CATALYSIS

VOLUME VI

Alkylation, Isomerization, Polymerization, Cracking and Hydroreforming

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REINHOLD PUBLISHING CORPORATION
NEW YORK
CHAPMAN & HALL, LTD., LONDON

Library of Congress Catalog Card Number: 54-6801

REINHOLD PUBLISHING CORPORATION

Publishers of Chemical Engineering Catalog, Chemical Materials Catalog, "Automatic Control," "Materials in Design Engineering," "Progressive Architecture"; Advertising Management of the American Chemical Society

Printed in the U.S.A. by
The Waverly Press, Inc., Baltimore, Md.

PREFACE

Volume VI of the present series has, for convenience, been designated as "hydrocarbon catalysis". It is concerned with the rearranging, cracking, and polymerization of hydrocarbon molecules over catalysts which function in part, at least, by virtue of their acidic nature. The entire context deals in detail with the theory and practice of carrying out catalytic reactions that have become essential parts of the petroleum industry. Specifically, it covers alkylation (Chapter 1), isomerization (Chapter 2), polymerization (Chapters 3 and 4), cracking (Chapter 5) and hydroreforming (Chapter 6).

The final chapter, on hydroreforming, is the only one in this volume dealing with catalytic hydrogenation and dehydrogenation. It is concerned with the new "dual-function" catalysts that embody both a hydrogenating-dehydrogenating catalyst and components having acidic reaction centers. This chapter contains considerable new material that is being published for the first time. It presents a timely discussion of certain catalytic processes that are the newest and probably the most important in the petroleum industry.

As far as possible, this Volume, like Volumes I through V, includes discussions of the theory and mechanism, as well as the factual matter of each of the catalytic reactions covered. The theory for hydroreforming in Chapter 6 is, unfortunately, not as completely worked out as that for the topics in Chapters 1 through 5. The subject matter is so new that it has not yet been studied in great detail from the standpoint of reaction mechanisms. Nevertheless, even in this instance, the factors influencing activity are fairly well understood and the probable mechanism of the catalytic reactions are pointed out.

For this volume, as for the previous ones, the editor wishes to thank all of the contributing authors for their fine cooperation. Without the guiding background of experience that each of them possesses, a critical presentation of the various catalytic processes here discussed would not have been possible. Special thanks are due the Socony Mobil Oil Co. for releasing for publication a great deal of new material on hydroreforming.

Paul H. Emmett

October 1, 1958
Baltimore, Md.

CONTENTS

CHAPTER 1

CATALYTIC ALKYLATION OF PARAFFINS WITH OLEFINS

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INTRODUCTION

The alkylation of paraffins with olefins under the influence of an acid catalyst was first reported in 1935[24]. The first plant based on this reaction was built and put into operation in 1938. The development of other processes and the installation of additional plants for the manufacture of high octane fuel by this reaction continued at a rapid pace. It was given special impetus during World War II, and by 1946 a total daily production of about 7,000,000 gallons of alkylate was attained[34]. Concurrently, intensive research on the fundamental mechanism of the alkylation reaction was under way. While much progress has been made in understanding the fundamental chemistry of the alkylation reaction, it cannot be said that it is completely understood.

Thermal alkylation, initiated by high temperature and pressure or by the combined effect of temperature, pressure and a promoter (alkyl halide or aliphatic nitro compound), is excluded from the scope of this discussion. This type of alkylation is a vapor phase free-radical reaction. The chemistry of such systems and a summary of the literature have been presented elsewhere[45].

After World War II, the need for alkylate in large volumes was reduced sharply as a result of the drop in aviation fuel requirements. Some alkylation plants were shut down. Others continued to operate, manufacturing alkylate for commercial aviation fuel or for motor fuel. The octane levels of premium motor fuels were such as to be attainable without using large amounts of alkylate.

Within the last few years the octane levels of premium motor fuels have increased so rapidly that a resurgence of interest in alkylation has occurred.

This is shown by the approximate domestic producing capacity[34] for alkylate, as follows:

	Approximate Capacity B/SD
October, 1946	171,000
January, 1955	236,000
January, 1956	263,000
January, 1957	273,000
Early 1959 (est.)	334,000

In a little more than a decade the capacity will be about double that at the end of World War II. This renewed interest in alkylate is due to its excellence as a motor fuel component for manufacturing a premium fuel with an octane number (F-1) in the range 95 to 105. Alkylate has a high clear octane number, excellent lead susceptibility and desirable burning and volatile properties.

It is the purpose of this chapter to provide a perspective of the progress that has been made in the fundamental chemistry of the alkylation reaction and to present in detail, with a critical evaluation, all those ideas which have contributed to an understanding of the reaction. Since concentrated sulfuric acid and anhydrous hydrofluoric acid are the principal catalysts used in industrial processes, most of the research has been done with these. Of the alkylation capacity existing in 1957, about 78 per cent was from sulfuric acid plants and 22 per cent from hydrofluoric acid plants. Other acids are, of course, capable of functioning as alkylation catalysts. Examples are the aluminum halides, boron trifluoride, boron trifluoride plus alkyl fluoride promoters, boron trifluoride with water or alcohols, or phosphoric acid, fluosulfonic acid, or chlorosulfonic acid. Thus, while much of the data bearing on mechanism interpretation have been obtained with hydrofluoric acid or sulfuric acid, some of the most important information comes from experiments with other catalysts.

A similar situation exists with respect to the hydrocarbons concerned. Isobutane is the only isoparaffin to attain any industrial importance in alkylation, yet when compared with other isoparaffins, it is unique in several respects. The reactions of other isoparaffins have provided important information relating to the mechanism.

The butylenes and propylene are the principal olefins for industrial alkylation. Though ethylene alkylation has been practiced commercially, it has never attained large volume compared to butylene or propylene alkylation. Nevertheless, ethylene alkylation has been an important aspect of the mechanism work since its beginning.

FACTS CONFRONTING EARLY ALKYLATION THEORIES

The first reported case in which the alkylation reaction was observed was that between isobutane and ethylene catalyzed with boron trifluoride, water and nickel to yield hexanes[24].

These experiments were performed at 20 to 30°C and the products were paraffinic materials boiling over a wide range. Undoubtedly the long residence times, 21 to 40 hours, resulted in much subsequent reaction of the primary products. The molar ratio of ethylene to isobutane in the product ranged from 5.9:1 to 1.2:1 calculated from the respective amounts consumed. In the latter case, the greatest yield of low-boiling (below 437°F) product was obtained. Hydrogen fluoride was substituted for water in the catalyst. The hexane produced was believed to be 2,2-dimethylbutane. The product contained more even carbon-number molecules than odd carbon-number molecules.

Isobutane was shown to alkylate isobutylene under the same conditions to yield octanes and dodecanes plus other paraffins. Isopentane alkylated ethylene yielding heptanes plus paraffins from isopentane to dodecanes and higher.

No specific compounds were identified in the products in this work. The chemistry of the catalyst was not elucidated. It was shown, however, that hydrogen fluoride could be substituted for water in the catalyst mixture. The nickel was probably unessential.

The inability of *n*-paraffins to alkylate was pointed out in this work. Later work[6, 20] established that the principal hexane produced was not 2,2-dimethylbutane but an isomer, 2,3-dimethylbutane. This immediately raised the question of whether the isobutane underwent fission before its addition to the double bond of the olefin, or whether, after addition occurred, the primary product of this addition had rearranged in some way. As the reaction was extended to other olefins and other paraffins, a number of questions were raised which, it was apparent, any comprehensive theory of the mechanism of alkylation would have to explain. These demands of fact on theory can be listed here, for subsequent discussion, as follows:

(1) Isoparaffins, but not normal paraffins, would react.

(2) Isoparaffins, in the absence of olefins, were surprisingly stable with alkylation catalysts.

(3) A majority of the products were unexpected or rearranged compounds in that there was no way direct combination of the paraffin and olefin structures could yield the structures observed.

(4) A significant part of the product was of an unexpected and unexplainable molecular weight.

(5) Practically no normal paraffins were in the alkylate, nor were there any "neo" structures in it, e.g., neopentane, neohexane, etc.

(6) Olefin polymers appeared to be, in some cases, equal in reactivity to the monomers. In other cases, this was not so.

(7) Plant data showed that somewhat more than one mole of isoparaffin was disappearing per mole of olefin consumed.

(8) The isoparaffin-olefin ratio was preferably high, not less than 5 for best selectivity.

(9) Vigorous agitation was required for best results.

(10) Increased temperature resulted in less product in the expected molecular weight range, and more rearranged products.

(11) Minor differences between liquid acid catalysts were observed.

(12) Both hydrogen fluoride and sulfuric acid possessed optimum amounts of water and hydrocarbon contaminants.

(13) A volume of acid about equal to the volume of hydrocarbon was desirable.

(14) Polymerization of the olefin was a competitive reaction.

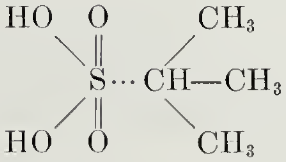
(15) Isomerization of olefins probably occurred, but the extent in any case was unknown and probably variable.

It is worth pointing out in passing that the development of a body of knowledge in alkylation embraces in chronology the development of highly precise analytical distillation methods and spectroscopic identification methods for hydrocarbons. The early work in alkylation was hampered by lack of such methods. The separation and identification of the components of complex and close-boiling hydrocarbon mixtures was a problem for which no good solutions existed in 1935. Undoubtedly the alkylation problem and analytical problem had stimulating effects on each other.

Activation of the Isoparaffin

The role of the isoparaffin was most intimately related to the question of its mode of activation. Since normal paraffins were inert, it was most likely that the tertiary C—H bond was the one reacting. Paraffins were shown[23] to undergo exchange with deutero-sulfuric acid. Although both normal paraffins and isoparaffins underwent exchange, in the case of the isoparaffins the tertiary hydrogen was believed to be the one exchanging. With respect to reactions involving C—C bonds, isoparaffins were particularly stable in the presence of concentrated sulfuric acid under alkylating conditions[33]. In excess isobutane at room temperature 2,2,4-trimethylpentane was inert except, presumably, for hydrogen exchange reactions. Under more severe conditions and in the absence of isobutane, 2,2,4-trimethylpentane did undergo extensive reaction[59], presumably preceded by an oxidation reaction. These results did not particularly help to resolve any problems, since catalysts such as hydrogen fluoride and aluminum chloride did not possess any oxidizing properties. Other methods were suggested[5, 12, 19, 33] by which the isoparaffin was activated. All of these used the observed products as a basis for deducing the manner in which the paraffin originally reacted. In all cases, a rather forced mechanism was involved, one which required a chemical behavior by the isoparaffin unknown at the time and still not demonstrated.

One suggestion[5] was that the isoparaffin formed an activated complex with the acid, e.g.



This led to fission of the isoparaffin into suitable fragments which added to the olefin. Another suggestion[33] was that the isoparaffin dissociated into a methyl "fragment" and—for isobutane—an isopropyl fragment. No distinction was made between ionic or free radical species. Similar suggested cleavages[12, 19] of the isoparaffin molecule failed to give a consistent explanation of the observed products.

Variation in the Olefin

All of the monoolefins from ethylene through the butylenes were studied extensively in the alkylation reaction, and the products from such experiments form the main basis for interpretation of the mechanism. However, valuable tests of various hypotheses were provided by work on higher olefins such as pentenes, diisobutylene, and polymers of propylene and butylenes.

Ethylene was observed to be the most difficult olefin to alkylate. Its alkylation could not be catalyzed with anhydrous hydrogen fluoride or concentrated sulfuric acid without going to temperatures so high that prohibitive amounts of cracking occurred. Hydrogen fluoride and powdered nickel[24], aluminum chloride[1, 40, 50], alkyl fluoride-boron trifluoride[26], boron trifluoride-hydrogen fluoride-water[2] were found to be effective catalysts. The temperature varied with the catalyst. Nominal temperature ranges for these catalysts are shown in Table 1.

As the temperature increased, the 2,3-dimethylbutane content of the hexane fraction decreased due to additional isomerization. The total yield of hexanes also decreased whereas the yield of isopentane increased.

Some of the first product analyses from concentrated sulfuric acid alkylation for various other olefins are shown in Table 2[6].

More precise quantitative results for the same catalyst and olefins obtained later are shown in Table 3[33]. The agreement is generally good.

The multiplicity of products was striking. Isomerization has obviously

TABLE 1. NOMINAL TEMPERATURES REQUIRED FOR ALKYLATING ISOBUTANE WITH ETHYLENE

Catalyst	T, °C	Remarks
Alkyl fluoride + BF_3[26]	−80 and higher	No hexanes made except 2,3-dimethylbutane
$AlCl_3$ + HCl[40]	−15 to 0	Intermediates isolatable. No isomerization of 2,3-dimethylbutane
$AlCl_3$ + HCl[1] or $AlCl_3$ + Ethyl chloride[50]	25	Substantial isomerization of 2,3-dimethylbutane
BF_3 + HF + H_2O[2]	40–45	Extensive isomerization of 2,3-dimethylbutane
Ni + HF + BF_3[24]	20–30	Considerable isomerization and some disproportionation

TABLE 2. PRODUCTS FORMED IN VARIOUS ISOPARAFFIN-OLEFIN ALKYLATIONS

Isoparaffin	Olefin	Main Products
Isobutane	Propylene	2,3-, 2,4-dimethylpentane; 2,2,4-trimethylpentane; 2,3-dimethylbutane
Isobutane	Butene-1 Butene-2 Diisobutene	2,2,4-trimethylpentane; 2,5-, 2,4-dimethylhexane; 2,2,5-trimethylhexane; 2,3-dimethylbutane; 2-methylpentane; (2,2,6-trimethylheptane?); isopentane.
Isopentane	Propylene	2,3-, 2,4-, 2,5-dimethylhexane; isobutane.
Isopentane	Butene-2 Diisobutene	2,2,5-trimethylhexane; isohexanes (probably mainly 2-, 3-methylpentanes); (2,2,6-trimethylheptane?).
2-Methylpentane	Butene-2 Diisobutene	(2,2,6-trimethylheptane?); isobutane; isopentane.

been extensive, but there was no reliable basis for selecting primary products of alkylation. The consistent appearance of isopentane and 2,3-dimethylbutane was characteristic.

That anhydrous hydrogen fluoride displayed much the same product distribution was shown by later work[27], presented in Table 4, designed to be done at relatively short contact times.

In the experiments of Table 4, isopentane was observed in all cases in small amounts. Examination of this table shows some difference from Table 3, probably due to the shorter contact times and lower temperatures used with the hydrogen fluoride. The large yield of high boiling product with propylene is prominent. Big differences between the butylene products can

Table 3. Composition of Alkylation Products from Sulfuric Acid Catalysis

Reactants	Products Obtained	Percentage (Wt.)
Isobutane and propylene	Propane	Trace
	2,4-dimethylpentane	8–12
	2,3-dimethylpentane	62–66
	2,2,4-trimethylpentane	5–9
	2,3,4- or 2,3,3-trimethylpentane	6–10
Isobutane and butene-2	Isopentane	Trace
	2,3-dimethylbutane	4–6
	2,2,4-trimethylpentane	34–38
	2,3,4- or 2,3,3-trimethylpentane	51–55
	Isobutane probably also formed	
Isobutane and pentene-2	Isopentane	6–8
	2,2,4-trimethylpentane	6–10
	2,3,4- or 2,3,3-trimethylpentane	8–12
	Isononanes	55–65
Isobutane and isobutylene	Isopentane	7–9
	2,3-dimethylbutane	8–10
	2,2,4-trimethylpentane	24–28
	2,3,4- or 2,3,3-trimethylpentane	30–34
	Isobutane probably also formed	
Isobutane and 2-methyl-butene-2	Isopentane	18–20
	2,3-dimethylbutane	5–7
	2,2,4-trimethylpentane	14–16
	2,3,4- or 2,3,3-trimethylpentane	15–17
	Isononanes	15–20
Isobutane and octenes from 2-ethyl-hexanol-1	Isopentane	3–5
	2,3-dimethylbutane	3–5
	2,2,4-trimethylpentane	12–16
	2,3,3-trimethylpentane	(?)
	3-methylheptane	35
	Isododecanes	(?)

be seen in contrast to earlier results which considered them essentially equal. The large yield of 2,3-dimethylhexane from butene-1 suggested a close similarity with ethylene alkylation, producing 2, 3-dimethylbutane.

The major products in every case were ones which could not be explained by direct combination of paraffin and olefin unless some dissociation of the paraffin preceded addition to the olefin. In some cases, even this could not explain all the products observed in the expected molecular weight. Isomerization was undoubtedly extensive.

Table 4. Compounds Produced by Alkylation of Isobutane with Pure Olefins, Catalyzed by Anhydrous Hydrogen Fluoride

Component in Alkylate	Volume per cent of Depentanized Alkylate			
	Olefin Used			
	Propylene	Isobutylene	Butene-1	Butene-2
2,3-Dimethylbutane	1.34	1.50	0.55	2.47
2-Methylpentane	0.25	0.92	0	0.52
3-Methylpentane	0	0	0	0
2,3-Dimethylpentane	43.40	2.73	1.74	1.35
2,4-Dimethylpentane	7.29	2.32	1.30	2.40
2,2,4-Trimethylpentane	3.73	48.97	29.47	37.90
2,2,3-Trimethylpentane	0	1.50	0.92	2.36
2,3,4-Trimethylpentane	0.92	9.38	14.14	19.39
2,3,3-Trimethylpentane	0.43	6.82	8.19	10.13
2,4-Dimethylhexane	0.24	3.31	4.93	2.58
2,5-Dimethylhexane	0.34	2.91	1.94	2.84
2,3-Dimethylhexane	0.40	2.41	25.22	3.40
2,2,5-Trimethylhexane	1.52	9.69	5.99	7.18
Uncalculated[a]	40.22	7.64	5.52	7.50
Temperature, °F	51	55	53	51
Contact time, min.	11.8	5.2	2.9	3.8
Isobutane/olefin ratio	4.67	5.16	4.75	5.57

[a] Unidentified paraffins boiling above about 125°C.

As analytical methods were improved, the occurrence of other paraffins outside the expected molecular weight was established. Tables 3 and 4 show that with isobutane, regardless of the olefin used, some isopentane, 2,3-dimethylbutane and 2,2,5-trimethylhexane were always formed. When isopentane was used in place of isobutane, then isobutane was formed. When a hexane was the reacting isoparaffin, Table 2 shows that isobutane and isopentane were produced. Even when butylenes were not used, 2,2,4-trimethylpentane was always a product when isobutane was the isoparaffin.

In all cases, material boiling above 125°C was invariably produced which could not be analyzed. This was due to the unavailability of a sufficient number of pure isomers for spectroscopic standards in the C_9 range. The use of isopentane and isohexane increased the amount of product in this high boiling range.

Table 5. The Alkylation of Isobutane with Olefin Polymers

Reactants	Products Obtained	Percentage (Wt.)
Isobutane and propylene trimers	Isopentane	2–3
	2,3-dimethylbutane	1–2
	2,2,4-trimethylpentane	15–20
	2,3,4- or 2,3,3-trimethylpentane	18–20
	Hydrogenated trimmers	45
Isobutane and butene dimers	Isopentane	6–7
	2,3-dimethylbutane	5–6
	2,2,4-trimethylpentane	60–65
	2,3,3- or 2,3,4-trimethylpentane	
	Hydrogenated dimers (?)	
	Isododecanes (?)	(?)
Isobutane and butene trimers	Isopentane	5–6
	2,3-dimethylbutane	3–5
	2,2,4-trimethylpentane	60–65
	2,3,4- or 2,3,3-trimethylpentane	
	Hydrogenated trimers	10–15
Isobutane and diisoamylene	Isopentane	10–12
	2,3-dimethylbutane	2–3
	2,2,4-trimethylpentane	20–25
	2,3,4- or 2,3,3-trimethylpentane	20–25
	Isodecanes	16–20

These tables also show the typical absence of normal paraffins and "neo" paraffins. In general, the amount of branching in the product was determined by the olefin. Propylene, regardless of the isoparaffin, produced mostly double-branched paraffins. Butene-1, under conditions where it was not allowed to equilibrate with butene-2 produced double-branched isomers, as shown in Table 4. Butene-2 produced more triple-branched isomers. Isobutylene consistently yielded predominantly triple-branched products.

The absence of normal and "neo" structures in the product probably means that the thermodynamic stability of the paraffins has little or no bearing on the final product distribution. If it did, large amounts of normal paraffins could be expected if equilibrium was attained. The branching in the "abnormal" molecular weights seemed to be independent of the olefin used.

The relative contributions of polymerization and alkylation were difficult to unravel. Data[33] shown in Table 5 suggest that the polymers were being directly hydrogenated in some way. The results were confusing, though, in that propylene trimers yielded substantial quantities of trimethylpentanes plus the ever-present isopentane and 2,3-dimethylbutane. Diisoamylene similarly yielded large amounts of trimethylpentanes and a fairly large amount of isopentane. Butylene polymers were hard to distinguish from the monomers based on their products.

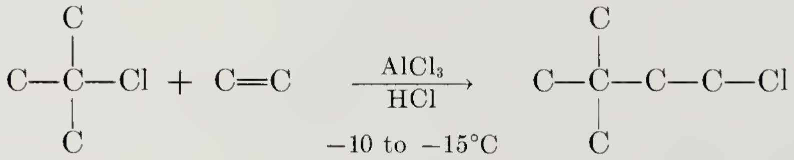
Primary Reactions of Alkylation

The conflicting and puzzling information outlined above was put into orderly arrangement by a study of the stages of ethylene alkylation[40]. Using aluminum chloride-hydrogen chloride as the catalyst, the following reactions were shown, by isolation of the intermediate products, to occur:

(1)

$$C-\underset{C}{\overset{C}{C}}-H + C=C \xrightarrow[HCl]{AlCl_3} C-\underset{C}{\overset{C}{C}}-Cl + C_2H_6$$

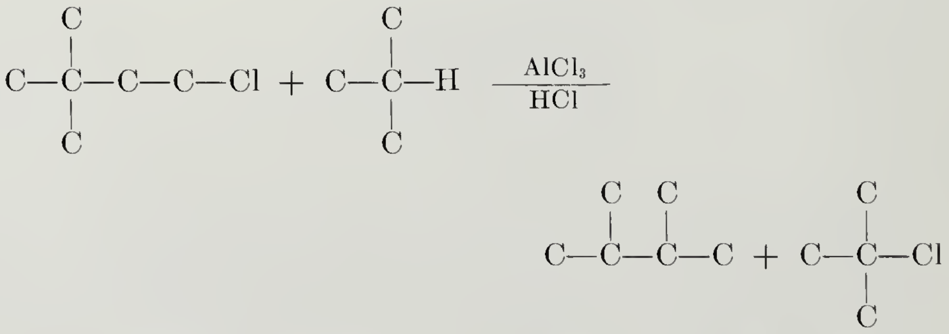
(2)



$$C-\underset{C}{\overset{C}{C}}-Cl + C=C \xrightarrow[HCl]{AlCl_3} C-\underset{C}{\overset{C}{C}}-C-C-Cl$$

-10 to -15°C

(3)

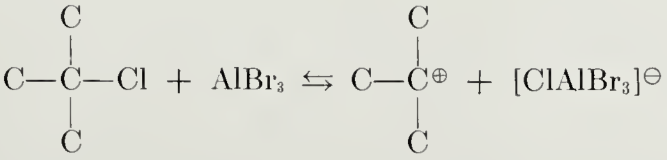


$$C-\underset{C}{\overset{C}{C}}-C-C-Cl + C-\underset{C}{\overset{C}{C}}-H \xrightarrow[HCl]{AlCl_3} C-\overset{C}{C}-\overset{C}{C}-C + C-\underset{C}{\overset{C}{C}}-Cl$$

The sequence was interpreted to mean that the ethylene and HCl first formed ethyl chloride which reacted with the isobutane to give *tert*-butyl chloride and ethane. Addition of the chloride to olefin followed. The neohexyl chloride reacted with more isobutane to produce a rearranged hexane and a new mole of *tert*-butyl chloride which could continue the sequence by addition to more olefin. The hydrogen-halogen transfer reaction shown here was demonstrated in greater detail shortly thereafter[3].

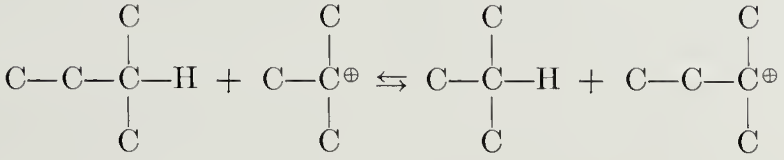
This study of hydrogen-halogen transfer reactions showed that the following *ionic* reactions occurred, exemplified by the reaction between *tert*-butyl chloride and isopentane:

(4)



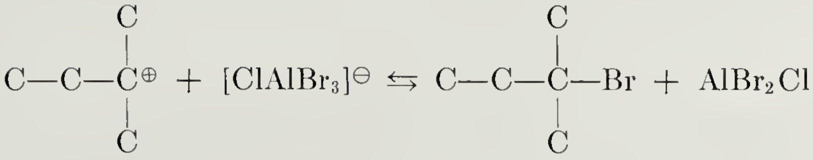
$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}Cl} + \mathrm{AlBr_3} \leftrightarrows \mathrm{C{-}\overset{C}{\underset{C}{C}}}^{\oplus} + [\mathrm{ClAlBr_3}]^{\ominus}$$

(5)



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}H} + \mathrm{C{-}\overset{C}{\underset{C}{C}}}^{\oplus} \leftrightarrows \mathrm{C{-}\overset{C}{\underset{C}{C}}{-}H} + \mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}}^{\oplus}$$

(6)



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}}^{\oplus} + [\mathrm{ClAlBr_3}]^{\ominus} \leftrightarrows \mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}Br} + \mathrm{AlBr_2Cl}$$

Isobutane and *tert*-amyl bromide were produced.

Isopentane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, and methylcyclohexane were shown to undergo hydrogen-halogen exchange with *tert*-butyl chloride under the influence of aluminum bromide. Paraffins without a tertiary C—H bond did not react. The reactions occurred very rapidly and at temperatures as low as −30°C.

To apply these results to systems of acid catalysts, isoparaffins and olefins, it was only necessary to assume that a proton from the acid added to an olefin to produce a carbonium ion. This concept had previously been used to explain polymerization of olefins[23, 55, 56]. If olefins were needed to initiate ion formation, then the stability of 2,2,4-trimethylpentane and isobutane in concentrated sulfuric acid in the absence of olefins was explainable. This also explained the instability of isoparaffins at higher temperature[59], where presumably oxidation produced an olefin or alcohol which initiated other reactions of the isooctane.

This work on ethylene contained most of the ideas needed to understand the primary reactions of alkylation. First, there is an initiating reaction in which a proton (in this case from hydrogen chloride) is added to the olefin. Then, the resulting ion reacts with the isoparaffin, producing a new ion and a paraffin derived from the olefin. The initiating reaction need occur only once. The third step is the addition of the new ion to the olefin to produce an ion of higher molecular weight. The fourth stage is the rearrangement of this ion. The fifth and last step is the saturation of these ions by reaction with the tertiary carbon-hydrogen bond of the isoparaffin to give the final product and to produce a new ion capable of propagating the chain.

These ideas were developed and applied to propylene and the butylenes in subsequent work[41, 42, 43]. The addition of *tert*-butyl chloride, isopropyl chloride, *tert*-amyl chloride, *tert*-butyl bromide and *tert*-amyl bromide to ethylene was shown[41] to occur readily. The principal product was the primary halide expected by addition of the alkyl halide to the double bond except in the case of isopropyl chloride. This yielded 1-chloro-3,3-dimethylpentane as the principal product. This can only be explained by postulating the formation of an amyl chloride which rearranges to *tert*-amyl chloride, which then adds to ethylene.

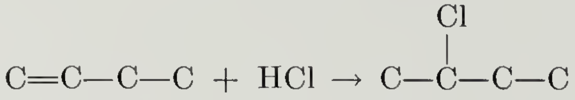
Some evidence of disproportionation was also found in the production of small yields of halides of unexpected molecular weight. For example, *tert*-butyl chloride and ethylene yielded small amounts of 1-chloro-3,3-dimethylpentane. This was believed to arise from the reaction

$$(7) \qquad 2\ t\text{-}C_4H_9Cl \rightarrow t\text{-}C_5H_{11}Cl + i\text{-}C_3H_7Cl$$

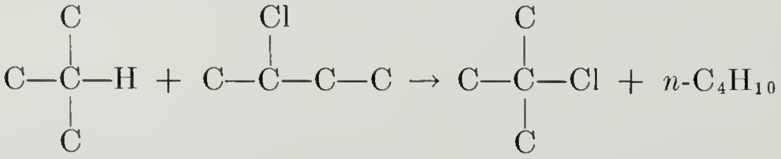
The tertiary halide condensations proceeded with ease at comparatively low temperatures (−15 to +5°C) in contrast to the condensation of primary or secondary halides. These halides gave low yield of addition products. Isomerization of the primary and secondary halides preceded their addition to the ethylene, as shown by the addition products.

More details of the reaction of 1-chloro-3,3-dimethylbutane with isobutane to yield 2,3-dimethylbutane and an expansion of the theory were given in a subsequent paper[42].

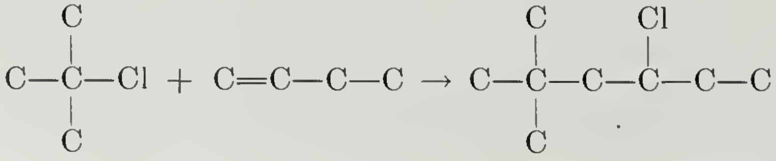
The complete mechanism was described and applied to butene-1, butene-2 and propylene in work with a catalyst consisting of the complex $AlCl_3 \cdot CH_3OH$[43]. Stated in general terms for butene-1, the sequence is as follows:

(8)


$$C{=}C{-}C{-}C + HCl \rightarrow C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C$$

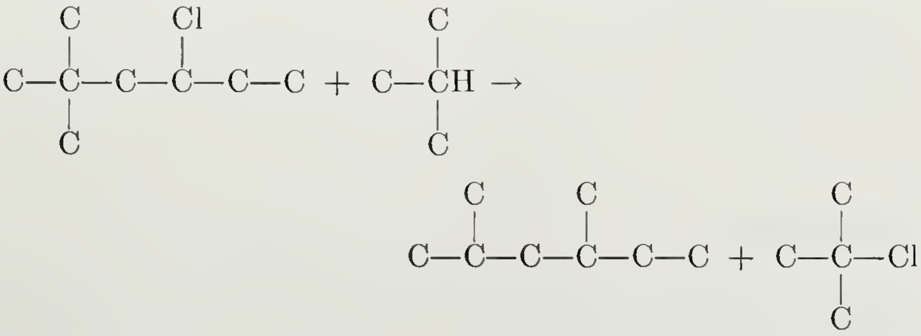
(9)


$$C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}H + C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C \rightarrow C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}Cl + n\text{-}C_4H_{10}$$

(10)


$$C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}Cl + C{=}C{-}C{-}C \rightarrow C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C$$

(11)



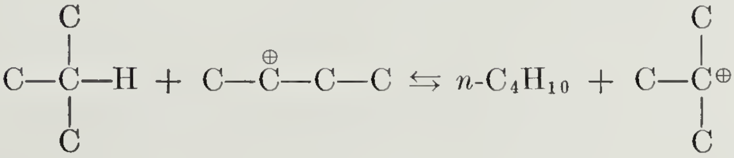
$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{\overset{Cl}{|}}{C}-C-C + C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}H \rightarrow C-\overset{\overset{C}{|}}{C}-C-\overset{\overset{C}{|}}{C}-C-C + C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-Cl$$

The last reaction involves the well-known Wagner-Meerwein rearrangement which was well understood in terms of carbonium ions. The alkylation sequence was also able to be expressed in terms of carbonium ions, as follows:

(12)

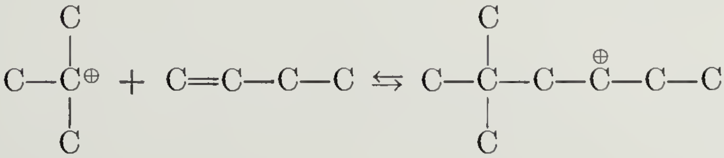
$$C{=}C-C-C + H^{\oplus} \rightleftarrows C-\overset{\oplus}{C}-C-C$$

(13)



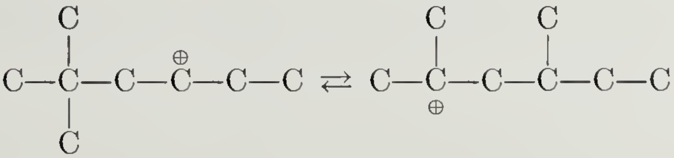
$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-H + C-\overset{\oplus}{C}-C-C \leftrightarrows n\text{-}C_4H_{10} + C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{}^{\oplus}$$

(14)



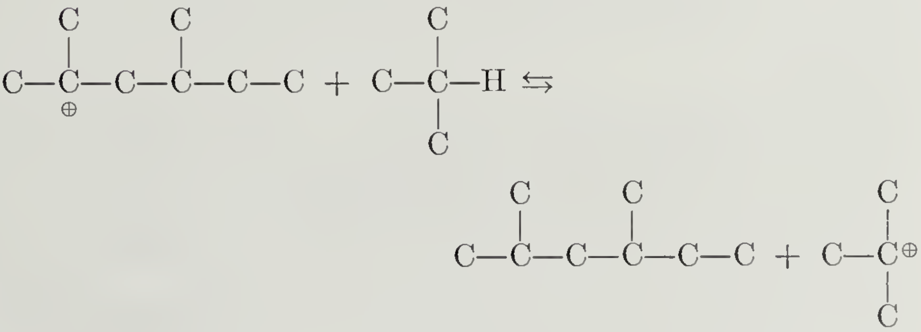
$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{}^{\oplus} + C{=}C-C-C \leftrightarrows C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{\oplus}{C}-C-C$$

(15)



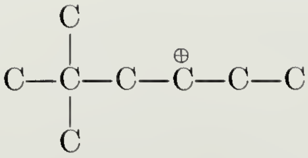
$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{\oplus}{C}-C-C \rightleftarrows C-\underset{\oplus}{\overset{\overset{C}{|}}{C}}-C-\overset{\overset{C}{|}}{C}-C-C$$

(16)



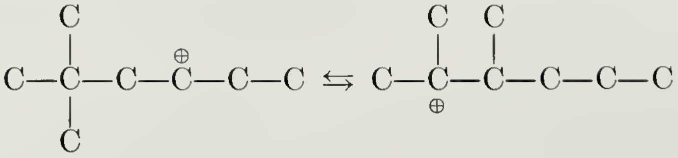
$$C-\underset{\oplus}{\overset{\overset{C}{|}}{C}}-C-\overset{\overset{C}{|}}{C}-C-C + C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-H \leftrightarrows C-\overset{\overset{C}{|}}{C}-C-\overset{\overset{C}{|}}{C}-C-C + C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{}^{\oplus}$$

Other isomerizations of



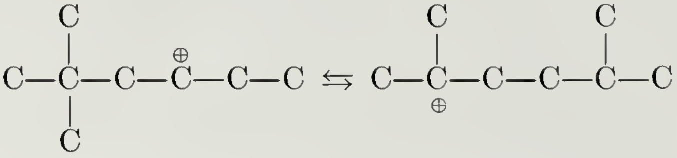
$$C-\underset{C}{\overset{C}{C}}-C-\overset{\oplus}{C}-C-C$$

could also occur:



$$C-\underset{C}{\overset{C}{C}}-C-\overset{\oplus}{C}-C-C \leftrightarrows C-\underset{\oplus}{\overset{C}{C}}-\overset{C}{C}-C-C-C \tag{17}$$

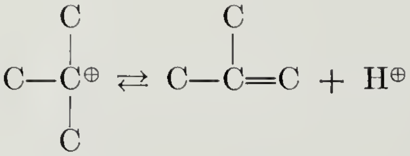
or



$$C-\underset{C}{\overset{C}{C}}-C-\overset{\oplus}{C}-C-C \leftrightarrows C-\underset{\oplus}{\overset{C}{C}}-C-C-\overset{C}{C}-C \tag{18}$$

These would yield 2,3-dimethylhexane and 2,5-dimethylhexane. The yield of 2,3-dimethylhexane was the second largest of the products from the butene-1 alkylation (see Table 4).

The trimethylpentanes observed could also have arisen from isomerization. It is more likely, however, that they arose from the isobutane, via this reaction:



$$C-\underset{C}{\overset{C}{C}}{}^{\oplus} \rightleftarrows C-\overset{C}{C}=C + H^{\oplus} \tag{19}$$

The isobutylene so produced was then alkylated to yield trimethylpentanes. That such a reaction can occur was shown later[16], and will be discussed in more detail subsequently.

Similar reactions can be written to apply to propylene and butene-2; and in general, the products predicted correspond to the major products observed. These can therefore be confidently considered to be the primary reactions of alkylation since they provide explanations for the following observations:

(1) The necessity for an isoparaffin: providing a tertiary C—H bond, which can undergo hydrogen transfer and continue the chain reaction.

(2) The need for an olefin to form ions initially to start the reaction.

(3) The large amount of rearranged products.

(4) The occurrence of octanes when not alkylating butenes, but when using isobutane.

(5) The saturation of olefin polymers by ion formation, followed by hydrogen transfer with an isoparaffin.

Other aspects of the reaction remained obscure, however, particularly the consistent occurrence of "abnormal" products such as isopentane and 2,3-dimethylbutane.

SECONDARY REACTIONS OF ALKYLATION

The data presented up to now establish the basis for a rational understanding of the main elements of alkylation. The process consisted of a sequence of ionic reactions comprising ion formation in the isoparaffin, addition to the olefin, isomerization of the new ion and hydrogen transfer with the isoparaffin to saturate the new ion and start a new cycle. Some evidence of secondary reactions, disproportionation, and "self-condensation" of isobutane existed, but their extent and nature were unknown.

The isomerization of branched paraffins had been studied before, but usually longer residence times and higher temperatures were needed than existed in alkylation reactions. Work[47] with a mixture of alkyl fluoride and boron trifluoride showed that the required isomerization could occur in very rapid reactions under conditions otherwise equivalent to alkylation.

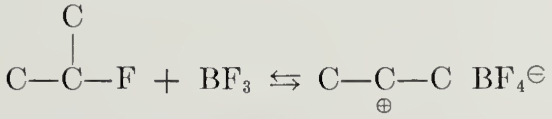
It had been shown[9] that an alkyl fluoride and boron trifluoride were able to produce carbonium ions

$$\mathrm{RF + BF_3 \leftrightarrows R^{\oplus} + BF_4^{\ominus}} \tag{20}$$

This reaction was used to promote other ionic reactions in mixtures of isobutane and isoparaffins found in alkylate[47]. The results of isomerizing hexanes and heptanes are shown in Table 6.

These experiments showed that the isoparaffins could be rapidly isomerized at temperatures of 20 to 30°C, provided the proper promoters were available. Normal paraffins did not react when exposed to an alkyl fluoride and boron trifluoride. The isoparaffins were completely unreactive in the presence of boron trifluoride only. The initiating reaction was therefore probably, in the case of isopropyl fluoride:

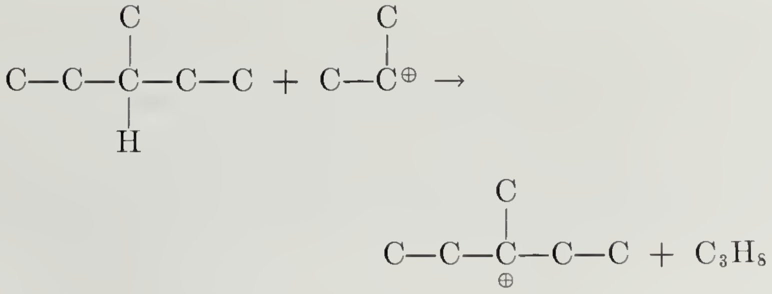
(21)



$$\mathrm{C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}F + BF_3 \leftrightarrows C{-}\underset{\oplus}{C}{-}C\ \ BF_4^{\ominus}} \tag{21}$$

The isoparaffins then reacted as follows:

(22)

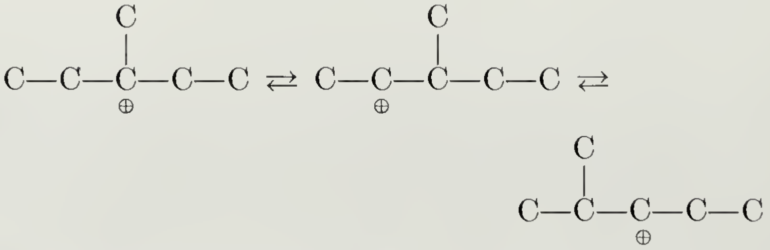


$$\mathrm{C{-}C{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle C}{|}}{C}}{-}C{-}C + C{-}\overset{\overset{\displaystyle C}{|}}{C}{}^{\oplus} \rightarrow C{-}C{-}\underset{\oplus}{\overset{\overset{\displaystyle C}{|}}{C}}{-}C{-}C + C_3H_8} \tag{22}$$

This reaction is irreversible since the propane has no tertiary C—H bond and in addition, tends to concentrate in the gas phase.

The hexyl ion so produced can isomerize:

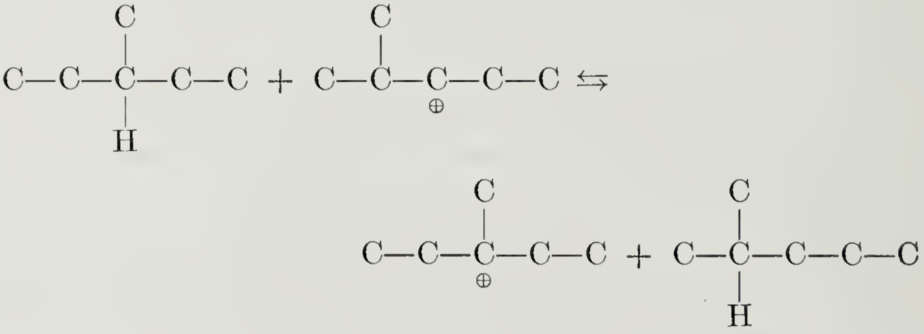
(23)



$$C-C-\underset{\oplus}{\overset{C}{C}}-C-C \rightleftarrows C-\underset{\oplus}{C}-\overset{C}{C}-C-C \rightleftarrows C-\overset{C}{C}-\underset{\oplus}{C}-C-C$$

The isomerized hexyl ion reacts with another isoparaffin to abstract a hydride ion, saturate itself, and initiate a new cycle:

(24)

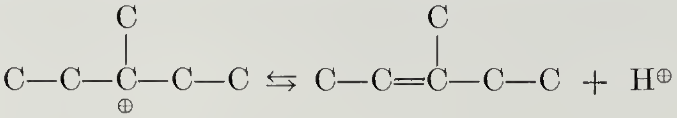


$$C-C-\overset{C}{\underset{H}{C}}-C-C + C-\overset{C}{C}-\underset{\oplus}{C}-C-C \leftrightarrows C-C-\underset{\oplus}{\overset{C}{C}}-C-C + C-\overset{C}{\underset{H}{C}}-C-C-C$$

Table 6 shows that one molecule of alkyl fluoride was able to promote the isomerization of 3 to 4 molecules of isoparaffin.

The chain-terminating step in such a sequence is probably the formation of an olefin by elimination of a proton from the carbonium ion:

(25)



$$C-C-\underset{\oplus}{\overset{C}{C}}-C-C \leftrightarrows C-C=\overset{C}{C}-C-C + H^{\oplus}$$

The proton reacts with $BF_4^{\ominus}$:

(26) $$H^{\oplus} + BF_4^{\ominus} \rightleftarrows HF + BF_3$$

This reaction is essential to maintain the electrical neutrality of the system.

The olefins so produced can polymerize under the influence of the hydrogen fluoride or boron trifluoride. Table 6 shows sizable yields of unidentified high-boiling hydrocarbons. In a system containing a large pool of free acid, such as in commercial hydrogen fluoride alkylation, such a chain-termination step is less likely to occur since the acid will tend to keep adding to the olefin. In such a case, the number of units in an isomerization chain would be much greater.

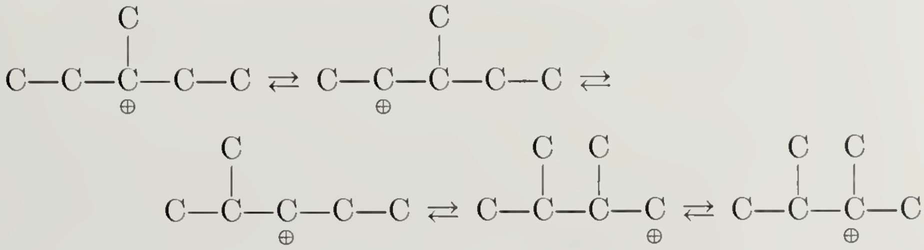
Table 6. Isomerization of Branched Hexanes and Heptanes Promoted by Isopropyl Fluoride-Boron Trifluoride

Isoparaffin Charged	3-Methylpentane	2-Methylpentane	2,3-Dimethylbutane	2,4-Dimethylpentane	2,3-Dimethylpentane
Vol. % in product					
Isopentane	—	—	2.8	—	—
2-Methylpentane	38.1	36.3	12.0	3.4	2.2
3-Methylpentane	37.9	18.0	4.1	4.4	—
2,3-Dimethylbutane	—	7.4	39.5	2.4	1.6
2,4-Dimethylpentane	—	1.1	5.6	32.3	38.2
2,3-Dimethylpentane	—	0.8	3.3	17.3	29.6
2-Methylhexane	3.1	5.2	1.4	2.1	3.4
3-Methylhexane	2.2	4.2	—	2.4	0.8
2,5-Dimethylhexane	—	—	3.7	4.0	1.3
2,4-Dimethylhexane	—	—	2.2	2.4	1.1
2,3-Dimethylhexane	—	—	2.3	0.6	—
2,2,5-Trimethylhexane	—	—	2.9	3.2	0.7
Moles isoparaffin converted/ mole alkyl fluoride	4.1	4.6	3.8	3.7	4.4
Vol. % High Boiling product[a]	16.8	23.5	14.2	21.5	20.6

[a] Boiling above about 125°C.

It is quite likely that the hexyl ions are convertible from one to another by the following sequence of proton and methyl shifts.

(27)



$$\mathrm{C{-}C{-}\underset{\oplus}{\overset{\displaystyle C}{\overset{|}{C}}}{-}C{-}C} \rightleftarrows \mathrm{C{-}\underset{\oplus}{C}{-}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}C} \rightleftarrows$$

$$\mathrm{C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}\underset{\oplus}{C}{-}C{-}C} \rightleftarrows \mathrm{C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}\overset{\displaystyle C}{\overset{|}{C}}{-}\underset{\oplus}{C}} \rightleftarrows \mathrm{C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}\underset{\oplus}{\overset{\displaystyle C}{\overset{|}{C}}}{-}C}$$

This requires that there be no way of going from the 3-methylpentane structure to the 2,3-dimethylbutane structure without going through the 2-methylpentane structure. The data of Table 6 are consistent with this requirement. No 2,3-dimethylbutane was formed when starting from 3-methylpentane, but some was formed when starting with 2-methylpentane. On the other hand, very little 3-methylpentane was formed starting with 2,3-dimethylbutane

2,3-Dimethylbutane is the preponderant hexane produced in all alkylates regardless of the olefin used. The reason for this has been the object of much speculation. It has been considered that it arose from isomerization of the methylpentanes. It is not the favored hexane thermodynamically.

Table 7. Disproportionation of Isoparaffins Promoted by Boron Trifluoride + Isopropyl Fluoride

Isoparaffin	Isobutane 2.90 moles	Isopentane 1.72 moles	2-methylpentane 1.41 moles
Temperature	0°C	0°C	27°C
Moles isopropyl fluoride	0.65	0.31	0.29
Moles isoparaffin reacted	0.95	1.28	1.15
Moles reacted/mole fluoride	1.46	4.45	2.79
Moles produced			
Propane	—	0.23	0.11
Isobutane		0.52	0.095
Isopentane	—	—	0.12
C_6	.039	0.22	—
C_7	.072	0.104	0.125
C_8	.23	0.092	0.068
C_9 and heavier	18.2 g	19 g	27.8 g
Vol. % of depentanized product			
2,3-Dimethylbutane	5.3	3.4	—
2-Methylpentane	1.2	15.7	43.4
3-Methylpentane	—	8.7	16.0
2,4-Dimethylpentane	8.8	2.6	—
2,3-Dimethylpentane	4.4	1.7	—
2-Methylhexane	—	5.6	7.1
3-Methylhexane	—	4.4	2.4
2,2,4-Trimethylpentane	18.2		—
2,2,3-Trimethylpentane	3.6		—
2,3,3-Trimethylpentane	9.1		—
2,3,4-Trimethylpentane	2.7		—
2,4-Dimethylhexane	2.5		—
2,5-Dimethylhexane	8.2		—
2,3-Dimethylhexane	2.4		—
2-Methylheptane			1.4
3-Methylheptane			5.7
4-Methylheptane			0.7

The data of Table 6 suggest that 2,3-dimethylbutane does *not* arise principally from isomerization of other hexanes. There is, instead, evidence that 2,3-dimethylbutane is the precursor of the other hexanes. The proportions 2,3-dimethylbutane: 2-methylpentane: 3-methylpentane in Column 4 of Table 6 are 3.3:1.0:0.34. The ratio of these compounds in 3 butene alkylates[18] averages 2.9:1.0:0.35, a remarkably close agreement. When isomerizing other hexanes, one does not obtain such ratios. This suggests that the methylpentanes arise from the 2,3-dimethylbutane. The latter must therefore come from some other reaction.

The experiments shown in Table 6 with 2,3-dimethylbutane, 2,4-dimethylpentane and 2,3-dimethylpentane show that products of higher and lower molecular weight can be produced. These products appear to be characterized by a degree of branching the same as the starting material. These "disproportionation" reactions were studied in another series of experiments[48] using an alkyl fluoride-boron trifluoride as the promoter.

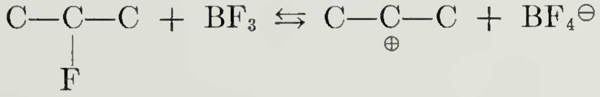
Typical disproportionation results are shown in Table 7. These results were obtained by treating a mixture of the isoparaffin in question and an alkyl fluoride with small amounts of boron trifluoride at 0 to 25°C. The reaction occurred as rapidly as the boron trifluoride could be introduced. Heat was evolved and a small amount of insoluble lower layer separated.

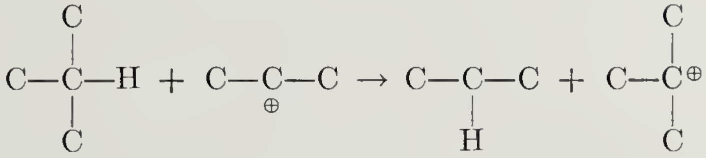
The disproportionation reaction can be exemplified by the conversion of isopentane to isobutane and a hexane:

(28)
$$2\ i\text{-}C_5H_{12} \leftrightarrows i\text{-}C_4H_{10} + i\text{-}C_6H_{14}$$

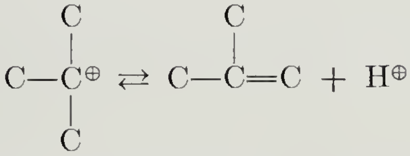
The isobutane and isohexane so produced can undergo further reaction. For this reason the stoichiometry predicted by the above equation is not discernible in the data of Table 7.

One other evident reaction in these experiments is condensation of the isoparaffin with itself, a "self-alkylation" reaction. Thus, isobutane promoted by isopropyl fluoride and boron trifluoride produced octanes, principally 2,2,4-trimethylpentane. The isopropyl fluoride has apparently not contributed to this condensation. A plausible mechanism appears to be:

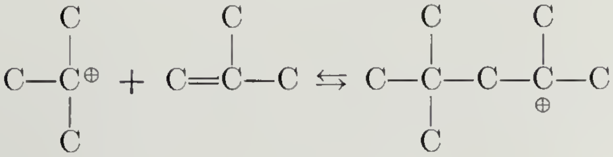
(29)

$$\mathrm{C{-}\underset{\underset{F}{|}}{C}{-}C + BF_3 \leftrightarrows C{-}\underset{\oplus}{C}{-}C + BF_4^{\ominus}}$$

(30)

$$\mathrm{C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}H + C{-}\underset{\oplus}{C}{-}C \rightarrow C{-}\underset{\underset{H}{|}}{C}{-}C + C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{}^{\oplus}}$$

Some of the *tert*-butyl ion so produced reacts as

(31)

$$\mathrm{C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{}^{\oplus} \rightleftarrows C{-}\overset{\overset{C}{|}}{C}{=}C + H^{\oplus}}$$

The isobutylene can be alkylated by other *tert*-butyl ions

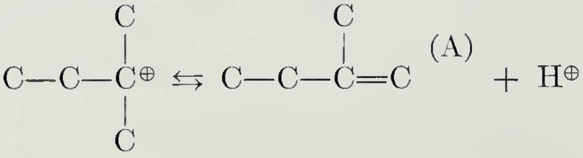
(32)

$$\mathrm{C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{}^{\oplus} + C{=}\overset{\overset{C}{|}}{C}{-}C \leftrightarrows C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}C{-}\overset{\overset{C}{|}}{\underset{\oplus}{C}}{-}C}$$

This undergoes the hydrogen transfer and isomerization reactions of a typical alkylation. The identity and quantity of paraffins formed from isobutane in the self-alkylation of isobutane is independent of the alkyl fluoride used[16]. This reaction has been studied and will be discussed later.

Isopentane also undergoes a self-alkylation reaction which is apparently followed by disproportionation. The decane formed by condensation undergoes cleavage to yield isobutane, hexanes and heptanes.

Generation of a *tert*-amyl ion proceeds by the same reactions as shown above for isobutane. The ion has two ways of losing a proton, however.

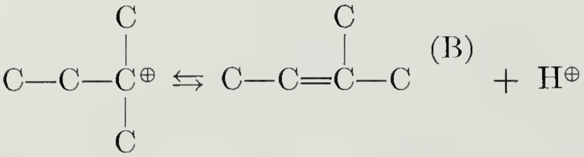
(33)



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{}^{\oplus} \leftrightarrows C{-}C{-}\overset{C}{C}{=}C}\ \text{(A)} + \mathrm{H}^{\oplus}$$

or

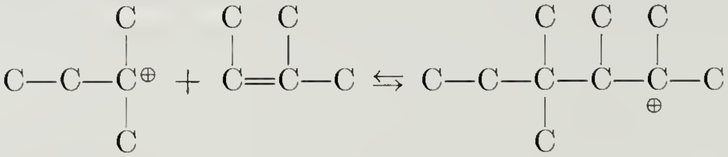
(34)



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{}^{\oplus} \leftrightarrows C{-}C{=}\overset{C}{C}{-}C}\ \text{(B)} + \mathrm{H}^{\oplus}$$

It has been shown by dehydration of *tert*-amyl alcohol[57] that the ratio of B/A is about 7:1. The subsequent reaction of the *tert*-amyl ion will therefore be with the trimethylethylene, principally

(35)

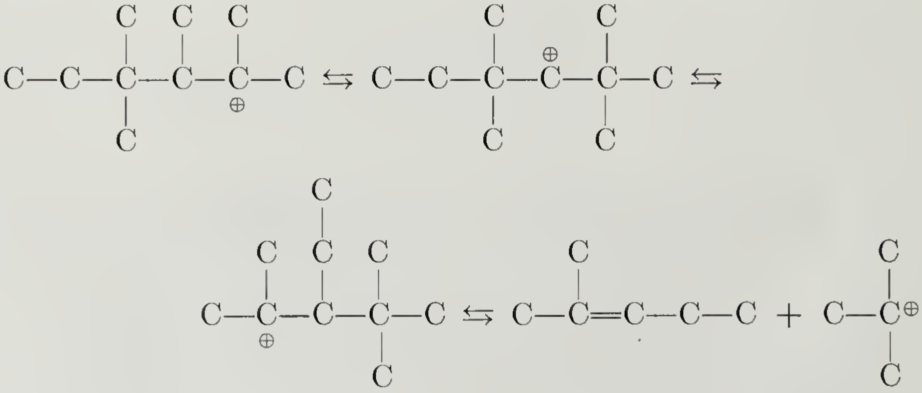


$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{}^{\oplus} + \overset{C}{C}{=}\overset{C}{C}{-}C \leftrightarrows C{-}C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{\underset{\oplus}{C}}{-}C}$$

This ion was shown[58] to cleave readily into C_5 fragments; in other words, the above reaction tends strongly to reversal.

A rearrangement of the ion, however, can occur which displaces the equilibrium to the right:

(36)



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{\underset{\oplus}{C}}{-}C \leftrightarrows C{-}C{-}\overset{C}{\underset{C}{C}}{-}\overset{\oplus}{C}{-}\overset{C}{\underset{C}{C}}{-}C \leftrightarrows}$$

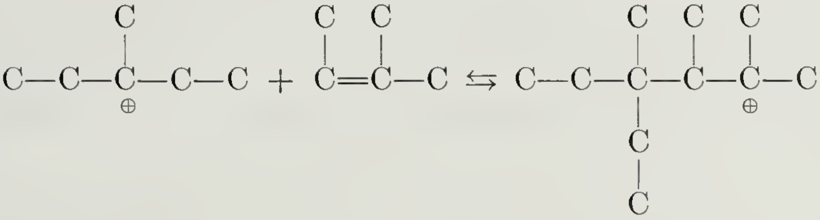
$$\mathrm{C{-}\overset{C}{\underset{\oplus}{C}}{-}\overset{\overset{C}{C}}{C}{-}\overset{C}{\underset{C}{C}}{-}C \leftrightarrows C{-}\overset{C}{C}{=}C{-}C{-}C + C{-}\overset{C}{\underset{C}{C}}{}^{\oplus}}$$

The *tert*-butyl ion, in a solvent of isopentane, becomes saturated yielding isobutane, generating a *tert*-amyl ion to propagate the chain reaction. The hexene can add a proton, derived from cleavage of a *tert*-amyl ion, and then react directly with isopentane or rearrange first and then react with isopentane. In either case, a hexane is produced and another chain-propagating *tert*-amyl ion is generated.

The data of Table 7 are consistent with this sequence. Per mole of isopentane reacted, 0.4 moles of isobutane and 0.17 moles of hexane appeared. The distribution of hexane isomers resembles that obtained by isomerization of 2-methylpentane in Table 6.

The heptanes are obtained in smaller yield, 0.08 moles per mole of isopentane reacted. They are predominantly single branched, suggesting that they are originally produced from single-branched structures. This probably occurs as follows. A *tert*-hexyl ion reacts with trimethylethylene:

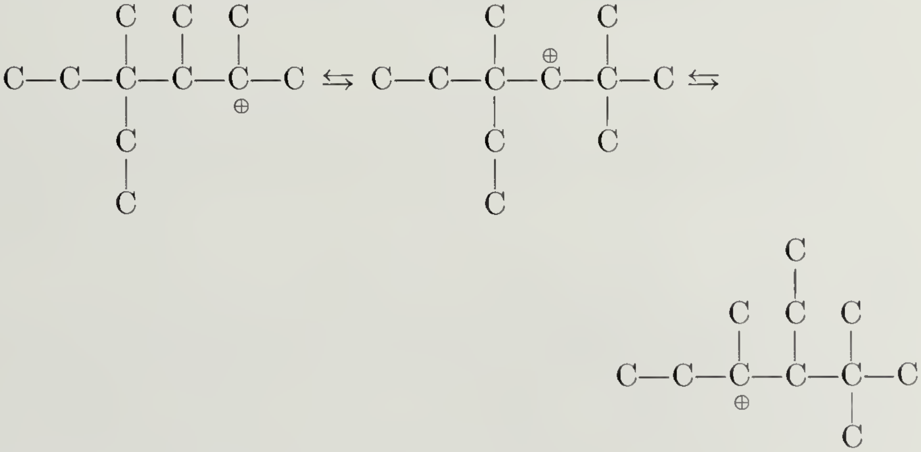
(37)



$$\mathrm{C{-}C{-}\underset{\oplus}{\overset{C}{C}}{-}C{-}C} + \mathrm{\overset{C}{C}{=}\overset{C}{C}{-}C} \leftrightarrows \mathrm{C{-}C{-}\underset{C-C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{\oplus}{\overset{C}{C}}{-}C}$$

This undergoes rearrangement as follows:

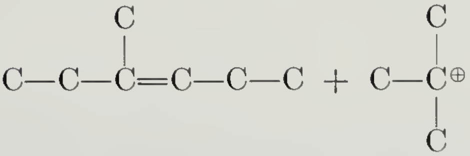
(38)



$$\mathrm{C{-}C{-}\underset{C-C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{\oplus}{\overset{C}{C}}{-}C} \leftrightarrows \mathrm{C{-}C{-}\underset{C-C}{\overset{C}{C}}{-}\overset{\oplus}{C}{-}\underset{C}{\overset{C}{C}}{-}C} \leftrightarrows \mathrm{C{-}C{-}\underset{\oplus}{\overset{C}{C}}{-}\overset{C-C}{C}{-}\underset{C}{\overset{C}{C}}{-}C}$$

The rearranged ion undergoes cleavage to yield

(39)



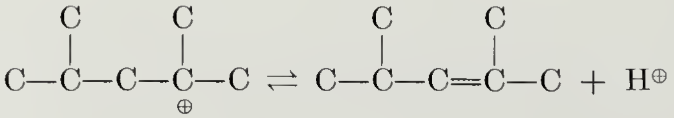
$$\mathrm{C{-}C{-}\overset{C}{C}{=}C{-}C{-}C} + \mathrm{C{-}\underset{C}{\overset{C}{C}}{}^{\oplus}}$$

The *tert*-butyl ion yields isobutane on reaction with isopentane and the heptane is saturated as before to yield a methylhexane.

The greater conversion of isopentane per mole of alkyl fluoride in comparison to isobutane can also be explained in terms of the above reactions. The ion produced from self-alkylation of isobutane is the 2,2,4-trimethylpentyl ion. This is more stable than the decyl ions produced from isopentane. More of the octyl ion is saturated by reaction with isobutane than decyl ions. Thus, only *one* new ion is produced in the saturating reaction in the case of isobutane. The decyl ions are more prone to cleave, even after rearrangement. In so doing, they produce two species which can ultimately cause a molecule of isopentane to react. As a result, many more molecules of isopentane react.

Table 7 shows that the octanes produced from 2-methylpentane are principally single branched. This is predictable by applying the same reasoning to reaction of a heptyl ion (single branched) derived from the above sequence and trimethylethylene. This leads to the generalization that the products of disproportionation have the same degree of branching as the starting paraffin. Table 6, although intended to show isomerization, shows the disproportionation results also. In the case of 2,4-dimethylpentane, double-branched hexanes and octanes are predicted via the following sequence:

(40)



$$\mathrm{C-\overset{C}{\overset{|}{C}}-C-\underset{\oplus}{\overset{C}{\overset{|}{C}}}-C \rightleftharpoons C-\overset{C}{\overset{|}{C}}-C{=}\overset{C}{\overset{|}{C}}-C + H^{\oplus}}$$

(41)

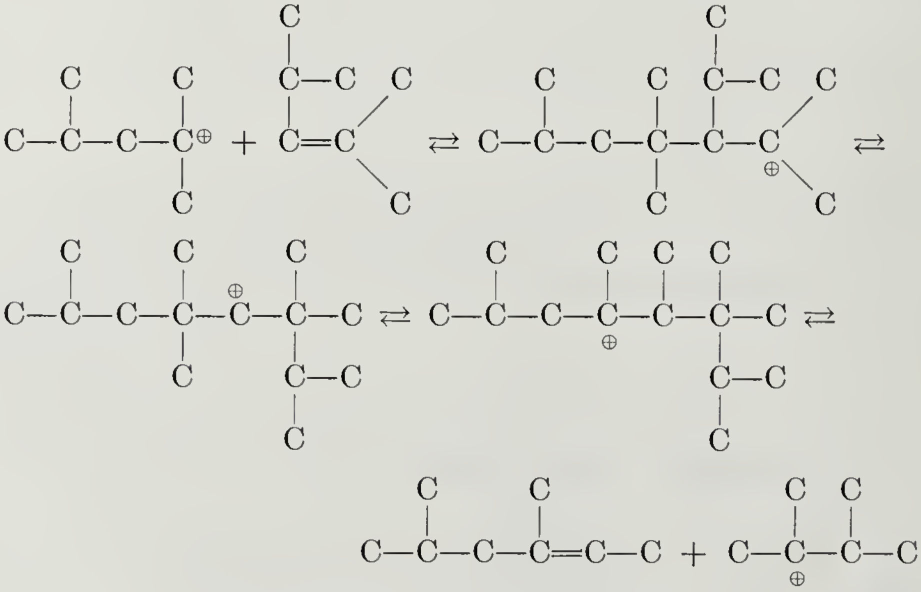


Table 6 shows a much larger relative concentration of 2,3-dimethylbutane in the hexane fraction from disproportionating double-branched heptanes than is obtained from disproportionating isopentane in Table 7.

Comparing disproportionation products from 2-methylpentane and 2,3-dimethylbutane, one finds that there are no singly-branched octanes from the 2,3-dimethylbutane, while from 2-methylpentane *only* single-branched octanes are obtained.

These reactions, except with isobutane, have differed from alkylation conditions in that they have not had present a large excess of isobutane. The final stage in these investigations was the study of these reactions in a solvent of isobutane[49].

Table 8 shows the results of reacting isobutane with various pure hexanes as promoted by *tert*-butyl fluoride and boron trifluoride. These data indicate that isobutane and the hexane are reacting to yield at least one mole of isopentane, and sometimes more than one, per mole of hexane reacted. This is in distinct contrast to the data of Table 7 where, for example, in the case of 2-methylpentane, the hexane gave equal molar yields of isopentane and heptanes. Broadly speaking, the reactions appear to be:

TABLE 8. REACTIONS OF ISOBUTANE WITH HEXANES PROMOTED BY TERT-BUTYL FLUORIDE AND BORON TRIFLUORIDE

T = 25–30°C 0.47 Moles Hexane 0.3 Moles tert-butyl fluoride

0.06 to 0.08 Moles of Boron trifluoride

Isoparaffin	3-Methylpentane	2-Methylpentane	2,3-Dimethylbutane
Moles reacted	0.235	0.230	0.110
% of original	50	49	24
Moles isobutane reacted	0.53	0.57	0.38
Moles produced			
Isopentane	0.26	0.26	0.10
Heptanes	0.05	0.054	0.04
Octanes	0.057	0.080	0.111
$\frac{\text{Moles isobutane consumed}}{\text{Mole hexane reacted}}$	2.26	2.48	3.46
$\frac{\text{Moles isopentane produced}}{\text{Mole hexane reacted}}$	1.10	1.13	0.92

(42) $2i\text{-}C_6 \rightarrow i\text{-}C_5 + i\text{-}C_7$ in the absence of isobutane

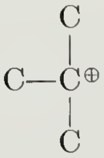
and

(43) $i\text{-}C_4 + i\text{-}C_6 \rightarrow 2i\text{-}C_5$ in the presence of isobutane.

Failure to show the exact stoichiometry of the last equation is due to the fact that side reactions of the intermediate pentenes detract from the yield of isopentane.

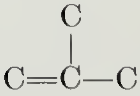
The sequence of reactions is believed to involve the following ions and their corresponding olefins, in the case of 3-methylpentane:

(A)



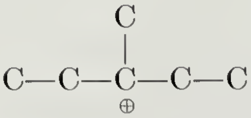
$$C-\underset{C}{\overset{C}{C}}{}^{\oplus}$$

(B)



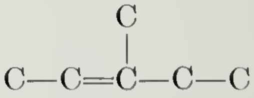
$$C=\overset{C}{C}-C$$

(C)



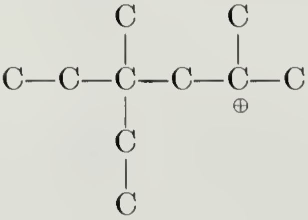
$$C-C-\underset{\oplus}{\overset{C}{C}}-C-C$$

(D)



$$C-C=\overset{C}{C}-C-C$$

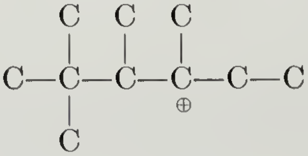
Combination of (A) and (B) ultimately yields 2,2,4-trimethylpentane which was observed as the principal octane. Combination of (C) and (D) has been shown to result in disproportionation to yield isopentane and heptanes. Combination of (C) with (B) leads to:



$$C-C-\underset{\underset{C}{C}}{\overset{C}{C}}-C-\underset{\oplus}{\overset{C}{C}}-C$$

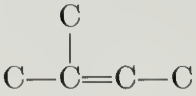
This type ion does not cleave readily into lighter fragments and saturation of this ion may be responsible for the high-boiling saturates invariably found in these reactions.

The addition of *tert*-butyl ion to (D) leads to the previously shown ion:



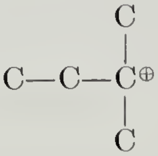
$$C-\underset{C}{\overset{C}{C}}-\overset{C}{C}-\underset{\oplus}{\overset{C}{C}}-C-C$$

which after rearrangement cleaves to yield:



$$C-\overset{C}{C}=C-C$$

and



$$C-C-\underset{C}{\overset{C}{C}}{}^{\oplus}$$

The latter ion is saturated to yield isopentane. Some of the trimethylethylene is saturated to isopentane, but the bulk of it appears to be alkylated or polymerized to higher boiling products.

Table 8 shows that 2,3-dimethylbutane is less inclined to enter into these reactions than the methylpentanes, reacting only one-half as much. This is in line with its lessened reactivity for isomerization and disproportionation.

The applicability of these reactions to the alkylation reaction was shown by a direct experiment using 2-methylpentane, isobutane, isobutylene, and anhydrous hydrogen fluoride[49]. The reactant proportions were:

2-Methylpentane	0.47	moles
Isobutane	2.12	"
Isobutylene	0.36	"
Anhydrous hydrogen fluoride	10.6.	"

The results were as follows:

Moles hexane reacted	0.28
Moles isobutane reacted	0.64
Moles isobutylene reacted	0.36
Moles produced:	
Isopentane	0.19 or 0.5 per mole hexane reacted
Heptanes	0.046
Octanes	0.159

Less than one mole of isopentane was produced per mole of hexane consumed, and the yield of octanes is somewhat larger than when promoted by *tert*-butyl fluoride and boron trifluoride. Apparently the slower speed of reaction in the hydrogen fluoride case is responsible for the change in product distribution.

The nonanes invariably observed in alkylation are 2,2,5-trimethylhexane and 2,2,4-trimethylhexane. These can be explained as arising from an alkylation of isobutane by one of the trimethylethylene isomers which have been mentioned as being obtained in lower yield than expected.

The condensation of isobutane with itself to form trimethylpentanes has already been referred to[16, 43, 44]. It is probably rightly considered as a secondary reaction of the alkylation system even though it does have a very important effect on the final alkylate composition. The occurrence of the over-all reaction was observed when isoparaffins, particularly isobutane, were in contact with such systems as alkyl halides and aluminum halides[43, 44], secondary or tertiary alcohols and concentrated sulfuric acid[32], secondary or tertiary alcohols and concentrated hydrogen fluoride[17] and alkyl fluorides with boron trifluoride[48]. The exact stoichiometry was shown by work with isobutane, isopropyl fluoride and boron trifluoride at −80°C[16]. It was shown that for each mole of boron trifluoride charged, 2 moles of propane were formed and 4 moles of isobutane consumed. The normally liquid hydrocarbons produced consisted principally of 2,2,4-trimethylpentane with small amounts of material in the C_5 to C_7 range. The balanced equation would seem to be:

$$BF_3 + 2i\text{-}C_3H_7F + 4i\text{-}C_4H_{10} \xrightarrow{-80°C} 2C_8H_{18} + 2C_3H_8 + BF_3 + 2HF \tag{44}$$

The 2:1 ratio between isobutane consumed and propane formed is confirmation of the sequence proposed for this reaction:

$$i\text{-}C_3H_7F + BF_3 \leftrightarrows i\text{-}C_3H_7^{\oplus} + BF_4^{\ominus} \tag{45}$$

$$i\text{-}C_4H_{10} + i\text{-}C_3H_7^{\oplus} \rightarrow t\text{-}C_4H_9^{\oplus} + C_3H_8 \tag{46}$$

$$t\text{-}C_4H_9^{\oplus} \leftrightarrows i\text{-}C_4H_8 + H^{\oplus} \tag{47}$$

$$t\text{-}C_4H_9^{\oplus} + i\text{-}C_4H_8 \leftrightarrows C_8H_{17}^{\oplus} \tag{48}$$

$$i\text{-}C_4H_{10} + C_8H_{17}^{\oplus} \leftrightarrows t\text{-}C_4H_9^{\oplus} + C_8H_{18} \tag{49}$$

The fact that exactly 2 moles of isopropyl fluoride were converted per mole of boron trifluoride was unexpected and not a necessary consequence of the above reaction sequence. The reaction

$$BF_4^{\ominus} + H^{\oplus} \rightleftarrows HF + BF_3 \tag{50}$$

should be a means of regenerating boron trifluoride for additional reaction. If this happened, no constant relation between boron trifluoride and isopropyl fluoride reacted should be obtained.

The explanation for these observations was concluded to be the formation of a crystalline complex $2HF:BF_3$ which was stable and insoluble at −80°C. The melting point of this complex was observed to be 56 to 58°C[21]. Thus, boron trifluoride at −80°C could only convert enough isopropyl fluoride to liberate 2 moles of hydrogen fluoride, i.e., 2 moles of isopropyl fluoride, before being removed from the system as solid $2HF \cdot BF_3$. At higher temperatures, the complex dissociates and, at 0°C, as much as 7.5 moles of isopropyl fluoride and 15 moles of isobutane can be reacted per mole of boron trifluoride.

Present Concept of Alkylation Mechanism

As a result of the work presented above, certain attributes of the alkylation mechanism have been established. It appears to be an ionic reaction, and is best understood in terms of carbonium ion chemistry. Whether the reaction occurs in the catalyst phase, hydrocarbon phase, or in the interface is not conclusively known. The results with alkyl fluoride-boron trifluoride systems, where the second (acid) phase is very small, where it appears as a result of reaction, and where the reactions are extremely rapid, suggest that it occurs in the hydrocarbon phase. The necessary sequence is:

1. Formation of ions by addition of a proton to olefins, ionization of an alkyl halide, or other means of producing ions.
2. Generation of ions from the isoparaffin (usually isobutane) by a hydrogen transfer reaction.
3. Addition of ions to olefins present, forming higher molecular weight ions.
4. Saturation of the heavier ions by hydrogen transfer reactions with isoparaffins present, before or after isomerization.
5. Continuation of the reaction chain by means of the ions produced in the final hydrogen-transfer step.

These primary reactions have secondary reactions which occur consecutively and simultaneously with the primary reactions. The secondary reactions are:

1. Condensation of the original isoparaffin with itself, "self-alkylation."
2. Reaction of the original isoparaffin with produced isoparaffins to yield isoparaffins of intermediate carbon content.
3. Disproportionation of produced isoparaffins to yield isoparaffins of higher and lower molecular weight.
4. Polymerization of the initial olefin followed by saturation of the polymer through hydrogen-transfer reactions.

Effects of Major Variables

How does this conception of the alkylation reaction explain the effects of major variables on the reaction? A qualitative explanation can be made for most major variables. Those to be considered are:

1. Catalysts
2. Temperature variation
3. Isoparaffin variation
4. Olefin variation
5. Ratios of catalyst, olefin and isoparaffin

Catalysts. The catalyst is important in at least two respects: (1) its ability to add a proton to an olefin (or the stability of the ester) and (2) its ability to abstract a hydride ion from a paraffin. The balance of these properties will determine the properties of the catalyst and the course of the alkylation reaction.

The stability of the ester formed with the olefin is greatest in the case of ethylene. Consequently, this is a good olefin to show how various acid catalysts can be differentiated. With concentrated sulfuric acid, the ester is quite stable and no alkylation occurs. With hydrogen fluoride, the ester, ethyl fluoride, is also quite stable, and in the absence of any promoter, little or no alkylation occurs. The use of a promoter[24, 26] facilitates the ionization of the ester; for example, $C—C—F + BF_3 \rightarrow C—C^{\oplus} + BF_4^{\ominus}$ and the chain reaction of alkylation ensues. Systems which can react with boron trifluoride to produce hydrogen fluoride[51] presumably function in this manner. Aluminum chloride reacts with traces of water to produce hydrogen chloride which adds to ethylene. The ethyl chloride is then ionized by more aluminum chloride

$$C—C—Cl + AlCl_3 \rightleftarrows C—C^{\oplus} + AlCl_4^{\ominus} \tag{51}$$

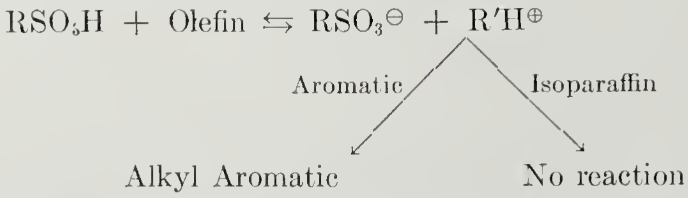
The ability of a catalyst to transfer a proton to an olefin is important not only in determining whether alkylation occurs but also in determining the degree of saturation or the amount of polymer in the alkylate. Hydrogen fluoride and sulfuric acid are about equal in this respect with hydrogen fluoride perhaps slightly more active. Aluminum chloride-hydrogen chloride is less active than these. As a result, hydrogen fluoride and sulfuric acid produce less high-boiling alkylate and a more saturated product. As long as the reaction

$$H^{\oplus} + \text{Olefin} \rightleftarrows \text{Ion} \tag{52}$$

is far to the right, less opportunity for formation of olefin from high-molecular-weight ions will exist.

The ability of an acid to transfer a proton to an olefin is dependent on more factors than are contained in the olefin or acid. Thus, alkane sulfonic acids cannot catalyze paraffin-olefin alkylation[39]. However, they can catalyze aromatic alkylations. In other words, the entire system must be considered, and both the kinetics and free energy of formation of the end-product can influence the apparent properties of the acid:

(53)



$$RSO_3H + \text{Olefin} \leftrightarrows RSO_3^{\ominus} + R'H^{\oplus}$$

The ability of an acid to transfer a proton to an olefin is undoubtedly influenced by the amount of water present. Both hydrogen fluoride and sulfuric acid possess optimum quantities of water for best results as alkylation catalysts, about 8 per cent for hydrogen fluoride and 4 per cent for sulfuric acid. Above the optimum amount, undue polymerization occurs at the expense of alkylation. Below this amount, increased complexity of product occurs.

The existence of optimum amounts of water and acid-soluble oil in the acid phase[29] can be readily associated with the ionization of the ester. If the acid concentration drops too low, ionization is insufficient. If the oil content is too low, the solubility of the ester is adversely affected. If the water content is too low, the ionization of the acid itself may be decreased, resulting in less ready addition to the olefin.

The same considerations apply to tertiary olefins. In dilute acidic solution, the only reaction is hydration to the corresponding alcohol[28, 30, 31]. This is because in aqueous or dilute acid, water is the principal species which can react with a carbonium ion. As the acid concentration increases, the water concentration decreases and the carbonium ion can react with other hydrocarbons present. When only olefins are present, polymerization occurs. When isoparaffins are present, hydrogen transfer reactions can occur. The need for a mole ratio of 5:1 for the isobutane-olefin ratio indicates that the olefin probably reacts 2 to 3 times more readily than the isoparaffin. If aromatics are present, they react most rapidly of all with the carbonium ions[14]. In the case of isobutane, benzene and an isopropyl ion, it has been estimated[14] that the isopropyl ion reacts 350 times more rapidly with the aromatic than with the isoparaffin.

The stability of the ester is, of course, a function of temperature, the ionization increasing as temperature is raised. Higher temperature can thus bring about alkylation of "refractory" olefins but other phenomena are encountered. Where the catalyst can also oxidize, as with sulfuric acid, the temperature may be high enough to cause some hydrocarbon oxidation. With all catalysts, higher temperature eventually causes greater catalyst consumption and formation of acid sludge. Finally, the product of alkylation becomes more complex due to increase in the secondary reactions.

Most catalysts, like hydrogen fluoride, are incapable of activating paraffins—even isoparaffins—until they are promoted by some co-catalyst. Boron trifluoride appears to be an effective co-catalyst for hydrogen fluoride[22]. Promoted by boron trifluoride and at temperatures somewhat above the usual for alkylation, hydrogen fluoride-boron trifluoride can cause paraffins, normal or branched, to react and undergo many of the reactions of isoparaffins demonstrated at lower temperatures when initiated by an alkyl fluoride and boron trifluoride. Butane, pentane and heptanes undergo extensive isomerization when exposed to such a catalyst. As evidence of the potency of such a catalyst, propane was converted to isobutane. This seems to require that hydrogen fluoride-boron trifluoride is capable of generating $\text{C—}\underset{\oplus}{\text{C}}\text{—C}$ from propane, something no other catalyst seems capable of accomplishing.

The reactions of hydrogen fluoride-boron trifluoride are strongly promoted by a trace of olefin, suggesting that the true catalyst is a complex of olefin-hydrogen fluoride-boron trifluoride, probably soluble in hydrocarbons.

Aluminum chloride is incapable of activating paraffins without hydrogen chloride unless an olefin or olefin precursor is generated by introducing oxygen. Concentrated sulfuric acid at room temperatures is incapable of activating paraffins at any appreciable rate. It is only when a higher temperature (*ca.* 60 to 100°C) is reached, and the oxidizing ability of sulfuric acid can be exerted that any extensive reaction occurs. This is preceded by some sulfur dioxide formation, and production of olefins or alcohols[11]. Only then can the proton transfer[13] to olefins occur to produce ions which then undergo the ionic reactions described before.

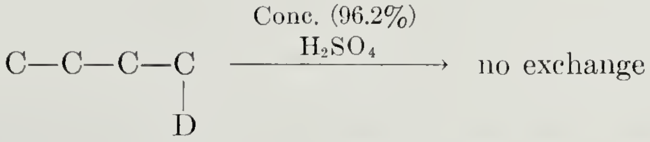
Table 9. Comparison of Volume Percentage Composition of Butene-2 Alkylates

Catalyst	$AlCl_3$[43]	$AlCl_3 \cdot CH_3OH$[43]	Anhydrous HF[27]
Temperature (°C)	30	28	20
Isopentane	17.4	Trace	Minor
Alkyl chloride	—	4.4	—
2,2-Dimethylbutane	5.4	—	—
2,3-Dimethylbutane	5.7	4.4	2.5
2-Methylpentane	6.6	—	0.5
3-Methylpentane	2.7	—	—
2,2,3-Trimethylbutane	1.0	—	—
2,2-Dimethylpentane	0.2	—	—
2,4-Dimethylpentane	5.5	3.7	2.4
2,3-Dimethylpentane	2.4	2.2	1.4
Methylhexane	5.7	—	—
2,2,4-Trimethylpentane	12.8	33.1	37.9
2,2,3-Trimethylpentane	1.3	0.6	2.4
2,3,4-Trimethylpentane	2.9	26.3	19.4
2,3,3-Trimethylpentane	2.6	16.3	10.1
2,4-Dimethylhexane	8.1	3.8	2.6
2,5-Dimethylhexane			2.8
2,3-Dimethylhexane	0.7	0.7	3.4
2,2-Dimethylhexane	0.5	—	—
Methylheptanes	3.6	—	—
C_9 +	14.9	4.5	7.5

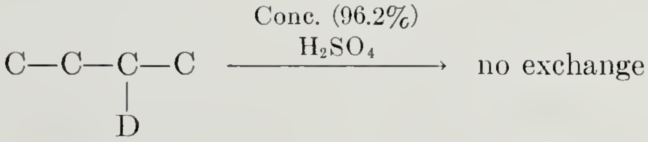
Thus, those catalysts which are capable of activating paraffins are prone to give alkylates with the greatest amount of isomerization and disproportionation in the product. This results, from a practical point of view, in alkylates with lower octane number, greater boiling range (particularly toward the higher boiling end), and greater consumption of catalyst and isobutane. For practical applications, anhydrous hydrogen fluoride and concentrated sulfuric acid have the appropriate activity.

Table 9 shows the effect of acid activity on product composition. The modified aluminum chloride, in the form of $AlCl_3—CH_3OH$, is a weaker acid and gives an alkylate approaching that from anhydrous hydrogen fluoride in composition. The low yield of 2,2,4-trimethylpentane from aluminum chloride is its most striking difference. It also has a more complex alkylate in terms of boiling range, molecular weight distribution, and number of isomers.

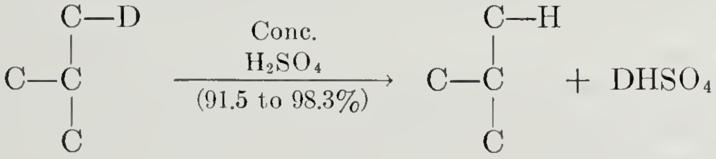
Hydrogen exchange reactions of the butanes show that the acid strength of sulfuric acid has a profound effect on the exchange rate[4]. With isobutane, the rate of exchange of the primary hydrogen increased 35 times in going from 91.5 per cent to 98.3 per cent sulfuric acid. Addition of traces of isobutylene caused large increases in the rate of exchange. The rates of exchange with the catalyst were quite slow, zero in the case of *n*-butane, in comparison to the rates of exchange between molecules. Thus, the following was observed:

(54)


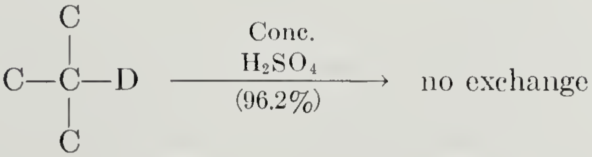
$$\mathrm{C{-}C{-}C{-}\underset{\underset{\displaystyle D}{|}}{C}} \xrightarrow{\text{Conc. (96.2\%)}\ \mathrm{H_2SO_4}} \text{no exchange}$$

(55)


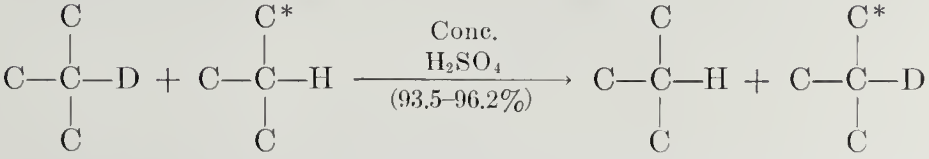
$$\mathrm{C{-}C{-}\underset{\underset{\displaystyle D}{|}}{C}{-}C} \xrightarrow{\text{Conc. (96.2\%)}\ \mathrm{H_2SO_4}} \text{no exchange}$$

(56)


$$\mathrm{C{-}\overset{\overset{\displaystyle C{-}D}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}} \xrightarrow[\text{(91.5 to 98.3\%)}]{\text{Conc.}\ \mathrm{H_2SO_4}} \mathrm{C{-}\overset{\overset{\displaystyle C{-}H}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}} + \mathrm{DHSO_4}$$

(57)


$$\mathrm{C{-}\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{-}D} \xrightarrow[\text{(96.2\%)}]{\text{Conc.}\ \mathrm{H_2SO_4}} \text{no exchange}$$

(58)


$$\mathrm{C{-}\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{-}D} + \mathrm{C{-}\overset{\overset{\displaystyle C^*}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{-}H} \xrightarrow[\text{(93.5–96.2\%)}]{\text{Conc.}\ \mathrm{H_2SO_4}} \mathrm{C{-}\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{-}H} + \mathrm{C{-}\overset{\overset{\displaystyle C^*}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{-}D}$$

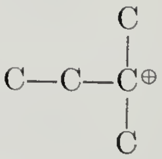
Similar results were obtained[54] with aluminum chloride-hydroged chloride in that no exchange of any hydrogen took place between ethane, propane, *n*-butane, or isobutane and the catalyst. Similar intermolecular exchanges of hydrogen and deuterium occurred, however. The fact that these exchanges can occur readily, and with no decrease in rate even when the activity of the catalyst for isomerization is decreasing by a factor of ten, indicates that the exchange reactions require much less activation of the hydrocarbon than isomerization or alkylation. Exchange results therefore have only limited application to the alkylation mechanism.

Temperature Variation. The temperature which an acid needs before it can activate paraffins determines how much of such activation will occur in the course of an alkylation reaction. Its relation to the ionization of olefin-acid esters has been mentioned. In general, the more readily paraffin ionization occurs, the more likely it will be that ions, and therefore olefins corresponding to the original paraffin, will be produced. As a result, the complexity of the alkylate will be increased. The combination of aluminum chloride-hydrogen chloride is the most active in this respect, and for this reason alkylates made with this catalyst are usually more complex than those produced with milder catalysts, other things being equal. Aluminum chloride-hydrogen chloride is, of course, more potent in causing further reaction of the primary products, and this alone is enough to make aluminum chloride-hydrogen chloride alkylates more complex.

The effect of temperature on individual reactions is thus not often clearly discernible due to the many conflicting and competing reactions. All the catalysts will of course be more active at higher temperatures. This means their attack on both original reactants and primary products will be greater. The total product will therefore be more complex. Isomerization reactions will be faster at higher temperatures. The olefin-ion equilibrium probably tends to be farther on the side of the olefin. These contribute more to the complexity of the product.

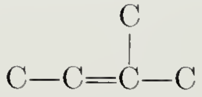
What is not known now is how the temperature coefficients of these reactions differ. Until such information is obtained, one can only say that higher temperature produces a more complex alkylate.

Isoparaffin Variation. The isoparaffin used is of course one of the principal factors in determining the complexity of the alkylate. Reference has been made to the fact that isobutane is, in a sense, unique among the isoparaffins. This is due to the fact that it has no secondary C—H bonds. When the *tert*-butyl ion is formed, it has a much lesser tendency to lose a proton than ions such as the *tert*-amyl ion. The latter contains a secondary C—H bond adjacent to the open sextet:



$$\begin{array}{ccccc} & & & & \mathrm{C} \\ & & & & | \\ \mathrm{C} & — & \mathrm{C} & — & \mathrm{C}^{\oplus} \\ & & & & | \\ & & & & \mathrm{C} \end{array}$$

This eliminates a proton more readily than the primary C—H bonds of the methyl groups. As a result, the olefin



$$C{-}C{=}\overset{\overset{\textstyle C}{|}}{C}{-}C$$

is produced and incorporated into the alkylate via direct alkylation or by polymerization, followed by hydrogen transfer. Isopentane alkylate is therefore characterized by higher consumption of the isoparaffin than is found with isobutane.

Isopentane alkylated with ethylene[52] using a $BF_3 \cdot H_3PO_4$ catalyst gave an alkylate having only 15 to 30 per cent of heptanes, the expected product. When alkylating with propylene[29] the octanes constituted only 26 per cent of the product, with 14 per cent heptanes. When alkylating isopentane with butene-1[33] only 45 per cent of the alkylate was nonanes. Alkylation of isopentane with 2-methyl butene-2[53] gave a very complex product ranging from isobutane to decanes. The structures were not determined. In all these cases, the yield of high-boiling (above the "normal" product) alkylate is also greater. A higher consumption of sulfuric with isopentane has also been observed[7].

Alkylation with branched hexanes has not been studied very much[33]. One can expect that the same principles will apply, and the alkylate should resemble isopentane alkylate. At the same time, isomerization and disproportionation of the original isoparaffins will occur. Neohexane behaves like a normal paraffin since it has no tertiary C—H bonds.

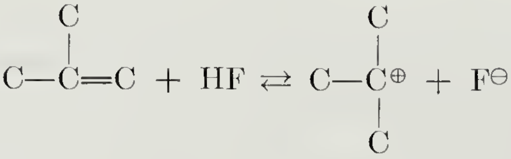
The most drastic change which can be made in the paraffin is to substitute a naphthene, especially one containing a tertiary C—H bond, for the isoparaffin. This has been studied using methylcyclopentane, cyclohexane and methylcyclohexane[36, 37, 46, 52].

Table 10 shows the comparative yields of isobutane-isobutylene alkylate and methylcyclopentane-isobutylene alkylate in a mixed alkylation reaction[46].

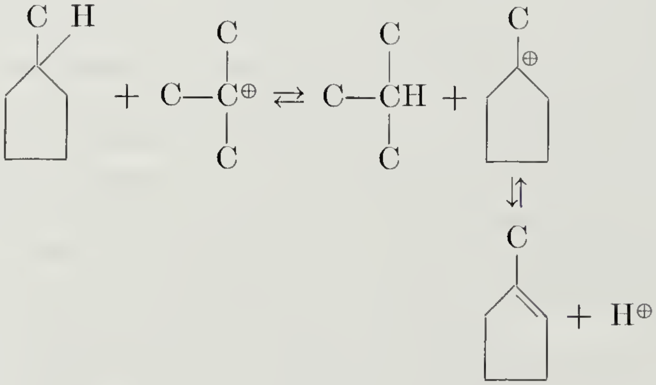
The methylcyclopentane reacts much more rapidly with the isobutylene than does the isobutane. In one case, even though it had only one-quarter the concentration of isobutane, it gave twice as much direct alkylation product. The methylcyclopentane conversion was never less than 87 per cent, while the isobutane conversion never exceeded about 25 per cent, and in one case was negative.

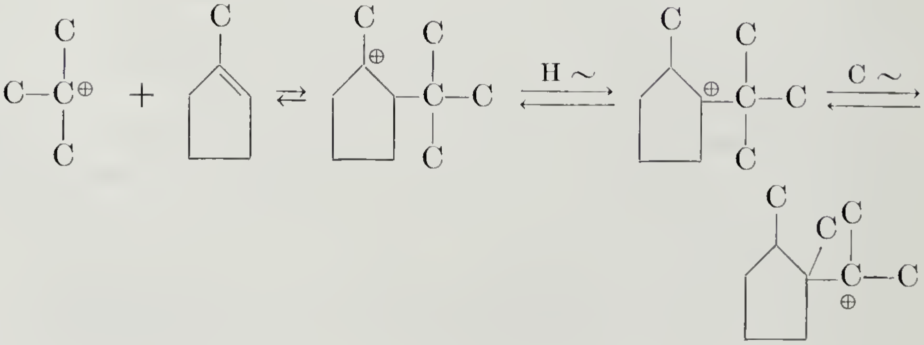
Another feature of the experiments of Table 10 was the formation of material boiling well above the usual alkylate range, even after allowing for normal yields of high-boiling alkylate. Physical property correlations indicated that this portion of the product was 90 to 100 per cent naphthenic. Dehydrogenation over platinum on charcoal showed 67 per cent dehydrogenation. The dehydrogenated product was shown by spectroscopic methods to be tetramethyl benzenes, including durene. Therefore, the alkylate contained tetramethylcyclohexanes in relatively large amounts.

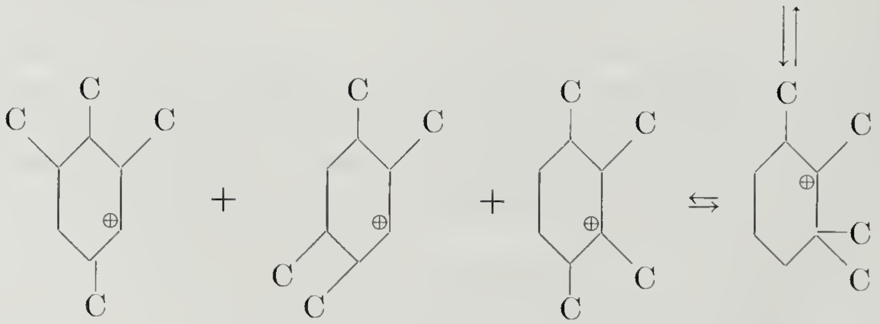
The sequence of reactions suggested for the formation of this material is as follows:

(59)


$$\mathrm{C{-}\overset{C}{\overset{|}{C}}{=}C + HF \rightleftarrows C{-}\underset{C}{\overset{C}{C^{\oplus}}} + F^{\ominus}}$$

(60)


(61)


(62)


This sequence allows for the formation of both cyclohexanes and cyclopentanes or geminal disubstituted cyclohexanes.

By appropriate competition reactions, it was shown[46] that large differences existed in the ease with which naphthenes and isoparaffins reacted in ionic systems. This order is as follows: methylcyclopentane > 2-methylpentane > isopentane > isobutane > methylcyclohexane. This is the same order as is observed in measurement of the rates of ionization of the corresponding tertiary alkyl chlorides[8]. The similarity between ionization of a chloride ion and loss of a hydride ion is evident.

This same investigation showed that in addition to the above, the alkylate produced in this reaction contained substantial amounts of substituted decahydronaphthalenes. These were believed to arise by a "self-alkylation" of the methylcyclopentane[15]. This can be explained by this sequence of reactions:

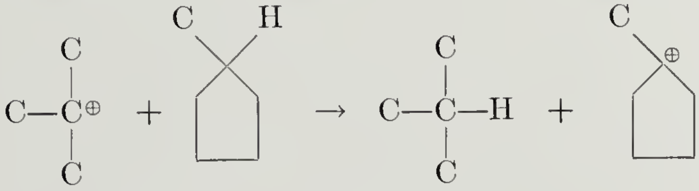
Table 10. Alkylation of Isobutane and Methylcyclopentane with Isobutylene at 20° to 25°C[41]

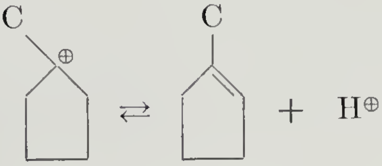
Catalyst: Anhydrous Hydrogen fluoride

Charge, moles				
Methylcyclopentane	0.12	0.506	1.03	2.00
Isobutane	3.67	2.01	2.89	1.48
Isobutylene	1.11	0.98	1.54	2.14
Mole Ratio $\frac{\text{Methylcyclopentane}}{\text{Isobutane}}$	0.0327	0.249	0.356	1.35
% Methylcyclopentane converted	100	100	95.2	87
% Isobutane converted	25	6	0	—[2]
% Octanes[1]	56	11	9	—
% C_4-alkylated methylcyclopentane	5	27	33	23.4

[1] Based on moles isobutylene charged.

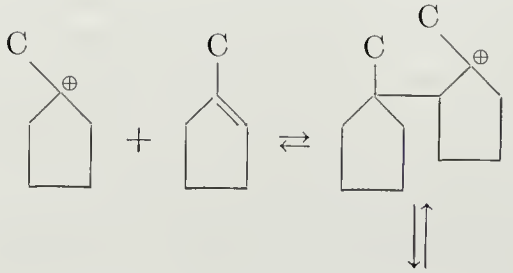
[2] 45% more isobutane was recovered than was charged due to hydrogen transfer to isobutylene.

(63) 

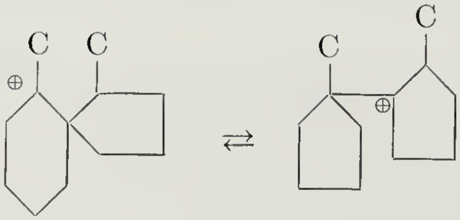
(64) 

The methylcyclopentyl ion adds to methylcyclopentene.

(65)

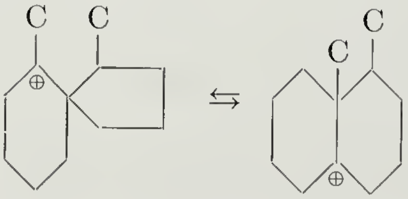


(66)



Isomerization of the second cyclopentyl ring gives the decalin structure

(67)



The last ion becomes saturated by reaction with methylcyclopentane, producing a Decalin and a new methylcyclopentyl ion to repeat the process.

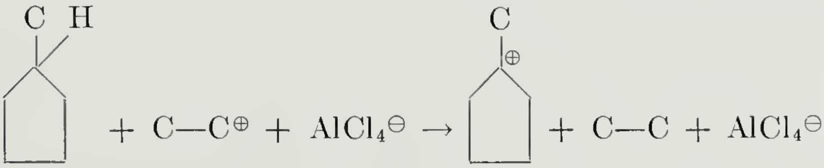
The reaction of methylcyclopentane with propylene in the absence of isobutane was investigated at −42°C using aluminum bromide promoted by hydrogen bromide[38]. Alkylated cyclohexanes with the general formula C_9H_{18} were one of the principal products. The other major product was a mixture of substituted decahydronaphthalenes which undoubtedly were due to the preceding sequence of reactions.

Methylcyclopentane and *n*-butylene[37] at 10 to 17°C catalyzed by sulfuric acid gave 1,3-dimethyl-5-ethylcyclohexane and 1,3-dimethyl-4-ethylcyclohexane. Some apparently naphthenic high-boiling product was also obtained. With the same system and isobutylene as the olefin more isobutane was formed and, from it, more octanes. These could also come from saturation of diisobutylene. Very little alkylated cyclohexane was obtained, but substantial yields of dicyclic and polycyclic products. Pentene-2 was similar to the butene. Very little direct alkylation occurred and much hydrogen transfer was observed, yielding isopentane and decane. Dicyclic and alkyl dicyclic products amounted to 41 per cent yield.

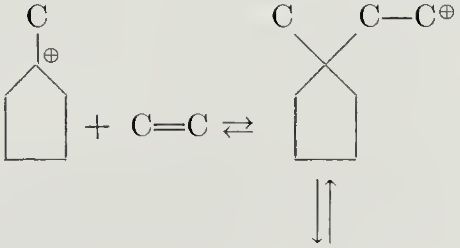
Hydrogen fluoride catalysis of methylcyclopentane and butylene[37] gave little alkylated cyclohexane and much hydrogen transfer.

When alkylating cyclohexane with ethylene[25] using aluminum chloride and hydrogen chloride, less dimerization of the naphthene, less hydrogen transfer, and more direct alkylation took place. The alkylate was chiefly dimethylcyclohexanes and tetramethylcyclohexanes. These products can best be explained by assuming that the cyclohexane first isomerizes to methylcyclopentane. This can then react as follows with the ethyl chloride-aluminum chloride complex:

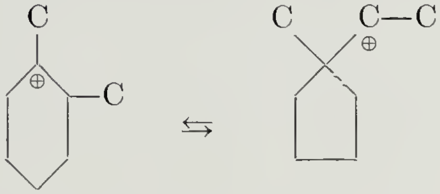
(68)



(69)



(70)



This is the ring expansion invoked earlier to explain the appearance of decalins in methylcyclopentane alkylate.

Methylcyclohexane was alkylated with propylene using aluminum chloride catalyst at −25°C and at 50°C[36]. The direct alkylate was not identified conclusively, but was certainly a substituted cyclohexane. Little or no dimerization of the naphthene occurred. This is confined to cyclopentyl rings. Apparently in this case, the methylcyclohexane alkylated before it could isomerize to ethylcyclopentane.

The inclusion of naphthenes in an alkylation reaction is therefore a major variation. The naphthenes react more readily than isoparaffins. They contribute more to hydrogen transfer reactions. Most important of all, the cyclopentane derivatives, or those naphthenes which can form cyclopentane derivatives under the conditions used, can undergo a dimerization or condensation reaction which leads to substituted decahydronaphthalene as a substantial part of the product.

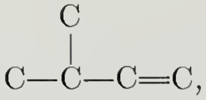
Olefin Variation. The effect of variation in the olefin used is almost wholly that due to the change in the carbon skeleton of the olefin. In other words, the olefins, except for isobutylene and ethylene, do not differ sufficiently in their rates of polymerization, ease of acceptance of protons, or other such factors to permit these to produce differences greater than those due to the fact that the structure is changed. For example, among the butylenes there is no profound change in molecular weight distribution of the alkylate at short contact times. Isobutylene and butene-2 alkylates are predominantly trimethylpentanes. Butene-1 alkylate is predominantly dimethyl-hexanes. Otherwise, the products are remarkably similar. The yield of "abnormal" products, or products of secondary reaction, is about the same. Butene-1 and butene-2 can give similar alkylates if the olefin is contacted with acid before encountering the isoparaffin. In this case, both butenes approach an equilibrium mixture which gives a mixed alkylate.

Ethylene is the only olefin which requires somewhat more severe conditions than the other olefins for its alkylation. This may be explained as due to the stability of the ester formed with the acid catalyst. Its rate of polymerization is very low and so the product has virtually no hydrogenated polymer.

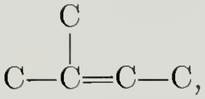
The alkylation of isobutane with propylene[35] poses no unusual problems in terms of the mechanism already given. The alkylate is chiefly heptanes (2,3-dimethylpentane and 2,4-dimethylpentane) with some decanes. This is consistent with other observations.

Pentenes, when alkylated, produce a complex alkylate with many "abnormal" products. This is due in part to the greater number of olefins possible in the pentene system:

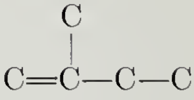
$C{=}C{-}C{-}C{-}C$, $C{-}C{=}C{-}C{-}C$,



$C{-}\overset{\overset{\displaystyle C}{|}}{C}{-}C{=}C$,



$C{-}\overset{\overset{\displaystyle C}{|}}{C}{=}C{-}C$,



$C{=}\overset{\overset{\displaystyle C}{|}}{C}{-}C{-}C$

Another contributing factor is that the primary alkylation products are more inclined to undergo rearrangement and cleavage than those from lighter olefins. Hydrogen transfer also occurs more readily than with lower olefins. Pentene-2[33], for example, produced an 11 to 15 per cent yield of isopentane. A branched olefin, 2-methyl-2-butene, yielded even greater amounts of isopentane. The saturation of propylene trimer and butylene dimers has already been mentioned.

Cyclic olefins can be considered to follow the sequence described above[46]. Methylcyclopentene, for example, can be expected to alkylate with isobutane to yield tetramethylcyclohexanes. Cyclohexene[33] apparently rearranges to methylcyclopentene and yields substituted cyclohexanes and substituted cyclopentanes in a manner already depicted. Hydrogen transfer seems to be low.

Monoolefinic polymers will undergo hydrogen transfer with the isoparaffin to yield a saturated product having the same structure as the polymer. The isoparaffin will simultaneously undergo self-alkylation. Thus, propylene trimer and isobutane yields nonanes and 2,2,4-trimethylpentane.

Ratios of Catalyst, Olefin and Isoparaffin. Variation in the ratios of catalyst, paraffin and olefin can produce profound changes in the character of the alkylate, some of which are obvious. Reduction of the molar ratio of isoparaffin to olefin much below 5 leads to some unsaturation in the product due to the polymerization of the olefin. In the case of sulfuric acid and hydrogen fluoride, a liquid volume about equal to that of the hydrocarbon phase has been found best. Reduction of the volume of acid below this level leads to more unsaturation and a greater yield of high-boiling alkylate in the product. A minimum-sized pool of acid is apparently required to keep the product saturated by hydrogen transfer reactions.

In the case of soluble catalysts such as an alkyl fluoride-BF_3 system, the characteristic feature is the rapid dissipation of the catalytic action so that the extent of the secondary reactions is not as great as with HF or H_2SO_4. In the latter case, high-boiling alkylate can be reacted to undergo cleavage and saturation of the lower molecular weight products. A pool of catalyst is available at all times for this purpose. With the alkyl fluoride-boron trifluoride catalysts, only a small pool of hydrogen fluoride-boron trifluoride is available after the first occurrence of reaction. Consequently, these alkylates are characterized by larger yields of high-boiling alkylate.

The unlikelihood of the isoparaffin reacting directly and rapidly enough with H_2SO_4 to provide a plausible alkylation sequence was indicated by experiments with optically-active hydrocarbons[10]. Exchange and racemization occurred at such a slow rate that, in comparison to known rates of alkylation, direct reaction between the isoparaffin and acid could not be involved. The acid strength (80 per cent) used in this work is considerably less than usual for alkylation, but the results are probably significant. They suggest that an alkylation sequence involving initial interaction of the acid and olefin is much more likely.

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CHAPTER 2

CATALYTIC ISOMERIZATION OF HYDROCARBONS

(Mechanisms, Kinetics, and Thermodynamics)

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INTRODUCTION

In 1942 a 500-page book[55] was needed to cover adequately the isomerization of hydrocarbons; and one much longer could be filled today. Therefore, this chapter is limited to consideration of certain theoretical and physical chemical aspects of the catalytic isomerization of five classes of hydrocarbons, namely, alkanes, alkenes, alkynes, naphthenes, and aromatics. The aspects considered are, broadly, mechanisms, kinetics, and thermodynamics.

No complete catalog of isomerization experiments, such as will be found in the monograph by Egloff, Hulla, and Komarewsky[55], which covers the literature through 1941, has been attempted here. The extensive patent literature on isomerization has been ignored; and only passing mention is made of the technological aspects[89]. Another omission worth mentioning is the considerable study that has been made of isomerization of terpene hydrocarbons. This field has aspects of special and growing interest and could well form the basis of a valuable monograph. Other omissions will be apparent to those acquainted with any of the many ramifications of the subject.

To balance these omissions, the list of references is probably longer than is absolutely needed for the stated objectives and therefore may serve to guide the reader to additional information about any subject in which he is particularly interested.

Noncatalytic Isomerization

Few hydrocarbon isomerizations take place in the absence of a catalyst. *n*-Octane has been reported to give isomers and olefins when passed through a porcelain tube at 450 to 600°[253]; but optically active 3-methylhexane was not racemized at 400°, despite slow thermal decomposition[293]. Noncatalytic *cis-trans* isomerization of 2-butene takes place without decomposition at 347 to 420°[124]; but interconversion of 1- and 2-butene[106] and 1- and 2-pentene[107] at 500 to 700° is accompanied by extensive decomposition. 1-Alkynes gave some isomeric 1,2-alkadienes when pyrolyzed at 500 to 600° but considerable decomposition also took place[105].

Noncatalytic isomerization appears to be limited almost entirely, therefore, to *cis-trans* rotation about the double bond and to shifts in the positions of multiple bonds. The fact that the latter type of isomerization requires temperatures which are high enough to cause concurrent pyrolysis suggests that the rearrangement under these conditions takes place by the same sort of mechanism as the pyrolysis[107].

General Aspects and Mechanisms

Survey of Isomerization Catalysts and Conditions

All inorganic catalysts may be broadly described as acidic (electron pair-accepting), basic (electron pair-donating), or *mono*-electronic (oxidative-reductive, hydrogen active). Catalysts having both acidic and electronic or both basic and electronic properties are also known. There are thus five classes of catalysts: acidic, basic, electronic, acidic-electronic, and basic-electronic. Furthermore, acids are not without basicity; and bases are not without acidity. The behavior of these substances under any circumstance is such as to focus attention on one of these attributes, its conjugate fading into the background so that its presence is likely to be forgotten. But their catalytic activity is probably more often than not to be ascribed to the presence of both of these conjugate properties in some degree.

Isomerization of hydrocarbons can be effected with catalysts representative of each of the aforementioned classes. Representative of basic catalysts active for isomerization are alkali metal hydroxides[12, 13, 63, 88, 115], amides[82a, 250], hydrides[309a], and organosodium compounds[131, 217b]. However, with basic catalysts, isomerization appears to be limited to shifts in the position of double bonds of olefins[12, 13, 82a, 217b, 250, 309a], and to certain alkyne-alkadiene interconversions[63, 88, 115, 131] (pages 101–102, 112–114). Representative of electronic catalysts active for isomerization are various forms of pure or supported nickel[29, 63a, 135, 270, 290, 316], palladium[315], or platinum[137, 144], and activated charcoal[48, 273]. With such catalysts isomerization appears to be limited to shifts in the position of double bonds[135, 137, 144, 270, 290, 315], interconversion of geometrical isomers of olefins[63a, 270, 273, 290] (pages 98–101), and inversion of configuration at a saturated carbon[29, 48, 316] (pages 44–51). The catalysts most generally effective for isomerization of hydrocarbons are acidic.

Acidic catalysts are either halides or chalcides (oxides or sulfides) and may be divided into three groups on the basis of chemical constitution, as follows: (1) acidic halides, (2) hydrogen acids, and (3) acidic chalcides. Representatives of each of these groups are listed below.

Acidic halides. Of these, aluminum chloride and aluminum bromide are most active and have been most widely used. Others are:

BF_3 (boron trifluoride) used in conjunction with a large amount of hydrogen fluoride, isomerized *n*-butane, *n*-pentane, and *n*-heptane at 32 to 85°[104] and polymethylbenzenes at 20 to 121°[121, 160] (pages 51–56, 107–110).

$FeCl_3$ (ferric chloride) isomerized 1,3-dimethyl-4-butylbenzenes to 1,3-dimethyl-5-butylbenzenes at 80 to 100° but unlike aluminum chloride[177, 180], it did not isomerize 1,3-dimethyl-4-propyl- and -4-ethylbenzene at 150°[179].

I_2 (iodine) isomerized 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene at about 55°[43], and brought about equilibrium between *cis*- and *trans*-1,3-pentadiene in 18 hours at about 45°[66].

$MgCl_2$ (magnesium chloride) isomerized 2,5-dimethyl-1,5-hexadiene to a conjugated diene with polymerization at 220°[101].

$ZnCl_2$ (zinc chloride) isomerized *n*-heptane and *n*-octane at 300 to 400°[202].

The acidic halides have been used on carriers and with solvents, with which they may be more or less strongly complexed. Thus zinc chloride deposited on pumice made an efficient catalyst for isomerization of straight-chain olefins to branched-chain olefins in the temperature range 250 to 375°[33, 198, 199]. A boron fluoride-ether complex slowly isomerized *cis*-stilbene to *trans*-stilbene at room temperature, but was much less active for this purpose than boron fluoride in carbon tetrachloride as a solvent. The rate of isomerization of *trans*-2-butene with boron fluoride-water mixtures was found to be markedly dependent upon water concentration and reached a sharp maximum at a $BF_3:H_2O$ ratio of about 2:1. At higher water concentrations the rate falls off very sharply and eventually complete poisoning results, presumably due to the formation of $BF_3 \cdot 2H_2O$[54a]. Magnesium bromide, prepared and used in anhydrous ether, has been observed to shift the position of the double bond of 1-dodecene toward the center of the molecule[5]. An 8 to 12 per cent solution of aluminum chloride in antimony trichloride, which is molten above about 70°, isomerizes *n*-butane and *n*-pentane[158]; and a commercial process using such a solution at 80 to 100° has been described[75]. Solutions of aluminum chloride in organic solvents, namely, acetone, benzophenone, ethyl or isopropyl ether, isopropyl acetate, and nitrobenzene, have been found to isomerize *n*-butane and *n*-pentane at 30 to 100°, provided that the molar ratio of aluminum chloride to solvent was greater than one[65]. A ternary alloy of aluminum chloride, cadmium sulfate and magnesium sulfate has been used to isomerize normal paraffins at 80°[189]. Results with these compositions do not differ qualitatively from those with aluminum chloride alone.

It has been amply demonstrated that a source of protons such as a hydrogen halide or water must be present, often in comparatively small amount, in order for the acidic halides to show catalytic activity[54a, 111, 134, 207, 265]. The proton source may in some instances be produced by oxidation of the substrate, as with ferric chloride[179] or iodine, or in promotion of aluminum halides with oxygen[219] (pages 56–57, 62–66). Their catalytic activity then resides in their ability to accept electrons in pairs and thereby to loosen protons in the proton source.

Hydrogen acids (*"Bronsted acids"*). These are definite molecules with readily ionizable protons. Sulfuric acid is typical and has been most widely used[30, 30a, 30b, 82, 122, 128, 155, 173, 234, 267, 269a] (pages 68–73). They are essentially fully hydrated chalcides (oxides) or can be regarded as derivatives of a fully hydrated chalcide. The organic sulfonic acids, for example, are derivatives of sulfuric acid. Some catalysts other than sulfuric acid representative of this group are compiled below.

$ClSO_3H$ (chlorosulfonic acid) racemized (+)3-methylheptane[82] at 0° and (+)3-methylhexane[30a] at −78° with shift of the methyl group to the "2" position in each case.

FSO_3H (fluorosulfonic acid) racemized (+)3-methylhexane at −78° with shift of the methyl group to the "2" position[30a].

$C_2H_5SO_3H$ (ethanesulfonic acid) racemized (+)3-methylheptane at 102 to 106°[82]. It appears to be less active, whereas the halosulfonic acids appear to be more active, than sulfuric acid[82].

$C_7H_7SO_3H$, (*p*-toluenesulfonic acid), in acetic acid solution, converted methylenecyclopentane to 1-methylcyclopentene[273a].

$C_{10}H_7SO_3H$ (β-naphthalenesulfonic acid) has been used to effect *cis-trans* interconversions in cycloöctene[322] and cyclononene[23] at 150° and in cyclodecene[22] at 170 to 180°. It was used in the presence of hydroquinone to retard oxidation.

Phosphoric acid (H_3PO_4) at 26 to 135°, aqueous perchloric acid (70 to 72 per cent $HClO_4$) at 21°, and aqueous benzenesulfonic acid (75 per cent $C_6H_5SO_3H$) at 76° isomerized 1-butene to 2-butene[113]. At 325 to 360°, phosphoric acid on pumice converted straight-chain olefins to branched-chain isomers[198, 200, 204, 205].

Acidic chalcides. The elements of Group VIA of the Periodic Table, namely, oxygen, sulfur, selenium, and tellurium, have been called "chalcogens" (kal'ko jens), a term analogous to "halogens," used for the elements of Group VIIA. Accordingly, compounds of these elements may be called "chalcides." Chalcide catalysts include a great variety of solid oxides and sulfides, the most widely used comprising alumina[1, 17, 18, 60, 79, 96, 97, 101, 135, 139, 145, 164a, 175, 184, 188, 312], silica[74, 312, 313], and mixtures[18, 187, 201, 203] of alumina and silica, either natural or synthetic, in which other oxides such as chromia[138, 141, 142, 142a, 142b, 146-9], magnesia[292], molybdena[39, 40, 83], thoria[21], tungstic oxide[39], and zirconia[21, 175], may also be present, and a sulfide of molybdenum (see below). A myriad of compositions is possible and it must be admitted that some have been used as catalysts, such as bauxite[18, 269, 292], floridin[73, 254-62], Georgia clay[97], and other natural aluminosilicates[73, 183, 269, 272a, 320], about which certain features of composition and structure remain unknown.

Some synthetic catalysts, other than silica-alumina compositions, representative of the acidic chalcide group are compiled below.

BeO converted cyclohexene to methylcyclopentenes at 450° and 1-octene to methylpentenes at 450°[3, 4, 314].

Cr_2O_3 isomerized 1,5-hexadiene to 2,4-hexadiene[140] and 1,2-hexadiene to 2,4-hexadiene and hexynes[149] at 225 to 250°.

P_2O_5 isomerized 1-phenyl-1-pentene to an unidentified isomer resembling phenylcyclopentane[54].

ThO_2 isomerized olefins at 398 to 440°[79].

TiO_2 isomerized straight-chain heptenes to methylhexenes at 450°[4].

$Al_2(SO_4)_3$ which may be regarded as $Al_2O_3 \cdot 3SO_3$, isomerized 1-butene to 2-butene at elevated temperatures[76, 273], and converted straight-chain olefins to branched-chain isomers in the temperature range 265 to 500°[73, 97].

Al_2O_3-Cr_2O_3, Al_2O_3-Fe_2O_3, Al_2O_3-CoO, and Al_2O_3-MnO (each 4:1 by weight) were used in a study of equilibrium among the three isomeric methylbutenes[60] at 294 to 370°.

Al_2O_3-Fe_2O_3 (9:1 by weight) isomerized cyclohexene to methylcyclopentenes at 300° provided hydrogen chloride was present[251].

Al_2O_3-Mo_2O_3 isomerized *n*-pentane at 460° and 33 atm. with molar ratios of hydrogen to pentane less than one[40].

Al_2O_3-V_2O_3 isomerized cyclohexene to methylcyclopentenes at 400 to 500°. The isomerization was accompanied by intermolecular hydrogen transfer on this catalyst, producing benzene and cycloalkanes[224].

Cr_2O_3-Fe_2O_3 shifted the position of double bonds and triple bonds in olefins, diolefins, and alkynes, apparently without alteration of the carbon skeleton in the temperature range 220 to 300°[136].

Molybdenum sulfide, variously designated as MoS_2[154, 181-2, 228, 232, 269] or MoS_3[163, 202], isomerized straight-chain paraffins[163, 181-2, 204], converted cyclohexane to methylcyclopentane[2, 71, 154, 232], decahydronaphthalene to dimethylbicyclooöctanes[227], and perhydrophenanthrene to perhydroanthracene[228] in the temperature range 370 to 430°.

A molybdenum sulfide-cobalt sulfide catalyst has been used to convert cyclohexane to methylcyclopentane at 500°[229].

In contrast to sulfuric acid, which may be regarded as a fully hydrated chalcide, the chalcides of this group are seldom very highly hydrated under conditions of use. However, adsorbed protons are probably essential to their activity as catalysts (pages 74–75). They are sometimes activated for use by treatment with aqueous mineral acid and then dried at a high temperature[17, 97, 164a, 188].

These substances possess the properties of being physically and chemically stable and catalytically active at temperatures approaching the threshold for thermal decomposition of hydrocarbons. Yet their acidity is not so great as to lead them to form stable complexes with unsaturated hydrocarbons, as do the aluminum halides, for example. For these reasons, they are frequently used at high temperatures and are preferred for isomerization of unsaturated hydrocarbons, which are polymerized by strongly acidic catalysts at low temperatures. Polymerization is thermodynamically disfavored by high temperatures.

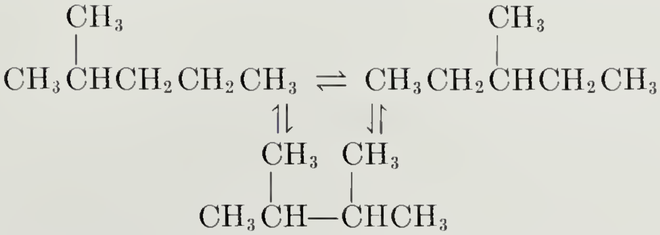
Chalcide catalysts are not very effective for isomerization of *saturated* hydrocarbons, unless they possess electronic as well as acidic properties. Electronic properties (hydrogen activity) may be imparted by the presence of a transition metal or transition metal oxide, such as cobalt[39], nickel[38, 39, 217a], and platinum[39, 90, 162a, 297a], or molybdena[39, 40, 83], tungstic oxide (WO_3)[39], and zirconia[21]. Less effective in conferring activity for isomerization of saturated hydrocarbons are the transition metals copper and iron[39]. The use of hydrogen with these catalysts is beneficial, perhaps essential, to isomerication of saturated hydrocarbons. Results obtained with one of these "acidic-electronic" (page 51) catalysts are presented in Tables 11, 12, 16, and 20; and their characteristics are further discussed on pages 72–95.

Isomerization of Saturated Hydrocarbons

The phenomena associated with catalytic isomerization of paraffins and cycloparaffins are similar; and these two classes of saturated hydrocarbons will be treated together. The main question to be answered here is how these substances, which classical organic chemistry and the etymology of the word "paraffin" tell us are chemically inert, are influenced by certain substances to undergo deep-seated structural changes at ordinary temperatures, sometimes very rapidly.

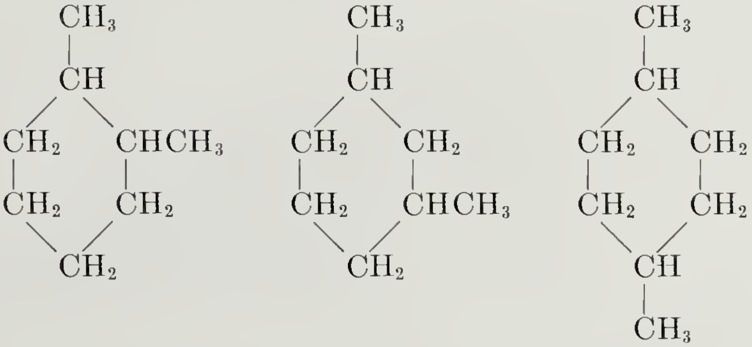
Phenomenological Aspects. The isomerization of a paraffin or cycloparaffin may comprise simply inversion of configuration at a saturated carbon or a more deep-seated isomerization with alteration of the carbon skeleton. Inversion of configuration is represented by the racemization of an optically active saturated hydrocarbon[30, 30a, 82, 100] or by the interconversion of *cis*- and *trans*-isomers of a cyclic saturated hydrocarbon[234, 249, 316]. These changes have been effected by catalysts of the "electronic" type as well as by acidic catalysts (pages 51–78).

It is convenient to distinguish two types of isomerization involving a change in carbon skeleton. These are: (a) interconversion of isomers having at least one tertiary carbon; and (b) interconversions involving an isomer with no tertiary carbon. Type (a) may be illustrated by interconversions among 2- and 3-methylpentanes and 2,3-dimethylbutane:

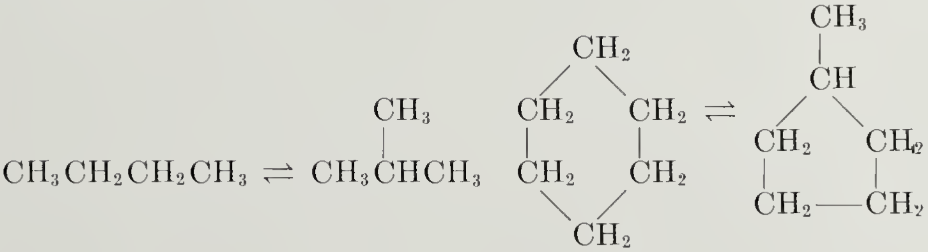


$$\begin{array}{c} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3 \rightleftharpoons CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \\ \upharpoonleft\downharpoonright \qquad \downharpoonleft\upharpoonright \\ CH_3\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array}$$

or by interconversions among the various dimethylcyclohexanes:



Type (b) may be illustrated by the butane-isobutane and cyclohexane-methylcyclopentane interconversions:



Type (a) isomerizations are "easier" than those of type (b). They can be effected by sulfuric acid at 25°[234, 267] and by a silica-alumina catalyst at 150°[187], conditions which appear to be ineffective for type (b) isomerizations (pages 68–73, 73–78). With catalysts which are capable of effecting both types of isomerization at moderate temperatures, such as aluminum chloride, type (a) isomerizations are faster than those of type (b)[59] (pages 51–56).

The isomerization of a paraffin may be accompanied by side reactions leading to paraffins of higher and lower molecular weight (disproportionation) and to unsaturated hydrocarbons that form a complex with the catalyst. The extent of these side reactions depends on the structure and molecular weight of the paraffin, on the temperature, on the percentage conversion, and on the catalyst. The side reactions can sometimes by suppressed by carrying out the isomerization in the presence of hydrogen under pressure[58, 80, 114, 126, 245], or in the presence of a small amount of an aromatic compound[58, 80, 156], a moderate amount of a cycloparaffin[58, 156], or a large amount of isobutane[58, 156, 247]. The nature and control of side reactions is discussed in more detail on pages 82–97.

A consideration of the extensive data on the isomerization of *cycloparaffins* leads to the following generalizations: (1) Alkylcyclopropanes do not undergo ring enlargement, but are isomerized to olefins[197] or polymerized[212] instead. (2) Alkylcyclobutanes, except methylcyclobutane[212], are partly isomerized and partly polymerized, depending on the structure[212, 274, 280] (pages 115–116). (3) Alkylcyclopentanes[34-7, 213, 216, 275-9, 281, 285, 287-9] and alkylcyclohexanes[34-7, 38, 319] are readily interconvertible with practically no side reactions at moderate conditions of temperature, time, and catalyst activity unless there is a long alkyl side chain. Cracking was extensive, for example, in the isomerization of *n*-amylcyclopentane with aluminum chloride at 150°[288], but not in the isomerization of *n*-butylcyclopentane under the same conditions[279]. (4) Cycloheptane[217, 286], cyclooctane[274, 282], and their alkyl derivatives[283] isomerize with ring contraction to alkylcyclohexanes mainly.

Results of isomerization of cycloparaffins thus reflect the stability of the cyclohexane ring relative to rings smaller or larger. Appreciable quantities of isomers having the cyclopentane ring appear in equilibrium mixtures only at elevated temperatures. This generalization covers the limited number of examples of isomerization of *bicyclic* saturated hydrocarbons as well as those having only one ring. Thus bicyclopentyl, treated with aluminum chloride, underwent a very exothermic reaction leading to the isomeric decahydronaphthalene[287a]. Decahydronaphthalene itself is converted to some extent to dimethylbicyclooctanes with five-membered rings only under forcing conditions[21, 117, 227, 317]. Hydrindan, treated with aluminum chloride at 170 to 230°, decomposed to monocyclic and paraffinic hydrocarbons[284]. Bicyclohexyl was partially converted to isomers having one or two cyclopentane rings by heating with aluminum chloride at 100°[150, 191].

Although cycloparaffin isomerization is practically free of side reactions, with the exceptions noted above in the case of small-ring compounds and those having a long alkyl side chain, deep-seated changes are brought about by isomerization catalysts under severe conditions. The behavior of hydrindan described immediately above is illustrative. Cyclohexane gave isobutane, dimethylcyclohexane, and bicyclic $C_{12}H_{22}$ hydrocarbons when heated with aluminum chloride and hydrogen chloride at 150° for 24 hours[112]. Unlike the reaction with a paraffin[86], no unsaturated hydrocarbon-catalyst complex was formed.

Isomerization with Electronic-type Catalysts. Isomerization of saturated hydrocarbons by means of catalysts with which acidic properties are not ordinarily associated appears to be limited almost entirely to inversion of configuration at a saturated carbon. Thus, optically active (+)3-methylhexane was racemized by nickel-on-kieselguhr in the presence of hydrogen at 103 to 154°[29], and *cis*-1,2- and 1,4-dimethylcyclohexanes were converted to their *trans* isomers on nickel at 175°[316]. A related observation is the racemization of optically active 2-phenylbutane on activated carbon at about 200°[48]. In one recorded instance of isomerization with change in carbon skeleton on such a catalyst, *n*-octane gave 15.6 per cent isomers when passed over a platinum-on-carbon catalyst in a stream of hydrogen at 310°[310].

The mechanism of these transformations is obscure. Hydrogen appears to be necessary and simultaneous exchange with hydrocarbon hydrogen occurs[29]. The relative rates of exchange and racemization are such as not to exclude a dehydrogenation-rehydrogenation mechanism for inversion on catalysts of this type[29].

Isomerization with Acidic Halides. *Need for Promoters.* Although aluminum bromide and aluminum chloride, *as ordinarily prepared and handled*, are catalysts for the isomerization of saturated hydrocarbons, it has been established that these substances are ineffective in the absence of a promoter or initiator. For example, pure aluminum bromide is ineffective on *n*-butane[134, 218], even at temperatures as high as 84°[99], and, in the absence of moisture, it has no effect on *n*-hexane[87], *n*-heptane[87], methylcyclopentane[265], cyclohexane[265], or cycloheptane[217]; and pure anhydrous aluminum chloride is ineffective on *n*-butane[218], *n*-pentane[78, 219], *n*-hexane[110], *n*-heptane[110], 2,2-dimethylbutane[129], or 2,2,4-trimethylpentane[110] at moderate temperatures. Furthermore, *n*-butane was not isomerized by boron fluoride-hydrogen fluoride at 50° unless a trace of olefin was present. It may be concluded, therefore, that certain substances, some of which may ordinarily be present as impurities, play an essential role in catalysis by the acidic halides.

Early Mechanisms. Early experiments with a high vacuum technique indicated that the hydrogen halides, alkali metal halides, boron fluoride, and organic halogen compounds would promote isomerization of *n*-butane by aluminum bromide[98]. Data obtained in these experiments are presented in Table 1. Furthermore, in the presence of hydrogen bromide and aluminum bromide, the rate of isomerization of *n*- or iso-butane seemed to be proportional to the concentration of $HAlBr_4$ which was calculated from the stoichiometry of the reaction

$$Al_2Br_6 + 2HBr \rightarrow 2HAlBr_4$$

on the assumption that the reaction has an equilibrium constant so large that the amount of $HAlBr_4$ produced was determined by the amount of that reagent added in limiting amount[134].

TABLE 1. EARLY-INDICATED PROMOTERS FOR ALUMINUM BROMIDE-CATALYZED ISOMERIZATION OF *n*-BUTANE[98, 206]

Promoter	Charge, moles/100 moles butane		Time (hr)	Isobutane formed (%)
	$AlBr_3$	Promoter		
a. Experiments at 25 ± 3°				
None	116[a]	—	360	2
HBr	10.4	13.5	96	14
HBr	29.5	7.6	72	17
HBr	3.7	4.0	149	38
NaBr	17.1	20.7	96	0.4
NaBr	6.1	6.1	286	10
NaCl	34.7	18.8	96	0.5
BF_3	15.6	1.8	95	>45
CH_3Br	10.6	16.0	96	11
b. Experiments at 84 ± 2°				
None	3.5	—	12	0
HBr	2.9	0.7	12	8
HBr	2.4	1.7	12	15
HCl	29.6	1.4	58.7	59
HCl	6.5	5.2	44.4	>69
NaBr	1.6	3.5	59	5
NaBr	3.0	10.2	44	12
NaCl	3.3	5.3	44	38–40
NaCl	2.8	8.1	35	31–36
BF_3	1.3	5.0	59	20
BF_3	2.8	10.6	44	42
$n\text{-}C_4H_9Br$	17.5	6.1	12	36

[a] 67°. *n*-Butane saturated with $AlBr_3$ (from Ref. 99).

On the basis of these observations, it was proposed that AlX_4^- is the catalyst and acts as both an acid and a base, aluminum exhibiting a coordination number greater than four when the AlX_4^- ion acts as an acid. The isomerization was visualized as in Figure 1[98, 206].

Stage 1. An oriented collision of the hydrocarbon with catalyst (AlX_4^-) produces a cyclic configuration with a carbon (designated C_1) within bonding distance of the aluminum and a hydrogen on C_3 (or C_4) within bonding distance of a halogen.

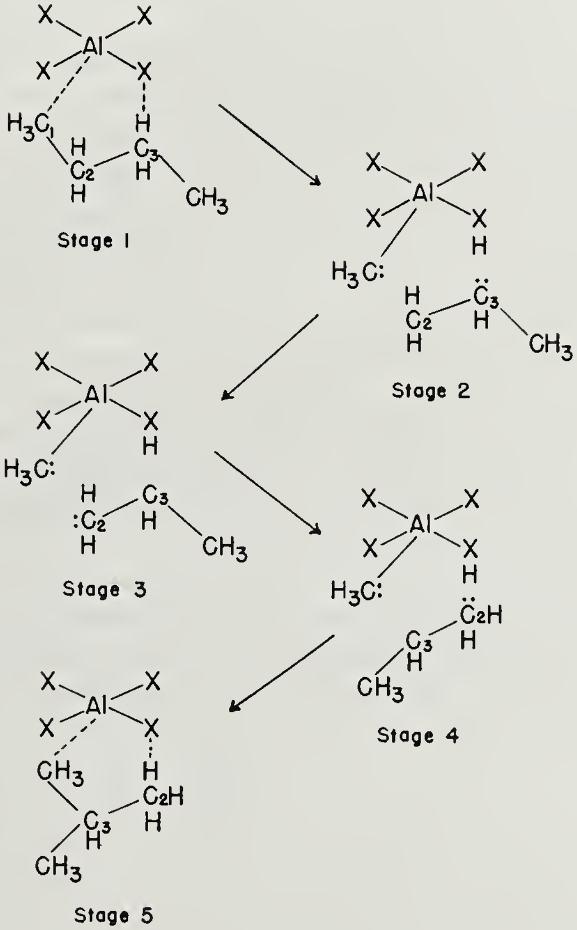


Figure 1. Mechanism of isomerization of *n*-butane, according to Heldman[98].

Stage 2. An activated complex is produced in which an alkyl fragment and a hydrogen from the hydrocarbon are loosely attached to AlX_4^- and the hydrocarbon residue is restrained from moving from the vicinity by residual attractive forces or by the cage effect if the isomerization is in the liquid phase.

Stage 3. A shift of an electron pair occurs within the hydrocarbon residue.

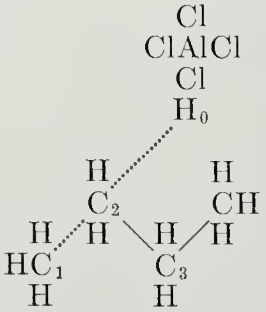
Stage 4. The hydrocarbon residue rotates with respect to AlX_4^- and its attached fragments.

Stage 5. Recombination of the hydrocarbon residue and the fragments from the catalyst gives a rearranged product.

In order to account for the promoting effect of BF_3 indicated by the data in Table 1, it was proposed that substances of the type $(Al_2Br_5)^+(BF_3Br)^-$ were formed, with $Al_2Br_5^+$ being an active catalyst. In order to account for the side reactions observed with higher homologs of butane and with butane at high temperatures, it was believed that the rotation (Stage 4) may become so violent at high temperatures as to result in separation of the hydrocarbon residue from the catalyst and its attached fragments; or with homologs larger than butane, a long tail on the rotating hydrocarbon residue may whip this fragment out of the reach of the catalyst[98].

A somewhat different picture of the isomerization reaction was drawn as the result of an isotopic tracer study of the exchange of hydrogen between the butanes and hydrogen or hydrogen chloride during aluminum chloride-catalyzed isomerization at 100 to 125°. Tritium, the radioactive isotope of hydrogen, was used as the tracer. The amount of exchange roughly paralleled the amount of isomerization; and exchange between hydrogen chloride and butane was large compared to that between hydrogen and butane. On the basis of these observations, it was assumed that in the presence of a suitable support the compound $HAlCl_4$ is formed, with a resultant weakening of the HCl bond, and the following mechanism of isomerization and exchange was proposed[225].

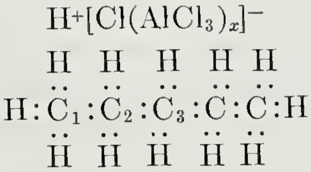
Stage 1. The butane contacts the catalyst mass so that the hydrogen of the $HAlCl_4$ (designated as H_0 in the diagram below) enters the bonding sphere of a carbon atom (designated as C_2) of the butane. This results in a weakening and partial rupture of the bond between C_2 and C_1.



Stage 2. The $AlCl_4$ takes a hydrogen from C_3.

Stage 3. A new bond forms between C_1 and C_3 to give the rearranged product. The isomerization of isobutane to *n*-butane can be readily pictured by the same steps in reverse order.

According to a similar mechanism[58], the catalyst, assumed to be a strong acid resulting from association of hydrogen chloride and aluminum chloride, $[HCl \cdot (AlCl_3)_x]$, becomes loosely associated with a paraffin somewhat as shown below for *n*-pentane:



$$\begin{array}{c} H^{+}[Cl(AlCl_{3})_{x}]^{-} \\ \begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ H & : & C_1 & : & C_2 & : & C_3 & : & C & : & C & : & H \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \\ & & H & & H & & H & & H & & H & & \end{array} \end{array}$$

The proton becomes attached to C_2 displacing C_1 as an alkyl positive ion. Meanwhile the anion of the strong acid takes a proton from C_3. The C_1 alkyl positive ion then becomes attached to C_3 to give the rearranged product. As long as the catalyst and hydrocarbon remain closely associated, no cracking occurs. Cracking occurs, according to this mechanism, when the C_1 alkyl positive ion moves further than some critical distance from the catalyst environment and picks off a hydrogen from an adjacent hydrocarbon molecule, thus stabilizing itself.

The foregoing ideas regarding the mechanism of catalytic isomerization of saturated hydrocarbons have not been very fruitful and have been largely discredited by subsequent findings, although the protolytic cracking described in the last paragraph may play a role in the action of aluminum chloride and hydrogen chloride on saturated hydrocarbons at high temperatures where no promoter is required and cracking is extensive. This possibility is discussed in more detail later (page 83).

In conflict with the foregoing mechanisms, experiments directed toward preparation of compounds between aluminum halides and hydrogen halides, such as $HAlX_4$, have only provided evidence that such compounds are not formed under the conditions of isomerization. A careful study of the system $AlCl_3$-HCl indicated no compound formation in the temperature range −120 to 300°[27]. The solubility of hydrogen bromide in *n*-butane was not increased by the addition of aluminum bromide; instead a slight decrease in solubility was found[64]. Hence it must be concluded that $HAlBr_4$ is not formed under these conditions. However, in the presence of a proton acceptor, "B," a "salt" of the hypothetical strong acid, $HAlX_4$, may be formed with the structure, $BH^+(AlX_4)^-$ [27].

Furthermore, although the data in Table 1 indicate that the hydrogen halides promote isomerization by aluminum bromide, subsequent work with rigorously purified reagents showed that isomerization of *n*-butane does not take place at moderate temperatures in the presence of either aluminum bromide-hydrogen bromide or aluminum chloride-hydrogen chloride. The addition of vanishingly small amounts of an olefin caused isomerization[218]. This effect is illustrated by the data in Tables 2 and 3. The isomerization of *n*-butane in the presence of aluminum bromide and hydrogen halides reported in Table 1 may have been due to the presence of traces of olefins as impurities in the butane used.

Oxygen was also found to be an effective promoter for the aluminum halides[186, 219], even in the absence of hydrogen halides and olefins. In comparison with the effect of oxygen, shown in Table 4, the promoting effects of alkali metal halides and boron fluoride indicated by the earlier data in Table 1 seem vanishingly small. That is, comparatively large amounts of the latter substances were used; yet only little isomerization occurred in some cases after a long period of time. It is conceivable the effects observed with these substances were actually due to oxygen introduced as air adsorbed on the crystalline substances or to some other very active promoter present in trace amounts as an impurity.

TABLE 2. EFFECT OF OLEFINS ON ISOMERIZATION OF n-BUTANE IN THE PRESENCE OF ALUMINUM BROMIDE-HYDROGEN BROMIDE AT 25°[218]

Experiment	1	2	3	4	5
Charge, moles/100 moles n-butane					
$AlBr_3$	10.0	9.3	9.3	9.3	9.3
HBr	0	2.3	2.3	2.3	2.3
"n-Butenes"	0	0	0.03	0.08	0.58
Reaction time, hr	508[a]	15	15	15	15
Isobutane formed, %	0	0.2	2.1	19.3	65.6

[a] Includes 8 hours exposure to sunlight.

TABLE 3. EFFECT OF OLEFINS ON ISOMERIZATION OF n-BUTANE IN THE PRESENCE OF ALUMINUM CHLORIDE-HYDROGEN CHLORIDE AT 100°[218]

Experiment	1	2	3	4	5
Charge, moles/100 moles n-butane					
$AlCl_3$	5.86				
HCl	3.05				
"n-Butenes"	0	0.013	0.05	0.09	0.28
Reaction time, hr	12				
Product composition, mole %					
n-Butane	99.9	87.6	87.0	82.8	72.3
Isobutane	<0.1	11.8	12.6	16.9	26.8
Pentanes and heavier	0.1	0.6	0.4	0.3	0.9

In view of the evidence against the formation of compounds such as $HAlX_4$ from aluminum halides and hydrogen halides, and in view of the necessity for olefins or their equivalent for isomerization of saturated hydrocarbons in the presence of aluminum halides and hydrogen halides, a mechanism that attributes isomerization to the action of these substances alone must be regarded as inadequate.

Application of Carbonium Ion Theory. It has been pointed out that organic reactions fall into three groups corresponding to three possible types of reaction intermediates, depending on whether the carbon atom at the site of reaction retains both, one, or none of the electrons in an electron-pair bond[91]. If carbon retains both the electrons, a *carbanion* is produced:

TABLE 4. EFFECT OF OXYGEN ON ISOMERIZATION OF *n*-BUTANE AND *n*-PENTANE IN THE PRESENCE OF ALUMINUM HALIDES AT 25°[a]

Experiment	Alkane	Charge, moles/100 moles alkane			Time (hr)	Isomerization (%)
		$AlBr_3$	$AlCl_3$[b]	O_2		
1	*n*-Butane	10.0	—	0	508[c]	0
2	"	11.0	—	0.06	192	7.5
3	"	11.0	—	0.06	21[d]	9.5
4	"	—	16.07	0.0168	121	29.9
5	"	—	17.40	0.0196	141	38.6
6	"	—	17.05	0.0112	16[e]	7.2
7	*n*-Pentane	—	23.0	0	257	1.0
8	"	—	23.0	0.013	96	27.5
9	"	—	24.3	0.007	9[e]	25.3

[a] Based on data in Ref. 219.

[b] The reaction tubes contained 123 parts by weight of activated coconut charcoal, 10–12 mesh, per 100 parts of aluminum chloride.

[c] Includes eight hours in sunlight.

[d] Includes four hours in sunlight.

[e] In sunlight without agitation.

$$-\overset{|}{\underset{|}{\mathrm{C}}}:\mathrm{X} \rightarrow -\overset{|}{\underset{|}{\mathrm{C}}}:^{-} + \mathrm{X}^{+}$$

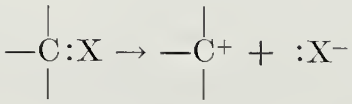
(*carbanion*)

If the electrons are divided equally by bond rupture during reaction, an organic *free radical* is produced:

$$-\overset{|}{\underset{|}{\mathrm{C}}}:\mathrm{X} \rightarrow -\overset{|}{\underset{|}{\mathrm{C}}}\cdot + \cdot\mathrm{X}$$

(*free radical*)

Finally, if carbon is stripped of an electron pair, a *carbonium ion* is produced:



$$-\overset{|}{\underset{|}{C}}:X \rightarrow -\overset{|}{\underset{|}{C}}{}^{+} + :X^{-}$$

(*carbonium ion*)

These three modes of reaction correspond well to the three fundamental types of catalysts differentiated on page 51, namely, basic, *mono*-electronic, and acidic. Thus it can be said that a basic catalyst very likely promotes reaction through formation of carbanions, a carbanion itself being a base; an electronic-type catalyst very likely promotes reaction through formation of free radicals or atoms, these being mono-electronic; and an acidic catalyst very likely promotes reaction through formation of carbonium ions, a carbonium ion being an acid (in the Lewis terminology, that is, an electron pair acceptor).

In a carbonium ion, one carbon has an "open sextet" of electrons. It was pointed out by Whitmore that most *intramolecular rearrangements* could be represented in terms of intermediates having such an "open sextet," as follows[298]:

$$:\underset{..}{\overset{..}{A}}:\underset{..}{\overset{..}{B}}:\underset{..}{\overset{..}{C}} \rightarrow \underset{..}{\overset{..}{B}}:\underset{..}{\overset{..}{C}}:\underset{..}{\overset{..}{A}}: \qquad (I)$$

The generalization was not restricted to systems in which atoms A, B, and C are all carbon; but in such systems, the intermediates would be carbonium ions. In work with neopentyl compounds, Whitmore and his students produced a parcel of evidence on which to base an argument that formation of an intermediate with an "open sextet" is necessary for intramolecular rearrangement. That is, rearrangement may occur when a carbonium ion is produced but not when a carbanion or a free radical is the reaction intermediate.

For example, rearrangement occurred in the reaction of neopentyl alcohol with hydrogen bromide to give *tert*-amyl bromide[304]; and the reaction of neopentyl iodide with silver hydroxide gave the rearrangement product, *tert*-amyl alcohol[307]. Most likely in these reactions there is removal of a negative group (hydroxyl or iodide) with the bonding electron pair to leave a neopentyl carbonium ion:

$$(CH_3)_3C—CH_2OH + HBr \rightarrow (CH_3)_3C—CH_2^+ + H_2O + Br^-$$

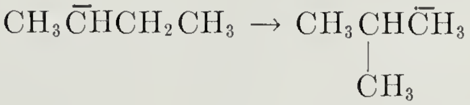
$$(CH)_3C—CH_2I + Ag^+ \rightarrow (CH_3)_3C—CH_2^+ + AgI$$

The neopentyl carbonium ion rearranges to the *tert*-amyl carbonium ion in accordance with (I), in each case leading to a rearranged product:

$$(CH_3)_3C\text{—}CH^+ \rightarrow (CH_3)_2\overset{+}{C}\text{—}CH_2CH_3$$

No rearrangement occurred in the following reactions: chlorination of neopentane[299], reaction of neopentyl chloride with sodium (Wurtz reaction)[303], formation and reactions of the Grignard reagent from neopentyl chloride and magnesium[299, 306], and the reaction of neopentyl iodide with alcoholic potassium hydroxide (produced neopentane)[307]. The most plausible mechanisms for these reactions involve the rupture of a C:X bond so as to leave one or both of the electrons with carbon to produce either a neopentyl *free radical* or a neopentyl *carbanion*.

Few exceptions to the rule that rearrangements occur with carbonium ion intermediates, not with free radicals or carbanions, have been found. The proposal[93] that catalytic isomerization involves rearrangement within a *carbanion*:



$$CH_3\bar{C}HCH_2CH_3 \rightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}\bar{C}H_3$$

must therefore be regarded as out of step with a great body of evidence and theory.

Now the isomerization of a saturated hydrocarbon is fundamentally an intramolecular rearrangement; therefore, it is logical to suppose it has a carbonium ion mechanism. That the rearrangement is intramolecular has been demonstrated most convincingly by experiments with isotopically labeled hydrocarbons. For example, the isomerization of propane-1-C^{13} to propane-2-C^{13} occurred with water-promoted aluminum bromide at room temperature with no detectable formation of molecules containing two C^{13} atoms[16]. The isomerization of butane-1-C^{13} to butane-2-C^{13} and C^{13}-containing isobutane occurred under similar conditions without formation of molecules containing more or less than one C^{13} per molecule[193]. These results establish that isomerization may be intramolecular with respect to carbon; but they do not require that the isomerization be intramolecular with respect to hydrogen. Other experiments have shown that considerable *inter*molecular transfer of hydrogen may take place during isomerization[102, 192, 267] (pages 68–79).

Before carbonium ion theory could be applied to the isomerization of saturated hydrocarbons, a mechanism for the formation of carbonium ions from them under isomerizing conditions had to be found. This was provided by the discoveries already mentioned relating to the effect of promoters, especially olefins, and by the discovery that, in the presence of aluminum halides, an extremely rapid exchange of halogen and hydrogen takes place between tertiary alkyl halides and saturated hydrocarbons having a tertiary hydrogen:

$$RX + R'H \xrightarrow{AlX_3} RH + R'X$$

For example, when a solution of *tert*-butyl chloride in isopentane was contacted with one containing an equimolar amount of aluminum bromide in a flow-type apparatus that permitted the mixture to pass quickly into a large volume of water, which destroyed the catalyst, all the *tert*-butyl chloride was converted and *tert*-amyl bromide was obtained in 50 to 70 per cent yields in the shortest reaction time obtainable (estimated to be 0.001 sec.).

This "halogen-hydrogen exchange" was interpreted as follows in terms of carbonium ions[11]:

$$(CH_3)_3CCl + AlBr_3 \rightleftharpoons (CH_3)_3C^+ + AlBr_3Cl^- \tag{II}$$

$$(CH_3)_3C^+ + HC(CH_3)_2CH_2CH_3 \rightleftharpoons (CH_3)_3CH + {}^+C(CH_3)_2CH_2CH_3 \tag{III}$$

$$AlBr_3Cl^- + {}^+C(CH_3)_2CH_2CH_3 \rightleftharpoons AlBr_2Cl + BrC(CH_3)_2CH_2CH_3 \tag{IV}$$

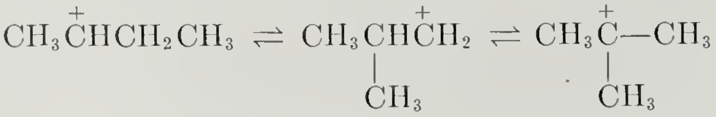
Reaction (III) is analogous to a carbonium ion rearrangement in which hydrogen migrates intramolecularly with its bonding pair of electrons from one carbon to an adjacent one carrying an "open sextet." Here, however, the shift of the "hydride" particle occurs at a collision between two different molecules. One result of such a process is that a saturated hydrocarbon is brought into an activated state in which it may undergo isomerization in accordance with well-established principles of carbonium ion rearrangements.

Accordingly, the isomerization of a saturated hydrocarbon has been represented as a chain reaction involving carbonium ions and is illustrated as follows with butane[20]:

Chain initiation:

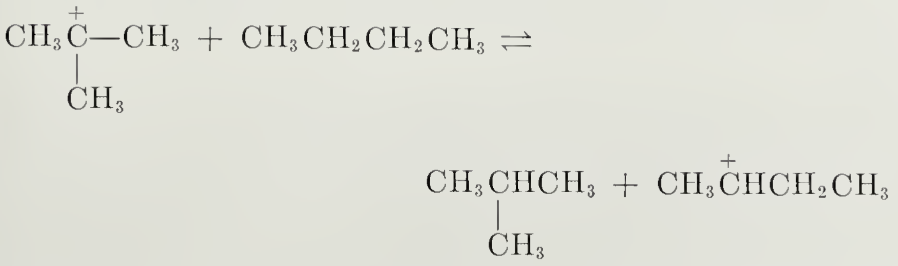
$$CH_3CH_2CH_2CH_3 + R^+ \rightarrow CH_3\overset{+}{C}HCH_2CH_3 + RH \tag{V}$$

Carbonium ion rearrangement:



$$CH_3\overset{+}{C}HCH_2CH_3 \rightleftharpoons CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{+}{C}H_2 \rightleftharpoons CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}{-}CH_3 \tag{VI}$$

Chain propagation:



$$CH_3\underset{\substack{|\\ CH_3}}{\overset{+}{C}}-CH_3 + CH_3CH_2CH_2CH_3 \rightleftharpoons CH_3\underset{\substack{|\\ CH_3}}{C}HCH_3 + CH_3\overset{+}{C}HCH_2CH_3 \qquad \text{(VII)}$$

Reactions (V) and (VII) are analogous to (III) of the halogen-hydrogen exchange mechanism. The rearrangements of (VI) are in accordance with Whitmore's generalization, (I).

Reaction (V) serves only to initiate the chain and therefore a substance that can furnish a carbonium ion in the presence of the catalyst need be present in only small amount. The need for traces of an olefin for isomerization of a saturated hydrocarbon by aluminum halides and hydrogen halides can thus be understood, since an olefin may be converted to a carbonium ion by addition of a proton from hydrogen halide:

$$CH_3CH{=}CHCH_3 + HCl + AlCl_3 \rightarrow CH_3\overset{+}{C}HCH_2CH_3 + AlCl_4^-$$

The necessity of hydrogen halide or equivalent proton source is implied here.[8] There is some evidence for such necessity. "In the absence of hydrogen bromide, aluminum bromide does not isomerize methylcyclopentane even in the presence of olefins[207]." The activity of an aluminum chloride catalyst for naptha isomerization was found to decline rapidly in the absence of hydrogen chloride. Addition of hydrogen chloride restored activity[58].

Alkyl halides are also effective promoters for isomerization by aluminum halides[98, 186, 210]. An alkyl halide may serve as a source of carbonium ions in the reaction:

$$RX + AlX_3 \rightarrow R^+ + AlX_4^- \qquad \text{(VIII)}$$

Data presented in Table 5 show that the effectiveness of the series of alkyl bromides, methyl, ethyl, and isopropyl, parallels their rates of solvolysis in aqueous formic acid; but the effectiveness of *tert*-butyl bromide is less than would be predicted from its rate of solvolysis. It may be that in the case of the first three alkyl bromides, ionization is the rate-controlling step in isomerization as in solvolysis, but with *tert*-butyl bromide, some other step, most likely the rearrangement of the carbonium ion from methylcyclopentane, is rate-controlling so that much of the *tert*-butyl bromide is destroyed by side reactions.

Bromine is an effective promoter for the isomerization of *n*-butane by aluminum bromide[186]. Presumably an alkyl bromide is formed by bromination of the hydrocarbon and serves as a source of carbonium ion by reaction (VIII).

As mentioned on page 56, oxygen promotes isomerization by aluminum halides. However, in experiments at 25°, both with *n*-butane[219] (Table 4) and with methylcyclopentane[209], isomerization was very slow in the presence of oxygen unless the reaction mixtures were exposed to sunlight or to radiation from a quartz cadmium-mercury arc lamp. The accelerating effect of radiation, which is shown by the data in Table 4, was greater in quartz than in "Pyrex" reaction tubes[209], indicating that frequencies in the ultraviolet region were particularly effective.

TABLE 5. PARALLELISM BETWEEN RATES OF SOLVOLYSIS OF ALKYL BROMIDES AND THEIR EFFECTIVENESS AS PROMOTERS FOR ALUMINUM BROMIDE-CATALYZED ISOMERIZATION OF METHYLCYCLOPENTANE

Alkyl Bromide	Charge, moles/100 moles methylcyclopentane			Cyclohexane produced,[a] (mole %)	10^5k_1[b]
	RBr	$AlBr_3$	HBr		
Methyl	0.113	2.03 ± 0.05	0.88	0	2.76
Ethyl	0.214	2.03 ± 0.05	0.79	1	3.15
Isopropyl	0.103	2.03 ± 0.05	0.40	18	61.9
tert-Butyl	0.103	2.03 ± 0.05	0.40	17	$(\sim 10^8)$

[a] Two hours at 25°. Isomerization data from Pines, Aristoff, and Ipatieff[210].

[b] Rate constants for first order solvolysis in 90 per cent aqueous formic acid at 100.2° from Bateman and Hughes[14].

Two hypotheses were advanced to account for the effect of oxygen[219]. Both provide for the formation of alkyl halide which serves as a source of carbonium ions according to reaction (VIII). One hypothesis is that oxygen reacts with the aluminum halide to yield free halogen and aluminum oxyhalide:

$$AlX_3 + \tfrac{1}{2}O_2 \rightarrow AlOX + X_2$$

The halogen then reacts with the saturated hydrocarbon to form alkyl halide. In support of this explanation, it was observed that aluminum bromide liberated bromine when treated with oxygen at 100° for one hour[219] or when irradiated in the presence of oxygen at ordinary temperatures[209]. Pretreatment of aluminum bromide with oxygen at 20 to 25° for several days followed by removal of the excess oxygen gave a product with which isomerization of *n*-butane occurred about as rapidly as in the presence of aluminum bromide promoted by oxygen[219].

A second hypothesis to account for the effect of oxygen is that the saturated hydrocarbon is oxidized in the presence of an aluminum halide to form an alcohol, for example

$$2C_4H_{10} + O_2 \xrightarrow{AlX_3} 2C_4H_9OH$$

This reaction is analogous to the observed oxidation of benzene to phenol by air in the presence of aluminum chloride[69]. An alcohol would be expected to react further and give an alkyl halide as follows[219]:

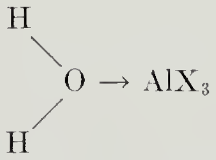
$$C_4H_9OH + AlX_3 \rightarrow C_4H_9OAlX_2 + HX$$

$$C_4H_9OH + HX \rightarrow C_4H_9X + H_2O$$

Table 6. Isomerization of *n*-Butane in the Presence of Aluminum Halides and Water[206, 295]

Experiment	1	2	3	4	5	6	7
Charge, moles/100 moles *n*-butane							
Aluminum bromide (as $AlBr_3$)	9.3	9.3	9.3	—	—	—	—
Aluminum chloride (as $AlCl_3$)	—	—	—	9.0	9.0	9.0	9.0
Water	0.3	27.9	56.0	9.0	27.4	36.5	54.2
Temperature, °C	25	25	25	100	100	100	100
Reaction time, hr	20	20	20	12	12	12	12
Product composition, mole %							
Isobutane	13.2	11.8	1.0	35.1	16.8	11.3	0
n-Butane	86.6	87.1	98.0	63.6	81.9	87.8	100
Pentanes and heavier	0.2	1.1	1.0	1.3	1.3	0.9	0

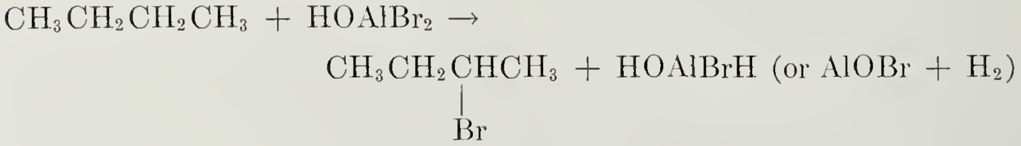
Another substance that converts the aluminum halides into catalysts active for isomerization of saturated hydrocarbons is *water*[265, 295]. The effect of water is interesting, since it is a base and might be expected to decrease the acidity of aluminum halides by formation of "salts" with the structure



However, experimental data presented in Table 6 show that as many as six moles of water per mole of aluminum halide (monomer) are required to destroy its catalytic activity completely.

In an effort to shed light on the mechanism of promotion by water, the reaction of water with aluminum halide in the absence of hydrocarbon was studied. The reaction was found to be exceedingly complex and not a simple one in which aluminum hydroxide and hydrogen halide were produced. For example, when water was added to aluminum bromide at liquid nitrogen temperature and the mixture was allowed to warm slowly, very little hydrogen bromide was generated until the temperature reached 75°, at which point a rapid evolution of hydrogen bromide occurred. Further heating to 100° resulted in additional slow evolution of hydrogen bromide. In general, with both aluminum bromide and aluminum chloride, the total amount of hydrogen halide produced depended on the time and temperature of heating and on the molar ratio of water to aluminum halide[295].

The products formed by the reaction of one, two, three, or four moles of water per mole of aluminum bromide, freed of hydrogen bromide evolved in 45 to 90 minutes at 100°, were effective for the isomerization of *n*-butane without further promotion[295]. In order to explain the catalytic activity of these substances and the promoting effect of water, it was postulated that hydroxyaluminum dihalide is formed and participates in a halogen-hydrogen exchange reaction with hydrocarbon analogous to that which occurs with alkyl halides (page 60):



$$\mathrm{CH_3CH_2CH_2CH_3} + \mathrm{HOAlBr_2} \rightarrow \mathrm{CH_3CH_2}\underset{\underset{\mathrm{Br}}{|}}{\mathrm{CH}}\mathrm{CH_3} + \mathrm{HOAlBrH}\ (\text{or } \mathrm{AlOBr} + \mathrm{H_2})$$

The alkyl bromide serves as a source of carbonium ions and initiates the isomerization chain reaction[295].

In support of this postulate may be cited the fact that small amounts of hydrogen bromide were produced during isomerization of *n*-butane by the water-aluminum bromide reaction product at 25°, even though the product had been freed of hydrogen bromide at 100° before its use in isomerization[295]. Furthermore, when deuteroxyaluminum bromide, prepared in the same manner from deuterium oxide and aluminum bromide, was used as a catalyst, isomerization of *n*-butane occurred with very little deuterium-hydrogen exchange, indicating that the bromine rather than the hydrogen of the catalyst is involved in the isomerization reaction[220].

Although the data already presented in Tables 2 and 5 demonstrate that neither hydrogen bromide nor methyl bromide is an effective promoter for aluminum bromide, isomerization of methylcyclopentane was found to take place in the presence of these substances if the reaction mixture was irradiated with ultraviolet light or if the temperature was high enough. Data obtained in these studies are presented in Table 7. In order to account for isomerization observed under these conditions, it was proposed that dissociation of hydrogen bromide or methyl bromide occurred, either photochemically or thermally, to produce atoms or, in the case of methyl bromide, a methyl radical and a bromine atom. The atoms (or methyl radical) then attacked the hydrocarbon to start a free radical chain reaction leading eventually to alkyl (or cycloalkyl) halide or to olefin, either of which may serve as an initiator of isomerization by the carbonium ion chain mechanism. Small amounts of benzene markedly inhibited isomerization under these conditions, presumably by combining with the atomic or free radical chain carriers[208].

According to this mechanism, hydrogen would be expected to result from reaction of the hydrocarbon with hydrogen atoms from the hydrogen halide. Hydrogen was in fact identified as one of the products in Experiment 4 of Table 7. The amount produced corresponded to conversion of 0.035 mole per cent of hydrocarbon to olefin or alkyl bromide. In that experiment, 24 per cent isomerization occurred in 9 hours; while in another experiment, conducted without irradiation and with 0.05 mole per cent of cyclohexene as promoter (but with 4.5 times as much aluminum bromide), 28 per cent isomerization occurred in 19 hours[207]. Although this comparison suffers from the inequality in the amounts of aluminum bromide used in the two experiments, it does indicate that a sufficient amount of a carbonium ion source may be produced by the postulated mechanism to account for the observed rate of isomerization.

TABLE 7. EFFECTS OF ULTRAVIOLET LIGHT AND TEMPERATURE ON ISOMERIZATION OF METHYLCYCLOPENTANE WITH ALUMINUM BROMIDE AND PROMOTERS[a]

Experiment[b]	1P	2P	3P	4Q	5Q	6P	7P	8P	9P	10P
Temperature, °C	27	27	27	27	27	49	56	80	25	25
Reaction time, hr										
Without irradiation	18[c]	—	—	—	—	18	24	24	18	9
With irradiation[d]	—	18	18	9	30	—	—	—	—	9
Charge, moles/100 moles MCP										
Aluminum bromide (as $AlBr_3$)	2.00 ± 0.04					2.00 ± 0.01			1.97	
Hydrogen bromide	1.00	0	1.00	1.00	1.00	0.50	0.89	0.89	—	—
Methyl bromide	—	—	—	—	—	—	—	—	0.95	0.95
Cyclohexane produced, %	0	0	18	24	29	0	6	26	2	20

[a] Based on Pines, Aristoff and Ipatieff[209, 210].

[b] P indicates a Pyrex, Q a quartz, reaction tube.

[c] This experiment was carried out in diffused light.

[d] A quartz cadmium-mercury vapor arc lamp was used for irradiation.

Irradiation with ultraviolet light did not cause isomerization of methylcyclopentane by aluminum bromide in the absence of hydrogen bromide or methyl bromide; but irradiation with high energy γ-rays caused isomerization of methylcyclopentane by means of aluminum bromide alone. Isomerization did not occur when pure methylcyclopentane or a mixture of methylcyclopentane and hydrogen bromide was irradiated with γ-rays; but some decomposition of the hydrocarbon was noted. Thus it appears that in γ-ray induced isomerization of methylcyclopentane by means of aluminum bromide alone, free radicals or bromine atoms are formed by γ-ray induced decomposition of the hydrocarbon or the aluminum bromide and initiate isomerization as in the reaction induced by ultraviolet light[215b].

The data presented in Table 8 show that isomerization of n-butane occurs in the presence of aluminum chloride and hydrogen chloride, provided the hydrogen chloride concentration or the temperature is high enough. Isomerization was brought about by aluminum chloride alone at 150°. Furthermore, increasing the hydrogen chloride concentration from three to seven mole per cent greatly increased the extent of cracking and this was accompanied by a high consumption of hydrogen chloride. Apparently, carbonium ions are produced under these conditions by direct attack of the hydrocarbon by the catalyst. A preliminary dissociation of hydrogen chloride into atoms, similar to that postulated for hydrogen bromide, is not excluded but does not seem likely because of the greater thermal stability of hydrogen chloride.

TABLE 8. EFFECTS OF HYDROGEN CHLORIDE CONCENTRATION AND TEMPERATURE ON ISOMERIZATION OF n-BUTANE BY ALUMINUM CHLORIDE[a]

Experiment	1	2	3	4	5	6
Temperature, °C	100	100	125	150	150	150
Charge, moles/100 moles n-butane						
Aluminum chloride (as $AlCl_3$)	8.91	8.84	9.26	9.18	9.50	9.05
Hydrogen chloride	5.87	17.6	3.24	0	3.10	7.12
Reaction time, hr	12					
Product composition, mole %						
Propane	—	—	0	—	3.3	57.9
Isobutane	0.1	14.1	16.3	11.1	62.4	23.4
n-Butane	99.8	85.0	83.1	88.2	31.8	13.8
Pentanes and heavier	0.1	0.9	0.6	0.7	2.5	4.4
HCl recovered, %	98	—	95	—	97	57

[a] Based on Pines and Wackher[218].

Two conceivable modes of attack of a saturated hydrocarbon by a proton source, such as aluminum chloride-hydrogen chloride, leading to a carbonium ion are illustrated by Eqs. (IX) and (X).

$$CH_3CH_2CH_2CH_3 + HCl + \tfrac{1}{2}Al_2Cl_6 \rightarrow CH_3CH_2\overset{+}{C}HCH_3 + H_2 + AlCl_4^- \quad (IX)$$

$$CH_3CH_2CH_2CH_3 + HCl + \tfrac{1}{2}Al_2Cl_6 \rightarrow CH_3CH_2CH_3 + CH_3^+ + AlCl_4^- \qquad (X)$$

Reaction (IX)[20] is analogous to the transfer of a hydride from a paraffin to a carbonium ion (reactions III and VII). It finds support in the fact that hydrogen is formed in small amounts during the initial stages of butane isomerization with a supported aluminum chloride catalyst and hydrogen chloride[20]. Furthermore, the reverse of (IX) may be involved in the inhibition of side reactions by hydrogen and in the regeneration of aluminum halides from hydrocarbon complexes by the use of hydrogen at 175° and 100 atm.[114]. These possibilities are discussed further on pages 83–85.

Reaction (X) is the protolytic cracking for which a more detailed mechanism was given on pages 54–55. It involves the penetration by a proton of the bonding sphere of a saturated carbon atom[225], and is analogous to what must occur in part when a cyclopropane or cyclobutane hydrocarbon dissolves in sulfuric acid at ordinary temperatures with ring opening. Such hydrocarbons are admittedly more susceptible to such *proton penetration* than paraffins and cyclopentanes or cyclohexanes; but it seems likely that this process is involved in the extensive cracking of butane by aluminum chloride-hydrogen chloride at 150° shown by the data in Table 8, and in the formation of paraffins from cyclohexane under the same conditions[112].

Although the pure aluminum halides are without effect on saturated hydrocarbons at moderate temperatures, reaction takes place if the temperature is high enough (Experiment 4, Table 8). Under these conditions, the aluminum halide may be dissociated slightly in either one or both of the following ways:

$$Al_2X_6 \rightleftharpoons 2AlX_3 \qquad (XI)$$

$$Al_2X_6 \rightleftharpoons AlX_2^+ + AlX_4^- \qquad (XII)^{130}$$

Both AlX_3 and AlX_2^+ would be powerful electron-pair acceptors and may serve to initiate a carbonium ion chain reaction by taking a hydride from a saturated hydrocarbon in the same way that a carbonium ion does (III and VII):

$$RH + AlX_3 \rightarrow R^+ + HAlX_3^- \qquad (XIII)^{298}$$

$$RH + AlX_2^+ \rightarrow R^+ + HAlX_2 \qquad (XIV)$$

It should be emphasized that the reactions illustrated by (IX), (X), (XIII) and (XIV) are believed to be important only at comparatively high temperatures. It may be that some dissociation of aluminum halide according to (XI) or (XII) is needed for any one of them to occur. Moreover, the "basic" properties of these halides (evident from the fact they are dimerized at low to moderate temperatures) may play an essential role in (IX), (X), (XIII) or (XIV) through coordination with the "acidic" carbonium ion. For an evaluation of this role to be profitable, however, more information is needed on which to base a comparison with other acidic halides. All that can be said now is that the aluminum halides exert a specific cracking action at about 150° which is not matched by certain other isomerization catalysts at about 400° (page 46).

Isomerization with Sulfuric Acid and Related Substances. Sulfuric acid isomerization of saturated hydrocarbons differs from isomerization in the presence of the acidic halides in two important respects. (1) No promoter or initiator is needed. (2) Only saturated hydrocarbons having at least one tertiary hydrogen are isomerized or produced by isomerization[30, 82, 128, 173, 192, 234, 267].

The reason no promoter is needed with sulfuric acid appears to be that sulfuric acid oxidizes saturated hydrocarbons[30, 82, 192, 300] and the oxidation product serves as an initiator. The oxidation has been represented as[192]

$$(CH_3)_3CH + 2H_2SO_4 \rightarrow (CH_3)_3C^+OSO_3H^- + SO_2 + 2H_2O \quad (XV)$$

and sulfur dioxide has been identified[30, 82, 267, 300]. Moreover, an induction period has been observed[192, 267]. The induction period is eliminated and the reaction rate is increased by purposeful addition of small amounts of olefins[82, 192] or sodium alkyl sulfates[82].

The oxidation occurs most readily with hydrocarbons having at least one tertiary hydrogen and very slowly or not at all with hydrocarbons having no tertiary hydrogen, such as 2,2-dimethylbutane[128], 2,2-dimethylhexane[82], and *n*-octane[82, 128]. Ethanesulfonic acid also oxidizes paraffins having at least one tertiary hydrogen, but more slowly than sulfuric acid[82]. Chlorosulfonic acid is a more vigorous oxidant and even oxidizes *n*-octane at 30°[82]. These acids also catalyze isomerization and give results similar to those obtained with sulfuric acid. Ethanesulfonic acid requires higher temperatures; but chlorosulfonic acid is effective at lower temperatures than sulfuric acid[82].

In addition to isomerization, there is a rapid exchange of hydrogen between sulfuric acid and saturated hydrocarbons having at least one tertiary hydrogen, observable by the use of isotopically labeled acid[30, 82, 109, 192, 248, 267] or hydrocarbon[192, 267]. Although early work[109] indicated that exchange took place between *n*-hexane or *n*-heptane and sulfuric acid-d_2, subsequent work has failed to detect appreciable exchange unless the hydrocarbon has at least one tertiary hydrogen[82, 192, 248, 267]. Nonoxidizing acids do not exchange hydrogen with saturated hydrocarbons[248].

In a study of the racemization, isomerization, and hydrogen exchange of optically active (+)3-methylheptane with sulfuric acid, it was found that the relative rates of the three reactions, that is, "atoms hydrogen exchanged"/"molecules (+)3-methylheptane racemized"/"molecules 3-methylheptane isomerized to 2-methylheptane," were about 30/2/1. That is, it appeared that almost all the hydrogen atoms in each molecule racemized underwent exchange with the acid[30, 82]. Subsequent extensive studies using isotopically labeled hydrocarbons and the powerful mass spectrometric method of analysis have confirmed and augmented the discovery of a high ratio of exchange to isomerization and have provided an extraordinarily detailed picture of the transformations which occur in saturated hydrocarbons in the presence of sulfuric acid[192, 267].

Each of the four monodeuterobutanes, namely, butane-1-*d*, butane-2-*d*, 2-methylpropane-1-*d*, and 2-methylpropane-2-*d*, was contacted for several hours with 96.2% sulfuric acid at 25° and then examined mass spectroscopically[192]. No change occurred in butane-1-*d*, butane-2-*d*, or 2-methylpropane-2-*d*; but 2-methylpropane-1-*d* was converted into ordinary isobutane (2-methylpropane-d_0). In another experiment[192], isobutane was contacted with sulfuric acid-d_2 (95 per cent acid, 99.5 atom per cent D) and then examined mass spectroscopically. It was found to contain isobutane-d_9 only, with the lone hydrogen attached to the tertiary carbon. Only after half the molecules had been converted to isobutane-d_9 did an appreciable amount of isobutane-d_8 begin to appear, because of isotopic dilution of the sulfuric acid-d_2, which was initially present in large excess. Isopentane was found to give only isopentane-d_8 and isopentane-d_{11} in the early stages of reaction with a large excess of sulfuric acid-d_2[267].

From these experiments, the following conclusions may be drawn[192, 267].

(1) No hydrogen exchange takes place between molecules of *n*-butane (intermolecular) or between the primary and secondary carbons of individual *n*-butane molecules (intramolecular).

(2) Neither intermolecular nor intramolecular exchange of hydrogen takes place between the primary and tertiary carbons of isobutane.

(3) The tertiary hydrogen of isobutane does not exchange with acid hydrogens, but the primary hydrogens do exchange.

(4) The minimum number of hydrogens in an isoparaffin exchanged with acid hydrogens is equal to the number of hydrogens (designated "contiguous hydrogens") attached to carbons adjacent to the tertiary carbon; for example, nine in the case of isobutane and eight in the case of isopentane.

Intermolecular exchange of tertiary hydrogens was demonstrated[192] by contacting a mixture of isobutane containing deuterium in the tertiary position (2-methylpropane-2-*d*) and isobutane containing carbon-13

(2-methylpropane-1-C^{13}) with sulfuric acid. Analysis by mass spectroscopy showed the exchange reaction

$$\mathrm{BD} + \mathrm{B'H} \rightleftharpoons \mathrm{BH} + \mathrm{B'D} \tag{XVI}$$

had occurred, where B represents *tert*-butyl and B′ represents *tert*-butyl labeled with C^{13}. This reaction is analogous to the aluminum-halide-catalyzed exchange of halogen and hydrogen between the *tert*-alkyl halides and isoparaffins described on page 60.

The mechanism that fits these observations is the following[30, 192].

(1) Carbonium ion chains are started by sulfuric acid oxidation (XV) or by the formation of carbonium ions from traces of contaminating olefin. For example:

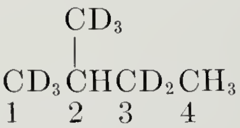
$$(\mathrm{CH_3})_2\mathrm{C{=}CH_2} + \mathrm{H_2SO_4} \rightarrow (\mathrm{CH_3})_3\mathrm{C^+OSO_3H^-} \tag{XVII}$$

(2) The chains are carried by shifts of hydride ions between carbonium ions and isoparaffin molecules. For example (*cf.* III and VII):

$$(\mathrm{CH_3})_3\mathrm{CH} + {}^+\mathrm{C(CH_3)_3} \rightleftharpoons (\mathrm{CH_3})_3\mathrm{C^+} + \mathrm{HC(CH_3)_3} \tag{XVIII}$$

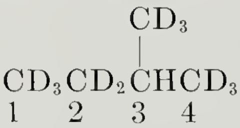
(3) During the existence of a carbonium ion any of its "contiguous hydrogens" (those attached to carbons adjacent to the positively charged tertiary carbon) may exchange with hydrogens of the acid. Apparently the exchange occurs at such a rate that equilibrium between "contiguous" hydrogens and acid hydrogens is established during the life of each ion.

(4) During the existence of a carbonium ion, rearrangement may occur by movement of an alkyl group and hydrogens, thus making new sets of hydrogens "contiguous." Thus the -d_8 and -d_{11} species formed from isopentane in early stages of the reaction with sulfuric acid-d_2 presumably have the structures (A) and (B) shown below.



$$\mathrm{CD_3C\overset{CD_3}{|}HCD_2CH_3}$$

(A)



$$\mathrm{CD_3CD_2C\overset{CD_3}{|}HCD_3}$$

(B)

(5) Chains are terminated by some irreversible side reaction of carbonium ions.

The mechanism requires that every molecule that has undergone primary hydrogen—acid hydrogen exchange will also have a new tertiary hydrogen acquired from another isoparaffin molecule; moreover, every molecule that has undergone tertiary hydrogen exchange will also have undergone hydrogen exchange with the acid. These predictions were verified as follows[192].

(1) The rate of approach to equilibrium in (XVI) was found to be the same (within a factor of 1.2) as the rate of attainment of equilibrium in

the reaction of isobutane containing a primary deuterium (2-methylpropane-1-*d*) with sulfuric acid:

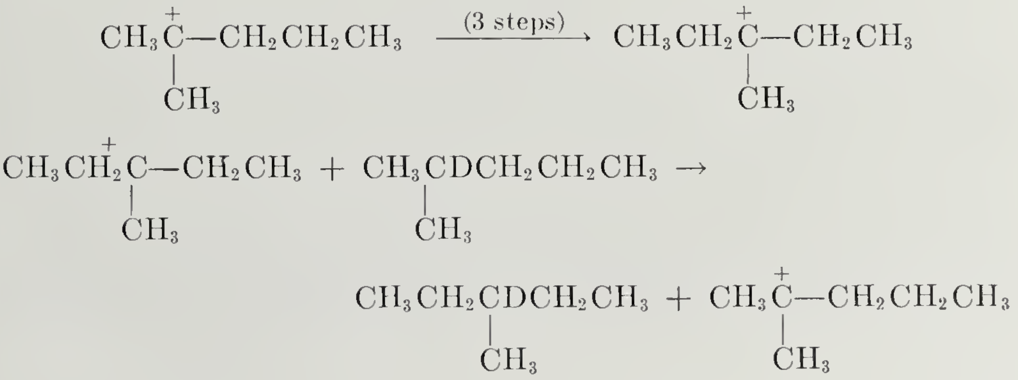
$$\text{2-methylpropane-1-}d + H_2SO_4 \rightleftharpoons \text{2-methylpropane} + HDSO_4 \qquad \text{(XIX)}$$

That is, the number of molecules per unit time undergoing tertiary—tertiary hydrogen exchange was the same as the number undergoing primary hydrogen—acid hydrogen exchange.

(2) When an equimolar mixture of 2-methylpropane-1-*d* and 2-methylpropane-2-*d* was contacted with sulfuric acid, no 2-methylpropane-1,2-d_2 was produced, although the 2-methylpropane-d_0 content increased and the 2-methylpropane-1-*d* content decreased (by the same amount). The non-formation of a -d_2 species in this experiment demonstrates that a molecule cannot be involved in tertiary—tertiary hydrogen exchange without exchanging all its primary hydrogens for acid hydrogens. Since the numbers of molecules per unit time participating in both exchanges are equal, it follows that the converse is also true. A molecule undergoing any hydrogen exchange undergoes both types of exchange, as required by the mechanism.

The mechanism has much in common with the chain mechanism of aluminum halide-catalyzed isomerization described on page 60. Although isomerization of butanes was not observed in the experiments described above (only molecules having at least one tertiary hydrogen are isomerized or produced by isomerization in the presence of sulfuric acid), isomerization was observed with higher homologs; and the results obtained with isotopically labeled hydrocarbons were completely in accord with the carbonium ion chain mechanism.

For example, when 2-methylpentane with deuterium in the tertiary position (2-methylpentane-2-*d*) was isomerized with sulfuric acid at 25°, only 3-methylpentane with deuterium in the tertiary position (3-methylpentane-3-*d*) was produced. Such a finding is difficult to understand unless it be supposed that the isomerization proceeds by way of a chain reaction perpetuated by the transfer of tertiary hydrogen (deuterium) between carbonium ions[267]:



$$CH_3\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_2CH_2CH_3 \xrightarrow{\text{(3 steps)}} CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_2CH_3$$

$$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_2CH_3 + CH_3\underset{\underset{CH_3}{|}}{C}DCH_2CH_2CH_3 \rightarrow$$

$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}DCH_2CH_3 + CH_3\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_2CH_2CH_3$$

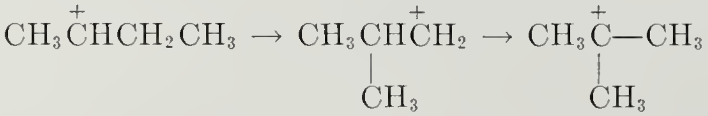
It is a curious fact that saturated hydrocarbons without at least one tertiary carbon have never been isomerized nor reported among the products of isomerization by sulfuric acid, especially since no such restriction exists for aluminum halide-catalyzed isomerization and both processes are now given essentially the same mechanism. It appears that a particular carbonium ion behaves differently in the presence of sulfuric acid and aluminum halide-hydrogen halide and it is difficult to understand why this should be so.

The fact is all the more curious when considered in the light of observations made in connection with sulfuric acid-catalyzed alkylation of saturated hydrocarbons by olefins, a reaction which has also been interpreted by a carbonium ion chain mechanism. For example, propane is produced from propylene during sulfuric acid-catalyzed alkylation of isobutane[157], isobutane as well as *n*-butane is produced from *n*-butenes, and isopentane is produced from 2-pentene during sulfuric acid-catalyzed alkylation of methylcyclopentane[214]. If the carbonium ion mechanism be accepted, these observations appear to demonstrate:

(1) Hydride transfer to a secondary (*i.e.*, non-tertiary) carbonium ion:

$$CH_3\overset{+}{C}HCH_3 + HC(CH_3)_3 \rightarrow CH_3CH_2CH_3 + {}^{+}C(CH_3)_3 \qquad (XX)$$

(2) Carbonium ion rearrangements involving non-tertiary ions:



$$CH_3\overset{+}{C}HCH_2CH_3 \rightarrow CH_3\underset{\displaystyle CH_3}{CH}\overset{+}{C}H_2 \rightarrow CH_3\underset{\displaystyle CH_3}{\overset{+}{C}}—CH_3 \qquad (VI)$$

(VI)

(An alternative mechanism for the formation of isobutane from *n*-butenes, which obviates the need for primary carbonium ions, is given on page 122.)

Excluding the idea that carbonium ions produced in the presence of sulfuric acid are somehow different from those produced in the presence of aluminum halide-hydrogen halide, which merely replaces one question by another, two explanations can be given for the fact that saturated hydrocarbons without at least one tertiary carbon are neither isomerized nor produced by isomerization in sulfuric acid.

(1) The fact is simply a consequence of differences in rates. The isomerizations which have been observed in sulfuric acid are those which take place most rapidly, and with sufficiently long reaction times, all products would be observed. It has been found, for example, that the isomerization of 2-methylpentane to 3-methylpentane is about 200 times faster than its isomerization to *n*-hexane in the presence of aluminum chloride at 100°[50]; and if this difference in rates holds for sulfuric acid, the amount of *n*-hexane in an isomerizate from 2-methylpentane might escape detection. In further

support of this explanation may be cited the fact that analytical data on a sulfuric acid isomerizate from 2,4-dimethylpentane did not exclude the presence of 2,2-dimethylpentane, a "forbidden" product[267]. However, this explanation does not seem very attractive. It attributes the absence of products without a tertiary carbon to a lack of diligent searching by the experimenters or to inadequacy of the analytical techniques. Furthermore, the isomerization of methylcyclopentane to cyclohexane proceeds about as rapidly as the isomerization of 2,2,4-trimethylpentane in the presence of aluminum bromide at 26° [41]; but methylcyclopentane is not isomerized by sulfuric acid[267], whereas 2,2,4-trimethylpentane is isomerized rapidly[173]. To suppose the difference in rates is greater in the presence of sulfuric acid than in the presence of aluminum halides is simply to restate the problem and raise the question, "Why?"

(2) An alternative explanation is suggested by the evident oxidizing action of sulfuric acid and a difference in structure between primary and secondary carbonium ions on the one hand and tertiary ions on the other. A non-tertiary ion has at least one hydrogen on the positively charged carbon; and this remaining hydrogen may be a site of attack for very rapid degradative oxidation by sulfuric acid (possibly through alkyl hydrogen sulfate formation). Tertiary ions would not be susceptible since they have no such hydrogen. If the oxidative degradation of primary and secondary ions were enormously more rapid than intermolecular hydride transfer, products having no tertiary hydrogen would never be formed. (The isomerizations that have been observed in the presence of sulfuric acid can be represented without intermediate formation of primary or secondary carbonium ions by use of "pi-complex" theory, as outlined later on pages 118–123.) This explanation finds some support in the observation that chlorosulfonic acid oxidizes *n*-octane without producing isomers[82]. If this oxidation involves a step analogous to (XV), it must be that further oxidation is even faster than carbonium ion rearrangement and stabilization by hydride transfer. However, this explanation would appear to be refuted by the formation of propane observed during sulfuric acid-catalyzed alkylation with propylene mentioned previously (XX).

Isomerization with Acidic Chalcides. It is now well established that the catalytic activity of silica-alumina and related substances is due to their acidity[84, 165, 272]. Their *stoichiometric acidity* can be measured by titration with alkali[38, 272]; and the *acid strength* of the surface of some of these solids can be gauged by color changes in adsorbed indicators[297]. As acids, they are "neutralized" by adsorption of alkali metal ions[38, 165] (essentially an ion exchange with hydrogen), ammonia[165], or quinoline[165]. Their catalytic activity has been related quantitatively to their stoichiometric acidity[165, 272] or to the degree of "neutralization" by nitrogen compounds[165].

The acidity may be due to constitutional hydrogen ions, or in the case of silica, for example, to physically adsorbed mineral acid[297]. The catalytic activity of molybdenum sulfide (page 47) has been attributed to the presence of a surface layer of hydrogen sulfide[94]. That is, the catalytically active acidic chalcides are not to be regarded as pure oxides or sulfides, the presence of hydrogen ion, sometimes in an amount too small to be detected by elementary analysis, being responsible for their catalytic activity. In the case of silica-alumina, for example, it has been pointed out that if an aluminum with a valence of three replaces a silicon in tetrahedral silica, another monovalent atom, such as hydrogen, will be necessary to satisfy the valences of oxygen[272]. Thus a structural unit in silica-alumina may be represented as in Figure 2. Ideally, then, maximum acidity and maximum activity would be realized with a catalyst of the composition $HAlSiO_4$. However, in the preparation of a silica-alumina catalyst by coprecipitation, a perfectly ordered arrangement into $HAlSiO_4$ hardly results, and some catalytically less active SiO_2 and Al_2O_3 are also formed. Consequently, in a series of synthetic silica-alumina catalysts, it was found that maximum activity (for cracking of gas oil) came with an Al/Si atomic ratio about two; and even though maximum acidity came at the expected Al/Si ratio of unity, it was only a fraction (2.43 milliequivalents H^+ per gram) of that expected for $HAlSiO_4$ (8.33 me. per gram)[272].

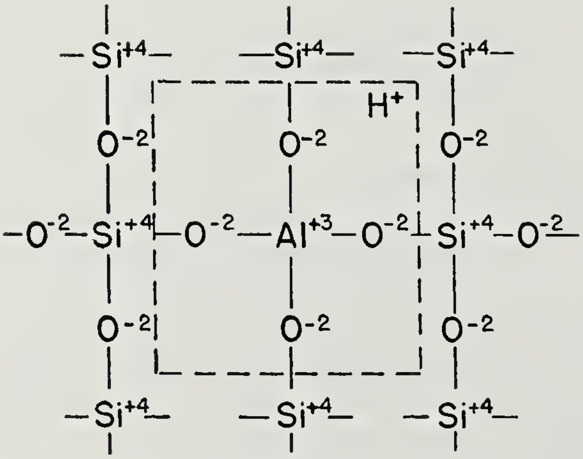


Figure 2. Two-dimensional representation of tetrahedral silica-alumina with constitutional hydrogen. (After Thomas[272].)

Adsorption of normal paraffins on a silica-alumina catalyst (Houdry S-46, 12.5 per cent Al_2O_3 (?)) has been found to be less than 0.005 millimole per gram[311] at temperatures above 150°, where such a catalyst is active for isomerization[187]. This is only one-tenth the amount of quinoline adsorbed at 315°[165], and only about one-hundredth the stoichiometric acidity of a closely similar catalyst[38].

The many reactions of hydrocarbons that will take place under suitable conditions on silica-alumina and related catalysts—cracking, isomerization, intermolecular hydrogen transfer, and polymerization—have been interpreted in terms of carbonium ions[84, 272]. As with aluminum halide-hydrogen halide in the case of a saturated hydrocarbon, a carbonium ion chain reaction may be initiated by addition of a proton from the catalyst to olefin present as an impurity or produced by a slight amount of thermal cracking at the high temperature often needed with these catalysts[272]. Alternatively, carbonium ions may be produced from saturated hydrocarbons by direct attack of the catalyst in a dehydrogenation[84] or protolytic cracking analogous to (IX) and (X).

TABLE 9. REACTIONS OF PARAFFINS ON SILICA-ALUMINA AT 150°[a]

Paraffin	H-D Exchange %[b]	Isomerization %	Cracking %
2-Methylbutane	94	—[c]	—
n-Hexane	0	0	0
2-Methylpentane	87	11	0
2,2-Dimethylbutane	—	0	0
2,3-Dimethylbutane	78	10[b]	5
n-Heptane[d]	0	0	0
2-Methylhexane	97	—	—
2,3-Dimethylpentane[d]	62	50[b]	30
2,4-Dimethylpentane[d]	70	22[b]	36
3,3-Dimethylpentane	0	0	0
2,2,3-Trimethylbutane	91	—[c]	—
2-Methylheptane	97	—	—
2,2,4-Trimethylpentane	—	3	92
2,3,3-Trimethylpentane	—	2	97
2,3,4-Trimethylpentane	—	2	94

[a] Based on Hindin, Mills, and Oblad[102, 166, 187]. Houdry S-45 silica-12.5 wt. per cent alumina was used. For the H-D exchange experiments, the catalyst was pretreated twice with 10 per cent by wt. of D_2O, with drying for one hour at 525° between treatments. Before each experiment, the catalyst was dried one hour at 525° (or 315° as noted), then cooled and treated with 0.5 per cent H_2O (or D_2O in the exchange experiments). The ratio of hydrocarbon to catalyst and the contact time (one hour) were the same in all experiments.

[b] Percentage based on products having the parent molecular weight only.

[c] Isomerization to the "3-methyl" isomer would not be detected.

[d] Catalyst dried at 315°.

As with sulfuric acid (pages 68–73), hydrogen exchange takes place between saturated hydrocarbons[102] and between saturated hydrocarbons and water[95, 102, 166] in the presence of silica-alumina. Some results of a study of these reactions at 150° are presented in Table 9. As with sulfuric acid at 25°:

(1) Hydrocarbons with no tertiary hydrogen do not exchange with wa-

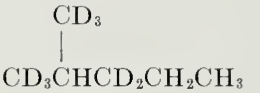
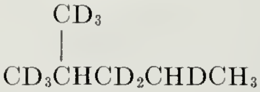
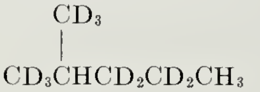
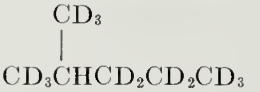
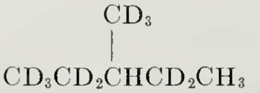
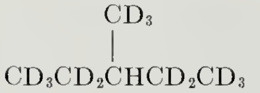
ter (D_2O) at 150°[166]. (Exchange is observed with such hydrocarbons above 200°[95].)

(2) The tertiary hydrogen of isobutane does not exchange with water below 120°[95] and slowly, if at all, at 150°[166].

(3) All primary hydrogens of isobutane exchange when any exchange[95, 102].

(4) Rapid intermolecular exchange of hydrogen between tertiary carbons occurs (demonstrated with a mixture of 2-methylpropane-2-*d* and 2-methylbutane at 150°[102]).

Table 10. Products of Reaction of 2-Methylpentane with Sulfuric Acid-d_2[267]

Product	Relative Amount
 $CD_3\overset{CD_3}{\overset{\vert}{C}}HCD_2CH_2CH_3$	1.0
 $CD_3\overset{CD_3}{\overset{\vert}{C}}HCD_2CHDCH_3$	0.8
 $CD_3\overset{CD_3}{\overset{\vert}{C}}HCD_2CD_2CH_3$	0.7
 $CD_3\overset{CD_3}{\overset{\vert}{C}}HCD_2CD_2CD_3$	0.8
 $CD_3CD_2\overset{CD_3}{\overset{\vert}{C}}HCD_2CH_3$	0.3
 $CD_3CD_2\overset{CD_3}{\overset{\vert}{C}}HCD_2CD_3$	0.3

In contrast to the exchange reactions with sulfuric acid at 25°:

(1) The tertiary hydrogen of higher homologs of isobutane is exchanged on a silica-alumina catalyst at 150° (although slowly)[166].

(2) With branched-chain paraffins having five or more carbons, *all* hydrogens, except perhaps a tertiary one, exchange with the catalyst when any exchange.[166] (With sulfuric acid, only "contiguous" hydrogens, and those brought into contiguity by rearrangement, exchanged (pages 68–73).)

Essentially the same mechanism as was used for sulfuric acid (pages 68–73) fits the observations on isomerization and exchange in the presence of silica-alumina[102], with the following modifications:

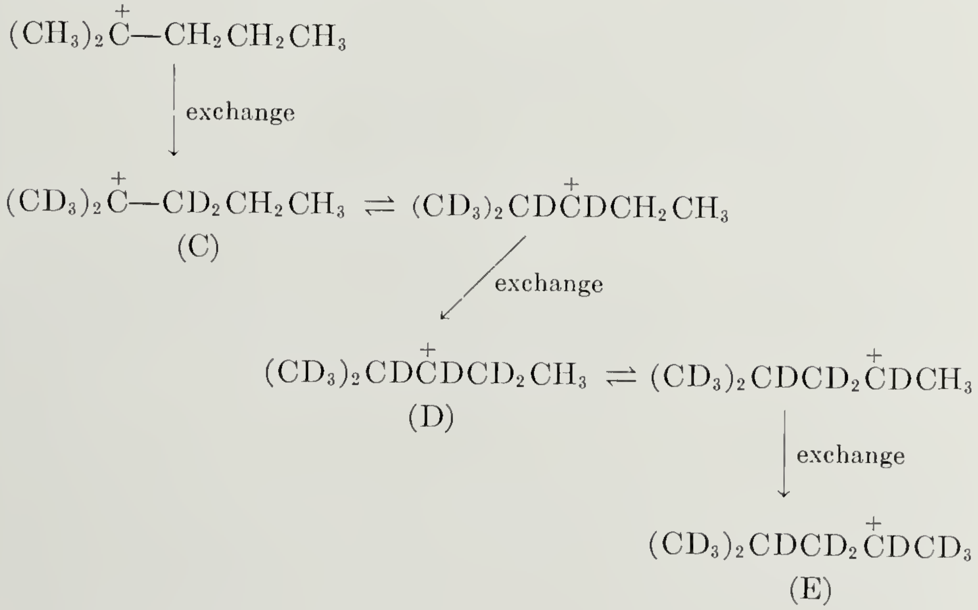
(1) The fact that the tertiary hydrogen of higher homologs exchanges slowly on silica-alumina at 150°, but not with sulfuric acid at 25°, has been

attributed to some hydride transfer between tertiary and secondary carbons at the higher temperature[166]:

$$CD_3CD_2\overset{+}{C}(CD_3)_2 + CD_3CD_2CH(CD_3)_2 \rightarrow CD_3CD_2CD(CD_3)_2 + CD_3\overset{+}{C}DCH(CD_3)_2$$

Because of the general leveling effect of temperature on competing reaction rates, the difference in reactivity of secondary and tertiary hydrogens would not be so great at 150° as at 25°.

(2) In order to account for exchange of all hydrogens in an isoparaffin (except possibly a lone tertiary one), without comparable isomerization, it was supposed that exchange of contiguous hydrogens takes place in secondary as well as in tertiary ions[166]:



$$(CH_3)_2\overset{+}{C}{-}CH_2CH_2CH_3 \xrightarrow{\text{exchange}} (CD_3)_2\overset{+}{C}{-}CD_2CH_2CH_3 \rightleftharpoons (CD_3)_2CD\overset{+}{C}DCH_2CH_3$$

(C)

$$(CD_3)_2CD\overset{+}{C}DCH_2CH_3 \xrightarrow{\text{exchange}} (CD_3)_2CD\overset{+}{C}DCD_2CH_3 \rightleftharpoons (CD_3)_2CDCD_2\overset{+}{C}DCH_3$$

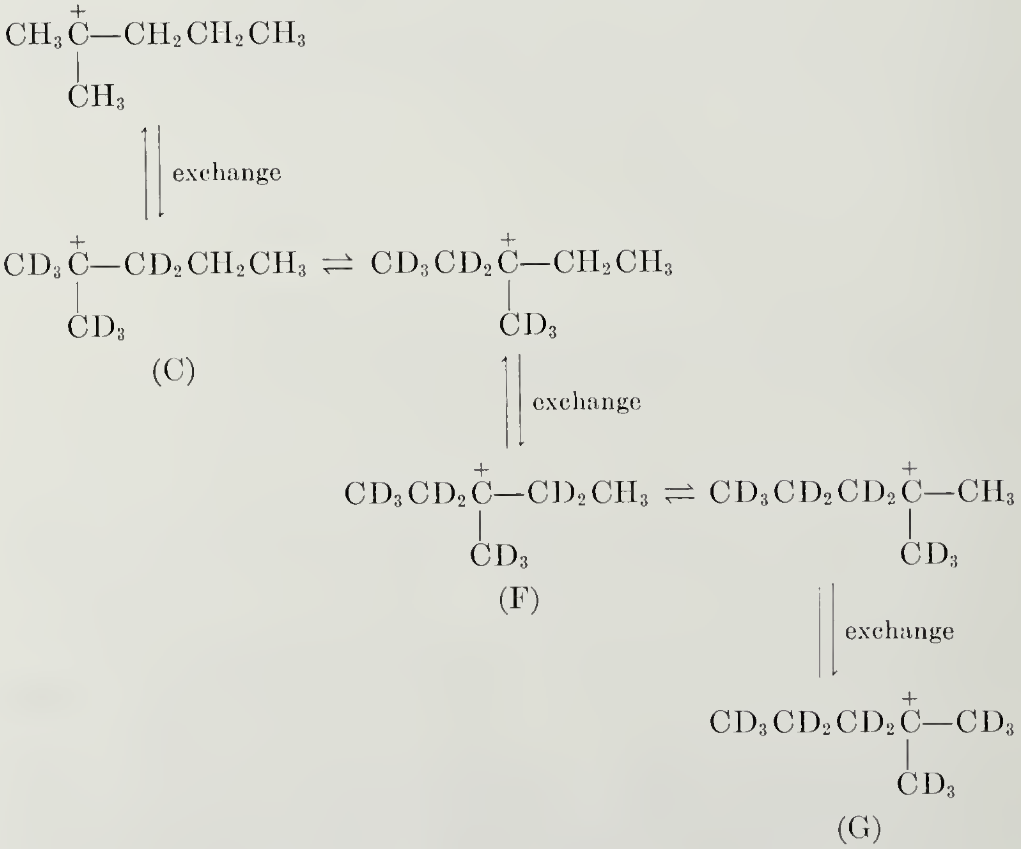
(D)

$$(CD_3)_2CDCD_2\overset{+}{C}DCH_3 \xrightarrow{\text{exchange}} (CD_3)_2CDCD_2\overset{+}{C}DCD_3$$

(E)

Because of the general leveling effect of increasing temperature on equilibria, the concentration of secondary carbonium ions would be greater at 150° than at 25°.

Although it was claimed that the ratio, "molecules exchanged"/"molecules isomerized," was much greater with silica-alumina than with sulfuric acid[166], a comparison of data in Tables 9 and 10 shows this need not be so. Data in Table 9 give 7.9 for this ratio in the case of 2-methylpentane in the presence of silica-alumina. Data in Table 10 give 6.5 for this ratio in the presence of sulfuric acid. These values are equal within the uncertainties in the several data. Bearing in mind that isomerization to 4-methylpentane would not be detected, an alternative mechanism for exchange of all hydrogens without comparable *observable* isomerization can be given without the need for exchange of contiguous hydrogens in secondary carbonium ions. That is, it seems likely that the following equilibria would be established in the presence of silica-alumina at 150° but not necessarily in the presence of sulfuric acid at 25° because under the gas-phase conditions employed with silica-alumina, and in view of the demonstrated very small adsorption of saturated hydrocarbons on silica-alumina[311], the chance of a carbonium ion's taking a hydride from another molecule must be much less than in the liquid-phase conditions employed with sulfuric acid:



$$CH_3\underset{CH_3}{\underset{|}{\overset{+}{C}}}—CH_2CH_2CH_3$$

$$\Big\updownarrow \text{exchange}$$

$$CD_3\underset{CD_3}{\underset{|}{\overset{+}{C}}}—CD_2CH_2CH_3 \rightleftharpoons CD_3CD_2\underset{CD_3}{\underset{|}{\overset{+}{C}}}—CH_2CH_3$$

$$\Big\updownarrow \text{exchange}$$

$$CD_3CD_2\underset{CD_3}{\underset{|}{\overset{+}{C}}}—CD_2CH_3 \rightleftharpoons CD_3CD_2CD_2\underset{CD_3}{\underset{|}{\overset{+}{C}}}—CH_3$$

$$\Big\updownarrow \text{exchange}$$

$$CD_3CD_2CD_2\underset{CD_3}{\underset{|}{\overset{+}{C}}}—CD_3$$

With (C), (F) and (G) in equilibrium, the amount of isomerization *observed* would be governed by the rate of acceptance of a hydride ion by (F) relative to (C) and (G). Both statistical and steric considerations suggest the former would be less than the latter.

A curious difference between sulfuric acid and silica-alumina on the one hand and aluminum chloride-hydrogen chloride on the other, is that exchange of hydrogen accompanies and is much faster than isomerization with the former but isomerization occurs without hydrogen exchange in the presence of aluminum chloride-hydrogen chloride at 25°[296]. [At 107 to 121°, exchange of hydrogen between hydrogen chloride and the butanes does occur during isomerization in the presence of aluminum chloride[225] (page 54.)] This difference has been attributed to the greater mobility of the catalyst[267] (sulfuric acid) or catalyst hydrogen[102] (silica-alumina) than in the case of aluminum chloride-hydrogen chloride.

Isomerization with Dual Function Catalysts. The data in Table 9 show that only paraffins having at least one tertiary carbon undergo isomerization or exchange with silica-alumina at 150°. As with sulfuric acid at lower temperatures, it appears these conditions are effective for Type (a) isomerizations (page 49), that is, those in which both reactant and product have at least one tertiary carbon, but not for Type (b), that is, those in which either reactant or product has no tertiary carbon[187]. At higher temperatures, Type (b) isomerizations are observed on silica-alumina, but only incidentally to extensive cracking, as shown by Expts. 1–4 of Table 11. However, a catalyst that has both *cracking* and *hydrogenation* activity is often effective for isomerization of saturated hydrocarbons at temperatures below those required for cracking. Such a catalyst can be made by combining a transition metal or transition metal oxide, such as cobalt[39], nickel[39, 217a], and platinum[39, 90, 162a, 217a, 297a], or molybdena[39, 40, 83], tungstic oxide (WO_3)[39], and zirconia[21], with an acidic chalcide cracking catalyst, such as alumina[40, 83, 162a] or silica-alumina[21, 39, 40, 162a, 217a, 297a]. These catalysts may be described as "acidic-electronic" (pages 51, 73).

Results obtained in the isomerization of *n*-hexane with such a catalyst are presented in Table 11 in comparison with results obtained with silica-alumina alone. They show that silica-alumina is a poor isomerizing catalyst; but the addition of 5 per cent of nickel greatly increases its isomerizing activity.

n-Heptane and *n*-octane also were isomerized in good yield with nickel-silica-alumina[39]. This catalyst therefore supplements the aluminum halides and catalysts like sulfuric acid, for with aluminum halides, cracking of *n*-heptane[114, 125] and higher normal paraffins[125] is not suppressed even by the use of hydrogen at high pressure; and with sulfuric acid-type catalysts, normal paraffins are not isomerized at all[82, 128, 192, 267]. Other results obtained with the nickel-silica-alumina catalyst are presented in Tables 16 and 20.

The results in Table 11 show that hydrogen is necessary for isomerization in the presence of the nickel-silica-alumina catalyst. The role of hydrogen here differs from its role as a suppressor of side reactions during aluminum halide-catalyzed isomerization (page 83) in that almost no reaction at all occurs with nickel-silica-alumina but cracking and isomerization do occur with aluminum halides in the absence of hydrogen.

In further studies it was found that sodium ions poison the nickel-silica-alumina catalyst for isomerization[38]. Sodium ions were introduced either by using sodium carbonate instead of ammonium carbonate during prepa-

Table 11. Effects of Nickel and Hydrogen on Isomerization of *n*-Hexane over a Silica-Alumina Cracking Catalyst[a]

Experiment[b]	1	2	3	4	5	6	7	8	9	10	11	12
Temperature, °C	315	374	431	485	328	355	385	412	311	367	396	422
Catalyst	SiO_2-12.8% Al_2O_3				SiO_2-Al_2O_3-5% Ni[e]							
Gas charged[c]	H_2				H_2				N_2			
Recovery, wt. % of charge	94.7	97.7	95.8	98.5	92.6	90.4	89.4	93.7	96.4	96.3	98.7	94.3
Product, moles/100 moles charge (no-loss basis)												
C_1–C_5	3.6	4.7	9.8	35.4	1.2	1.7	11.4	105.3	0.3	2.3	1.1	3.9
C_6 isomers	1.4	2.1	1.8	3.4	27.4	57.8	67.8	36.9	0.1	0.1	0.1	0.1
n-Hexane	96.2	95.3	92.4	76.2	71.8	41.2	23.2	12.7	99.7	98.8	99.6	98.6
Conversion, %	3.8	4.7	7.6	24.8	28.2	58.8	76.8	87.3	0.3	1.2	0.4	1.4
Efficiency, %	(37)[d]	(45)[d]	(24)[d]	(14)[d]	97	98	88	42	—	—	—	—

[a] Based on Ciapetta and Hunter[39].

[b] The pressure was 24.8 atm. and the liquid space velocity was 1.0 hr.$^{-1}$ in all experiments.

[c] Four moles/mole hexane charged.

[d] Values at low conversions are only approximate.

[e] Prepared by precipitating nickel carbonate on a commercial silica-alumina cracking catalyst containing 12.8 per cent alumina; and activated in a stream of hydrogen at 538°.

ration of the catalyst or by soaking an active catalyst in a sodium carbonate solution. The principal reaction with the catalyst containing sodium was demethanation:

$$CH_3CH_2CH_2CH_2CH_2CH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3 + CH_4$$

Since sodium ions undoubtedly replace the protons in the ionic lattice shown in Figure 2, these results show that a hydrogen ion as well as a hydrogenation component is necessary to make silica-alumina an efficient catalyst for isomerization of saturated hydrocarbons. Nitrogen bases present in the hydrocarbon feed to a platinum-containing alumina or silica-alumina catalyst poison it for isomerization of cyclohexane, presumably by tying up protons[162a].

The mechanism advanced to explain the isomerization of saturated hydrocarbons with these so-called dual function catalysts involves the formation of olefins as intermediates[38, 162a, 165a, 297a]. The function of the hydrogenation component is then to establish equilibrium between saturated hydrocarbon, olefin, and hydrogen. Only a small amount of olefin would be present at equilibrium under the conditions used. The function of the acidic component is then to isomerize the olefin, presumably via a carbonium ion mechanism. Rearranged olefin is then transported in the gas phase to a hydrogenation site where it is saturated with hydrogen. The following observations lend powerful support to these views:

(1) Olefins in the very small concentration permitted by thermodynamics have been detected by mass spectrometric means in *n*-hexane passed over a platinum catalyst at 373°[297a].

(2) Olefins, for example 1-hexene, underwent isomerization and hydrogenation on the nickel-silica-alumina catalyst at a lower temperature than that required for saturated hydrocarbons[38] (Table 12).

(3) Silica-alumina itself is an efficient catalyst for isomerization of olefins[297a].

(4) A mechanical mixture of particles of silica-alumina and particles of inert-supported platinum was about as effective for isomerization of *n*-heptane as a platinum-*impregnated* silica-alumina[297a]. The last observation, combined with calculations of diffusion rates, showed the ability of metal and acidic sites to act as independent, physically distinct catalysts with gas phase diffusion of intermediates (olefins) between different reaction sites supporting the over-all reaction rate[297a]. The mechanism may thus be summarized as follows:

$$\text{Saturate} \xrightleftharpoons[\text{site}]{\text{Metal}} \text{Unsaturate} \xrightleftharpoons[\text{site}]{\text{Acidic}} \begin{Bmatrix} \text{Rearranged} \\ \text{unsaturate} \end{Bmatrix} \xrightleftharpoons[\text{site}]{\text{Metal}} \begin{Bmatrix} \text{Rearranged} \\ \text{saturate} \end{Bmatrix}$$

An important difference between this mechanism and that for liquid phase isomerization with aluminum halides and sulfuric acid is the absence of a chain reaction involving transfer of hydride ion from hydrocarbon to carbonium ion. While it cannot be said that experimental evidence yet available excludes such a chain reaction with the dual function catalysts, the observed phenomena are as well accounted for without it. Indeed perhaps the necessity for hydrogen already alluded to can be regarded as evidence that saturation of carbonium ions cannot occur by hydride transfer. It has been suggested that the role of hydrogen with the dual function catalysts is "primarily to keep the catalyst surface clean of hydrocarbon residues and thus maintain its activity"[38]. If by "hydrocarbon residues" is meant "adsorbed olefin," then it would appear that the necessity for hydrogen is adequately explained by the mechanism outlined.

TABLE 12. HYDROGENATION AND ISOMERIZATION OF 1-HEXENE ON A NICKEL-SILICA-ALUMINA CATALYST[a]

Experiment[b]	1	2	3	4
Temperature[c], °C				
Top of catalyst	286	309	337	357
Bottom of catalyst	204	229	258	288
Recovery, wt. % of charge	97.6	97.6	98.2	97.8
Product, moles/100 moles charge (no-loss basis)				
C_1–C_5	3.4	4.7	9.5	17.3
Branched hexanes	17.0	29.0	41.1	45.4
n-Hexane	77.6	64.1	48.5	36.8
Heavier hydrocarbons	2.7	3.3	3.4	5.1
Conversion, %	22.4	35.9	51.5	63.2
Isomerization efficiency, %	76	81	80	72

[a] Based on Ciapetta[38].

[b] The catalyst was essentially the same as that used in Expts. 5–12 of Table 11. The pressure was 24.8 atm., the liquid space velocity was 1.0 hr^{-1}, and the molar ratio of hydrogen to hexene in the charge was four in all the experiments.

[c] Temperature control was difficult because of the exothermicity of hydrogenation.

Nature and Control of Side Reactions. Reference has been made in the foregoing discussion to the fact that isomerization of a paraffinic hydrocarbon is often accompanied by side reactions. These side reactions result in the formation of paraffins with both higher and lower molecular weights (disproportionation)[211] and unsaturated hydrocarbons that form a complex with the catalyst and reduce its activity. The extent of the side reactions and consequently the efficiency of isomerization, defined as follows:

$$\text{Efficiency } (\%) = \frac{\text{Mole \% isomers produced}}{\text{Mole \% hydrocarbon converted}}$$

depends on the structure and molecular weight of the paraffin, on the temperature, on the conversion, and on the nature of the catalyst. Of considerable practical and theoretical interest is the fact that the side reactions can sometimes be suppressed with consequent increase in the efficiency by carrying out the isomerization in the presence of hydrogen under pressure[58, 114, 126, 245], or in the presence of a small amount of an aromatic compound[58, 80, 156], a moderate amount of a naphthene[58, 156], or a large amount of isobutane[58, 156, 247].

The suppression of side reactions is of considerable practical importance in commercial applications not only because the efficiency of isomerization is increased, but also because catalyst life is greatly lengthened[58, 196, 247], presumably because the formation of unsaturated hydrocarbons that complex with the catalyst is repressed. The phenomenon is of theoretical interest—in the case of hydrogen because it demonstrates activation of hydrogen by acidic catalysts; in the case of an aromatic compound because of the magnitude of the effect, only a small amount of such a substance is needed; and in the case of a naphthene or isobutane because it is a rather exotic demonstration of chemical reactivity of these compounds, one saturated hydrocarbon profoundly influences the course of reaction of another!

For the reaction with an aluminum halide at moderate temperatures in the absence of a suppressor of side reactions, the following generalizations can be made:

(1) Butanes are isomerized without side reactions[98, 170, 218].

(2) Side reactions with higher molecular weight paraffins produce isobutane as a major product but no lower molecular weight paraffins (propane, ethane, or methane)[19, 31, 85-7, 219].

(3) The unsaturated oil concomitantly produced as a complex with the aluminum halide consists of unsaturated cyclic hydrocarbons resembling terpenes[111, 129, 247]. A consideration of these facts suggests that the ultimate reaction of a paraffin containing five or more carbons in the presence of an aluminum halide under conditions permitting removal of the reaction products may be represented as

$$C_nH_{2n+2} \rightarrow a i\text{-}C_4H_{10} + (1 - a)(C_5H_8)_x \qquad \text{(XXI)}$$

By use of this equation, the maximum attainable yield of isobutane from a paraffin of a given composition may be calculated. Some results are presented in Table 13[42]. In one recorded instance in which a paraffin was treated with an aluminum halide under conditions designed to give the maximum yield of isobutane, n-heptane was found to produce a maximum of 76 per cent of isobutane[86], in good agreement with the calculated value in Table 13. More commonly, reaction has not been carried to this extreme; and a complex mixture of products has been observed.

The distribution of products and the efficiency of isomerization of n-pentane under a variety of conditions are shown by the data in Tables 14–19. At room temperature with aluminum bromide (presumably promoted by air or alkene inadvertently present) an efficiency as high as 89 per cent was realized but this fell off with increasing conversion or with increased catalyst concentration[78] (Table 14).

TABLE 13. MAXIMUM YIELD OF ISOBUTANE FROM HIGHER MOLECULAR WEIGHT PARAFFINS ACCORDING TO REACTION (XXI)

Paraffin	Maximum Yield i-C_4H_{10} (%)
C_5H_{12}	90.8
C_6H_{14}	83.6
C_7H_{16}	76.4
C_8H_{18}	70.9
—	—
$C_{16}H_{34}$	58.2
—	—
C_nH_{2n} (limit)	45.5 (limit)

TABLE 14. EFFECTS OF REACTION TIME AND ALUMINUM BROMIDE CONCENTRATION ON THE EFFICIENCY OF ISOMERIZATION OF n-PENTANE[a]

Experiment[b]	1	2	3	4	5	6	7	8
Charge, mol %								
n-Pentane	97.18				98.48	94.72	91.06	85.95
$AlBr_3$	2.82				1.52	5.28	8.94	14.05
Reaction time, hr	22	51	95	169	26.2			
Loss and tar, wt. %	1.0	1.4	1.5	5.3	1.5	0.9	3.2	6.8
Products, liquid vol. %								
Butanes	1.5	2.8	5.0	8.8	1.5	6.1	10.2	14.1
Isopentane	40.8	51.0	55.9	44.2	27.2	53.5	46.8	40.4
C_6^+	2.5	3.4	3.4	5.9	2.8	3.1	5.4	4.9
Approximate conversion, %	46	59	66	64	33	64	66	67
Approximate efficiency, %	89	87	85	69	82	84	71	60

[a] Based on Glasebrook, Phillips and Lovell[78].

[b] All experiments carried out at room temperature.

Data in Table 15 show that side reactions resulting in the formation of methane, ethane, and propane are observed with aluminum chloride at 125°. These are almost completely eliminated by the use of hydrogen under pressure. At 150°, destructive hydrogenation sets in, resulting in large amounts of methane[114]. Similar phenomena are observed with a nickel-silica-alumina catalyst in the temperature range 371 to 407° (Table 16)[39]. The fact that n-pentane can be isomerized with high efficiency with a nickel-silica-alumina catalyst at such temperatures shows that the extensive

TABLE 15. EFFECT OF HYDROGEN ON EFFICIENCY OF ISOMERIZATION OF *n*-PENTANE AT ELEVATED TEMPERATURE[a]

Experiment	1	2	3	4	5	6	7	8
Aluminum chloride, type	Resublimed					Technical		
Gas, 100 atm. initial pressure	N_2	N_2	N_2	H_2	H_2	H_2	H_2	H_2
Temperature, °C	125	125	125	125	125	100	125	150
Charge, g								
n-Pentane	100	100	100	100	100	100	363	100
Aluminum chloride	10	10	10	10	10	10	35	10
Hydrogen chloride	0	9	0	2	10	0	0	0
Catalyst recovered, g	16	16	10	10	10	10	37	10
Product composition, mole %								
Methane	12.9	4.1	—	0.0	0.0	0.0	—	10.4
Ethane	0.0	3.5	—	0.0	0.0	0.0	3.3	5.0
Propane	0.0	21.0	0.0	0.0	0.0	0.0	2.5	5.4
Isobutane	27.6	28.0	0.0	0.0	0.5	3.2	0.0	1.4
n-Butane	18.4	9.8	0.0	0.0	0.0		0.1	2.5
Isopentane	5.5	8.0	2.8	22.4	61.0	14.2	84.9	65.2
n-Pentane	25.4	17.2	96.6	77.3	38.0	82.6	9.2	10.1
C_6^+	10.2	8.4	0.6	0.3	0.5	0.0	0.0	0.0
Approximate conversion, %[b]	71	80	3.4	23.7	62.0	17	91	88
Approximate efficiency, %[b]	9	11	82	94	98	84	96	86

[a] Based on Ipatieff and Schmerling[114].

[b] In computing conversion and efficiency, the product compositions were converted to wt. per cent and loss to catalyst tar was included in total conversion.

TABLE 16. EFFECT OF TEMPERATURE ON EFFICIENCY OF ISOMERIZATION OF *n*-PENTANE WITH NICKEL-SILICA-ALUMINA IN THE PRESENCE OF HYDROGEN[a]

Experiment[b]	1	2	3	4	5
Temperature, °C	343	371	382	393	407
Recovery, wt. % of charge	85.5	84.8	99.7	105.0	93.4
Products, moles/100 moles charge (no-loss basis)					
Methane	0.4	3.1	5.4	15.7	24.7
Ethane	—	—	0.5	1.9	3.4
Propane	2.3	1.5	2.3	5.4	7.9
Isobutane	0.6	2.5	1.4	3.0	1.9
n-Butane	0.1	1.9	4.1	9.3	13.2
Isopentane	5.4	31.3	41.8	43.4	41.1
n-Pentane	92.3	63.1	51.1	39.4	35.3
Conversion, %	7.7	36.9	48.9	60.6	64.7
Efficiency, %	70	85	86	72	64

[a] From Ciapetta and Hunter[39].

[b] For details of catalyst preparation, see Table 11, Note e. A total pressure of 24.8 atm., a liquid space velocity of 1.0 hr^{-1}, and an initial H_2/pentane molar ratio of four were used in all experiments.

degradation observed with aluminum chloride at 125 to 150° is not due to temperature alone, but is the result of specific cracking activity of the aluminum halide which is not matched by the nickel-silica-alumina catalyst.

The effect of benzene on the efficiency of isomerization of *n*-pentane with

Table 17. Effect of Benzene on Efficiency of Isomerization of *n*-Pentane with Aluminum Chloride-Hydrogen Chloride at 100°[a]

Experiment[b]	1	2	3	4	5	6
Feed[c]	A	B	B	B	B	B
Benzene, vol. % in feed	0.0	0.10	0.25	0.50	2.0	10.0
Product composition, mole % (benzene-free basis)						
Butanes	8.3	4.4	2.3	0.4	0.3	0.6
Isopentane	17.5	33.6	47.5	49.3	26.5	18.1
n-Pentane	67.9	57.3	47.3	48.4	71.3	79.8
C_6^+	6.3	4.7	2.9	1.9	1.9	1.5
Approximate conversion, %	27.5	34	44	43	20	11
Approximate efficiency, %	64	78	92	98	97	95

[a] Based on Mavity, Pines, Wackher and Brooks[156].

[b] All experiments were carried out in a continuous flow system at 34 atm. with a liquid hourly space velocity of 0.10, and with 0.10 mole HCl per mole of charge. The liquid feed, containing added benzene, was saturated with aluminum chloride at 77° before entering the reaction chamber at 100°.

[c] Commercial pentane feeds having the following compositions were used: Feed A: $n\text{-}C_5H_{12}$ 95.4, C_6^+ 4.6 mole per cent; Feed B: $i\text{-}C_5H_{12}$ 7.4, $n\text{-}C_5H_{12}$ 91.1, C_6^+ 1.5 mole per cent.

Table 18. Effect of Naphthenes on Efficiency of Isomerization of *n*-Pentane with Aluminum Chloride-Hydrogen Chloride at 100°[a]

Experiment[b]	0[d]	1	2	3	4	5	6
Naphthene[c]	—	None	MCP	CH	CH	MCH	D
Volume % in feed	—	—	10.0	5.0	10.0	10.0	10.0
Product composition, mole % (naphthene-free basis)							
Butanes	0.0	8.3	0.3	4	1.6	1.9	0
Isopentane	4.6	17.5	61	60	61	67	21
n-Pentane	95.4	67.9	35	32	34	27	72
C_6^+	0.0	6.3	3.7	4	3.4	4.1	7
Approximate conversion, %	—	27.5	60	63	61	68	23
Approximate efficiency, %	—	64	94	88	93	92	71

[a] Based on Mavity, Pines, Wackher and Brooks[156].

[b] See Note b, Table 17.

[c] MCP = methylcyclopentane; CH = cyclohexane; MCH = methylcyclohexane; D = decahydronaphthalene.

[d] Naphthene-free feed composition.

aluminum chloride-hydrogen chloride at 100° is shown by the data in Table 17. Small amounts of benzene increase the rate as well as the efficiency[156]. Large amounts of benzene inhibit isomerization in addition to suppressing side reactions. Considering both conversion and efficiency, about 0.5 vol. per cent of benzene represents an optimum. In one commercial process, optimum results are obtained with one mole per cent of hydrogen and only 0.2 vol. per cent of benzene[196].

TABLE 19. EFFECTS OF ISOBUTANE AND TEMPERATURE ON EFFICIENCY OF ISOMERIZATION OF *n*-PENTANE WITH WATER-PROMOTED ALUMINUM CHLORIDE[a]

Experiment[b]	1	2	3	4	5	6
Temperature, °C	54	71	93	54	71	93
Feed composition, wt. %						
n-Pentane	100			33.3 (28.6)[c]		
Isobutane	0			66.7 (71.4)[c]		
Reaction time, hr	4	4	4.1	2	2	2
Product composition, wt. %[d]						
Light ends	0.0	0.0	0.8	0.2	0.2	0.1
Isobutane	7.1	52.6	49.0	68.9	70.4	70.6
n-Butane	0.3	0.3	5.0	0.0	1.4	0.6
Isopentane	41.9	22.8	20.5	1.7	12.0	23.7
n-Pentane	45.5	2.7	5.0	29.2	16.0	5.0
C_6^+	4.9	16.0	12.8	0.0	0.0	0.0
Loss and catalyst oil	0.3	5.6	6.9	0.0	0.0	0.0
n-Pentane conversion, %	54.5	97.3	95.0	6[c]	48[c]	84[c]
Efficiency, %	92	23	22	94[c]	80[c]	91[c]

[a] Based on Sensel and Goldsby[247].

[b] In each experiment, there were used $AlCl_3$, 10.6 per cent of the weight of the hydrocarbon feed, and water, 2.3 per cent of the weight of the $AlCl_3$.

[c] The feed was made up to contain 33.3 wt. per cent *n*-pentane; but fractional distillation indicated 28.6 wt. per cent *n*-pentane. An average of these, 31.0 wt. per cent, was used in calculating *n*-pentane conversion and isomerization efficiency[12].

[d] Each datum is an average of two closely agreeing results.

Suppression of side reactions by various naphthenes is shown in Table 18 and by isobutane in Table 19. In contrast to the small amounts of benzene needed, rather large amounts of these saturated hydrocarbons are required for effective suppression of side reactions, the efficiency of the naphthenes occupying a position intermediate between those of benzene and isobutane. The data in Table 19 incidentally reveal that pentane isomerization is many times faster than butane isomerization.

Some insight into the mechanism of suppression of side reactions was obtained in a study of the action of aluminum bromide on 2,2,4-trimethylpentane at 26°[41]. In the absence of a suppressor, the product distribution, based on hydrocarbon converted, was as follows:

	(%)
Isobutane	18
Isopentane	6
Hexanes and heptanes	12
Isomeric octanes	26
Other products, including catalyst oil	38

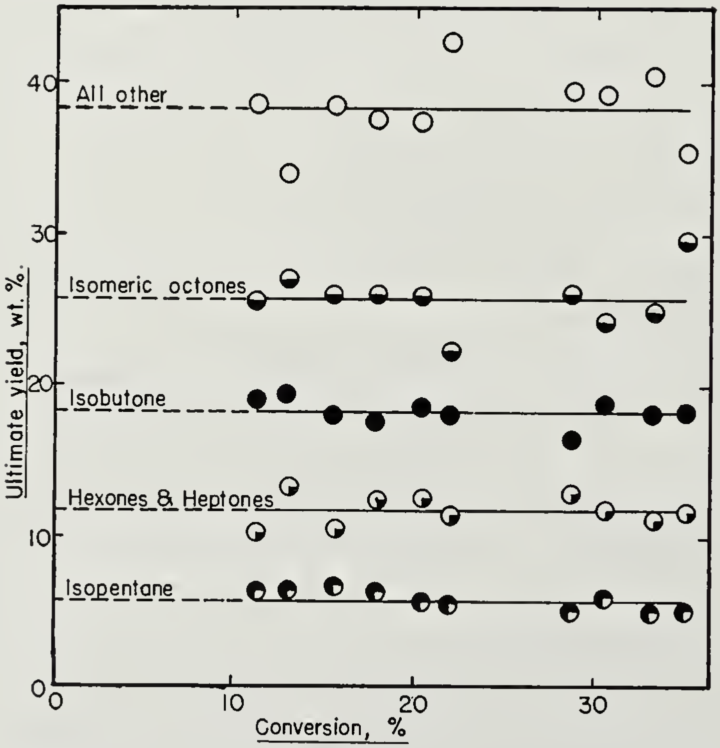


Figure 3. Distribution of products from aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane at 26°. (Condon[41])

This product distribution was substantially independent of the conversion in the range 11.8 to 35.1 per cent, as shown by Figure 3. As has frequently been observed in such reactions, methane, ethane, propane, and higher molecular weight *normal* paraffins were absent. The efficiency of isomerization under these conditions in the absence of a suppressor was therefore 26 per cent.

In the presence of added methylcyclopentane or *cis*-decahydronaphthalene, the efficiency of isomerization increased as shown in Figures 4 and 5[41]. Provided comparison was limited to a narrow range of conversion of the 2,2,4-trimethylpentane, the efficiency increased regularly with the amount of added naphthene initially present. This provision was necessary because the added methylcyclopentane or *cis*-decahydronaphthalene underwent

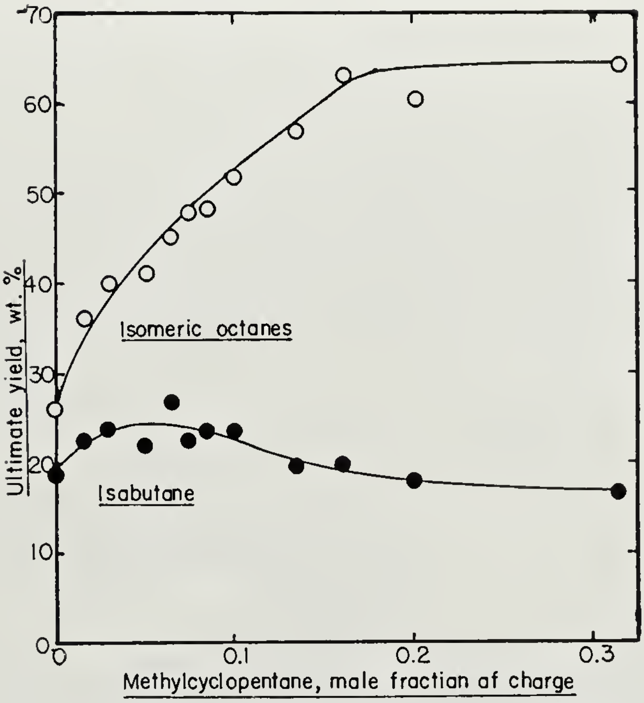


Figure 4. Effect of methylcyclopentane on yields of isomeric octanes and isobutane from aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane at 26°. (Condon[41]).

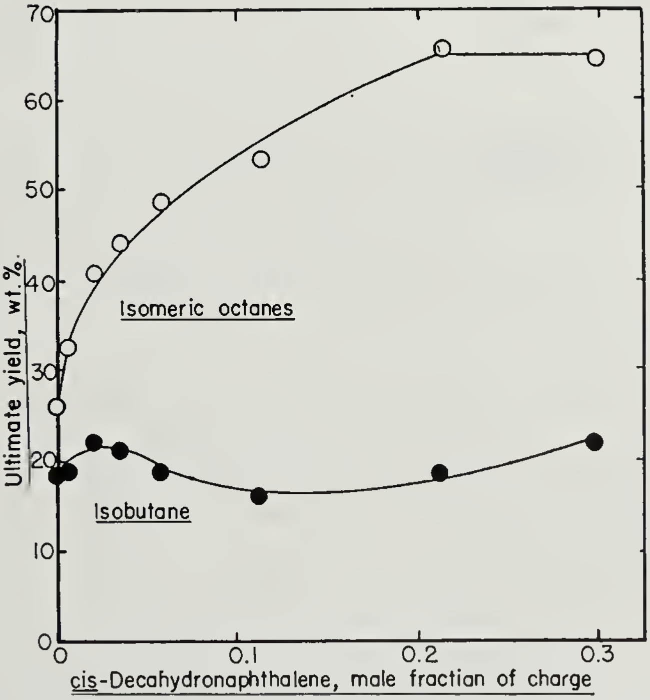


Figure 5. Effect of *cis*-decahydronaphthalene on yields of isomeric octanes and isobutane from aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane at 26°. (Condon[41]).

concomitant isomerization to cyclohexane and *trans*-decahydronaphthalene, respectively, and as is shown in Figure 6 these isomerization products were not effective suppressors of side reactions under the conditions used.

Figures 4 and 5 show that a maximum efficiency of 65 per cent was realized when the initial mole fraction of methylcyclopentane or *cis*-decahydronaphthalene was about 0.15 to 0.20. An increase in the amount of naphthene to a mole fraction about 0.3 failed to increase the efficiency. Furthermore, although an increase in efficiency can only result from a decrease in the yield of by-products, the yield of by-product *isobutane* was not appreciably decreased but was sometimes increased by the addition of methylcyclopentane or *cis*-decahydronaphthalene (Figures 4 and 5).

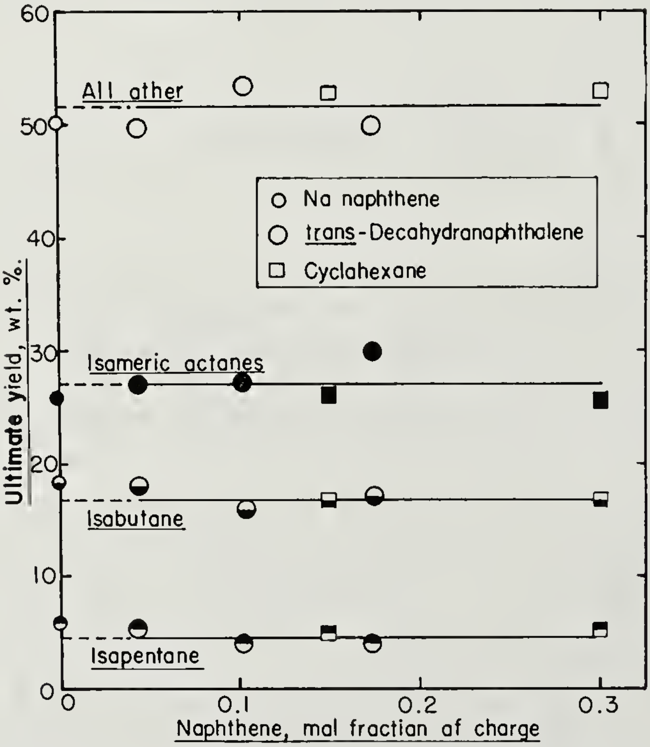


Figure 6. Effects of cyclohexane and *trans*-decahydronaphthalene on distribution of products from aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane at 26°. (Condon[41]).

These results were interpreted as follows[41]. The 2,2,4-trimethylpentane undergoes three primary reactions:

(1) Dealkylation to isobutane and isobutylene

$$C_8H_{18} \rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8 \qquad \text{(XXII)}$$

(2) Alkylation by the isobutylene produced in reaction (XXII)

$$C_8H_{18} + i\text{-}C_4H_8 \rightarrow C_{12}H_{26} \qquad \text{(XXIII)}$$

(3) Isomerization

$$C_8H_{18} \rightarrow C_8H_{18}' \qquad \text{(XXIV)}$$

The reactions are presumed to involve carbonium ion intermediates in conformity with the carbonium ion chain mechanism of isomerization[20] (page 57) and alkylation of saturated hydrocarbons[11]. By-products other than those shown are supposed to result from secondary reactions of the dodecane (or C_{12} carbonium ion intermediate) produced in (XXIII).

In the presence of a naphthene, (XXIII) is replaced, wholly or in part, depending on the concentration and reactivity of the naphthene, by alkylation of the naphthene:

$$C_nH_{2n} + i\text{-}C_4H_8 \rightarrow C_{n+4}H_{2n+8} \qquad \text{(XXV)}$$

and by hydrogen transfer from naphthene to isobutylene, resulting in an increased production of isobutane:

$$2C_nH_{2n} + i\text{-}C_4H_8 \rightarrow C_{2n}H_{4n-2} + i\text{-}C_4H_{10} \qquad \text{(XXVI)}$$

Such hydrogen transfer processes, with "dimerization" of the saturated hydrocarbon, are known to accompany acid-catalyzed reactions between olefins and naphthenes[214] or isoparaffins[157]. By reactions (XXV) and (XXVI), isobutylene is consumed that would otherwise consume 2,2,4-trimethylpentane by reaction (XXIII).

This interpretation is supported by the following quantitative correlation of the yield data. The production of 18 per cent of isobutane by reaction (XXII) requires by simple stoichiometry the consumption of about 35 per cent of octane. Another 35 per cent of octane will be consumed in reaction (XXIII). Thus, only about 30 per cent of octane is left for the isomerization reaction (XXIV). Actually, only 26 per cent of isomerization was achieved in the absence of a naphthene, indicating that another 4 per cent of octane was consumed by secondary reactions not delineated but required to produce the observed variety of products. In the presence of a naphthene, reaction (XXII) is not suppressed—it is difficult to see how it could be; and therefore the yield of isomers cannot exceed about 65 per cent, as was observed.

According to this interpretation, a suppressor of side reactions acts by consuming olefin that would otherwise produce by-products by a molecular chain reaction comprising alkylation and dealkylation. In extending this interpretation to other paraffins, the following two facts, previously mentioned, are highly significant: (1) Butanes isomerize without side reactions; and (2) by-products from higher molecular weight paraffins contain not less than four carbons. Both are true provided the reaction conditions are not too severe. From a consideration of these facts it must be concluded that, under mild conditions, breakdown of reaction intermediates (supposed to be carbonium ions) is limited to production of fragments (smaller carbonium ion and olefin) with at least four carbons. That is, all by-products must result from intermediates having at least eight carbons. During isomerization of a paraffin with less than eight carbons, such intermediates can be formed only by alkylation of the paraffin with olefin introduced into the reaction mixture or formed from the paraffin during the course of the reaction. As outlined on pages 55–57, a trace of olefin or olefin-generating substance is essential to low-temperature paraffin isomerization. In larger than trace amounts, olefins greatly decrease the efficiency of isomerization of n-pentane[58].

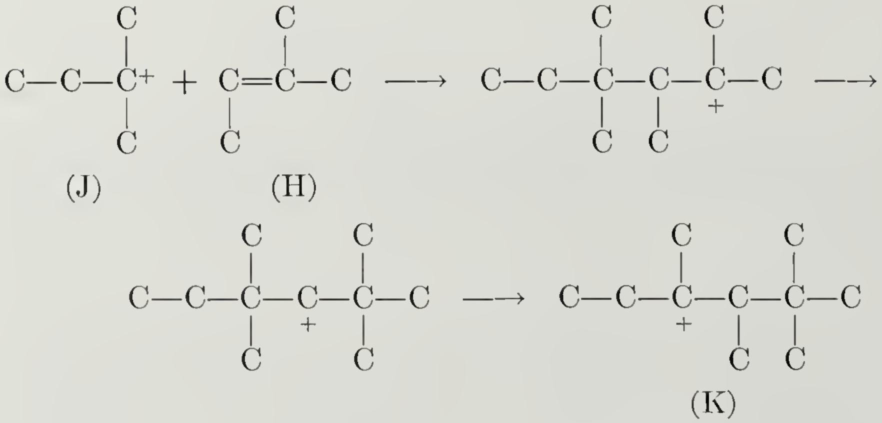
The formation of isobutane and hexanes from pentane, for example, may occur by the following molecular chain reaction:

$$C_5H_{12} + \underset{(H)}{C_5H_{10}} \rightarrow C_{10}H_{22}$$

$$C_{10}H_{22} \rightarrow i\text{-}C_4H_{10} + \underset{(I)}{C_6H_{12}}$$

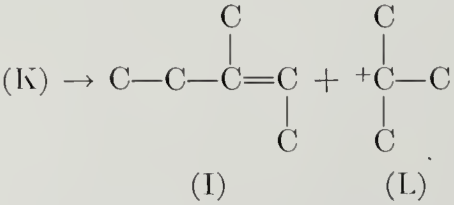
$$(I) + C_5H_{12} \rightarrow C_6H_{14} + (H)$$

which in turn has the following carbonium ion chain *mechanism* (hydrogens omitted):

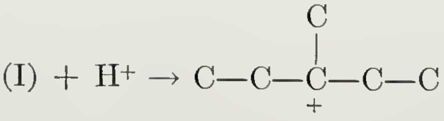


$$\underset{(J)}{\mathrm{C{-}C{-}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C^+}}}} + \underset{(H)}{\underset{\mathrm{C}}{\mathrm{C}}{=}\overset{\mathrm{C}}{\mathrm{C}}\mathrm{{-}C}} \longrightarrow \mathrm{C{-}C{-}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{{-}}\underset{\mathrm{C}}{\mathrm{C}}\mathrm{{-}}\overset{\mathrm{C}}{\underset{+}{\mathrm{C}}}\mathrm{{-}C} \longrightarrow$$

$$\mathrm{C{-}C{-}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{{-}}\underset{+}{\mathrm{C}}\mathrm{{-}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{{-}C} \longrightarrow \underset{(K)}{\mathrm{C{-}C{-}}\overset{\mathrm{C}}{\underset{+}{\mathrm{C}}}\mathrm{{-}}\underset{\mathrm{C}}{\mathrm{C}}\mathrm{{-}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{{-}C}} \qquad \text{(XXVII)}$$

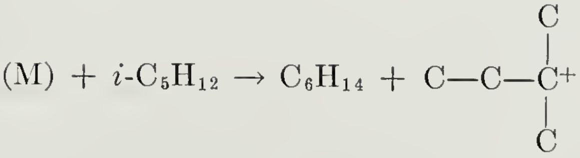


$$(K) \rightarrow \underset{(I)}{\mathrm{C{-}C{-}}\overset{\mathrm{C}}{\mathrm{C}}{=}\underset{\mathrm{C}}{\mathrm{C}}} + \underset{(L)}{{}^{+}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\mathrm{{-}C}} \qquad \text{(XXVIII)}$$



$$(\mathrm{I}) + \mathrm{H}^+ \rightarrow \mathrm{C{-}C{-}}\overset{\overset{\mathrm{C}}{|}}{\underset{+}{\mathrm{C}}}\mathrm{{-}C{-}C}$$

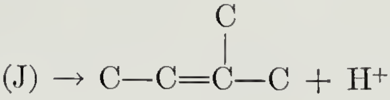
(M)



$$(\mathrm{M}) + i\text{-}\mathrm{C_5H_{12}} \rightarrow \mathrm{C_6H_{14}} + \mathrm{C{-}C{-}}\overset{\overset{\mathrm{C}}{|}}{\underset{\underset{\mathrm{C}}{|}}{\mathrm{C}^+}}$$

(J)

$$(\mathrm{L}) + i\text{-}\mathrm{C_5H_{12}} \rightarrow i\text{-}\mathrm{C_4H_{10}} + (\mathrm{J})$$



$$(\mathrm{J}) \rightarrow \mathrm{C{-}C{=}}\overset{\overset{\mathrm{C}}{|}}{\mathrm{C}}\mathrm{{-}C} + \mathrm{H}^+$$

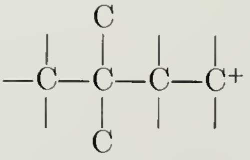
(H)

This carbonium ion mechanism is essentially the same as has been used to account for the formation of small amounts of 3-methyl-2-pentene (I) and polymers of isobutene during the sulfuric acid-catalyzed polymerization of olefins from dehydration of 3-methyl-2-butanol[53]. It makes use of the same intermediates and types of transformations as the carbonium ion chain mechanism for isomerization already described on page 57; and therefore involves no new postulates. The molecular chain reaction used here as an illustration is only one of many that may be going on simultaneously and give rise to the variety of products observed in the reaction of an acidic catalyst with a paraffin hydrocarbon. The picture that results is one of *coupled carbonium ion chain reactions.*

In interpreting the results with any particular paraffin, consideration of the relative rates of the isomerization and the alkylation-dealkylation chain reaction must play a large part. If the latter is rapid compared to the former, as would probably be the case with Type (b) isomerizations defined on pages 49–50, a low efficiency would be expected. However, if isomerization is rapid compared to alkylation-dealkylation, as would probably be the case with Type (a) isomerizations, a high efficiency would result. Hence the interconversion of 2- and 3-methylpentane can be accomplished with high efficiency with aluminum bromide at below room temperature; but similar treatment of 2,2-dimethylbutane yields chiefly isobutane and isopentane[19].

The fact that butane isomerization is remarkably free of side reactions at moderate temperatures is readily understood in terms of the alkylation-dealkylation mechanism with the restriction that dealkylation is limited to production of fragments with at least four carbons. Alkylation of butane with butylene introduced into the reaction mixture or formed by hydrogen transfer to olefin introduced into the reaction mixture gives first an eight-carbon product which, in principle, can only dealkylate so as to regenerate four-carbon fragments. Only by further alkylation of the eight-carbon primary alkylation product can there be produced intermediates capable of breaking down to other than four-carbon fragments. Inasmuch as the further alkylation is unlikely in the presence of a vast excess of butane, butane isomerization is practically free of side reactions.

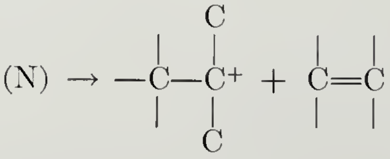
The important fact that products with less than four carbons are not formed at moderate temperatures is undoubtedly a consequence of the greater stability and ease of formation of tertiary carbonium ions compared to primary and secondary. Inasmuch as the simplest *tertiary* carbonium ion must have four carbons, it appears that a larger carbonium ion must maneuver, by a series of intramolecular rearrangements similar to those in (XXVII) above, until it has the structure



$$-\underset{|}{\overset{|}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C^+}}$$

(N)

which can break down by cleavage in the *beta* position to give a *tertiary* carbonium ion and an olefin as in (XXVIII):



$$(N) \rightarrow -\underset{|}{\overset{|}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C^+}} + \underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}$$

A similar phenomenon has been observed during acid-catalyzed depolymerization of highly branched olefins having eight or more carbons[176, 305] and has been given an identical interpretation[305].

When the structure of the hydrocarbon is such as to favor direct cleavage of this sort, as in the case of 2,2,4-trimethylpentane, a suppressor of side reactions is powerless to prevent it. Thus the yield of isobutane was not decreased by a naphthene in the experiments described above. And although *n*-octane is isomerized with high efficiency with a nickel-silica-alumina catalyst in the presence of hydrogen, 2,2,4-trimethylpentane is almost wholly converted to isobutane[39] (Table 20). With *n*-octane in Table 20, an increase in temperature may be regarded as synonymous with an increase in production of trimethylpentanes, the isomerization taking place in stepwise fashion through methylheptanes and dimethylhexanes to trimethylpentanes. An increase in temperature is therefore accompanied by a decrease in efficiency, the trimethylpentanes undergoing dealkylation and hydrogenation as rapidly as formed.

If the action of a suppressor of side reactions depends on its alkylation by olefins that would otherwise consume the paraffin being isomerized, its effectiveness would be expected to depend on its relative reactivity for alkylation. This is seen to be so by a comparison of the relative concentrations of benzene, a naphthene, and isobutane required for effective suppression of side reactions during pentane isomerization. In a competitive alkylation experiment, benzene has been found to be 350 times as reactive as isobutane toward a carbonium ion[44], the actual reactions under comparison being

Table 20. Effects of Hydrocarbon Structure and Temperature on Efficiency of Isomerization of Octanes with a Nickel-Silica-Alumina Catalyst[a]

Experiment[b]	1	2	3	4	5	6	7	8
Octane	*n*-Octane				2,2,4-Trimethylpentane			
Temperature, °C	316	348	364	380	259	288	320	336
Recovery, wt. % of charge	98.1	97.0	95.6	95.2	95.9	93.3	95.1	88.4
Products, moles/100 moles charge (no-loss basis)								
Methane	—	0.7	0.7	2.8	—	—	—	—
Propane	1.0	10.6	22.6	32.8	0.8	0.8	0.8	0.8
Butanes	1.2	30.3	56.8	85.2	3.2	12.4	58.3	76.5
Pentanes	1.0	12.6	22.8	37.2	—	—	—	—
Hexanes	0.7	0.5	0.3	0.8	—	—	—	—
Heptanes	0.3	0.2	0.3	0.3	—	—	—	—
Isomeric octanes	60.8	69.7	47.5	18.5	0.4	0.6	1.2	1.2
n-Octane	37.0	2.1	0.0	0.0	—	—	—	—
2,2,4-Trimethylpentane	—	—	—	—	98.2	92.9	69.0	59.1
Conversion, %	63.0	97.9	100.0	99.4	1.8	7.1	31.0	40.9
Efficiency, %	97	71	48	17	—	—	—	—

[a] Based on Ciapetta and Hunter[39].

[b] For details of catalyst preparation, see Table 11, Note e. For reaction conditions, see Table 16, Note b.

$$i\text{-}C_3H_7^+ + C_6H_6 \rightarrow i\text{-}C_3H_7C_6H_5 + H^+$$

and

$$i\text{-}C_3H_7^+ + i\text{-}C_4H_{10} \rightarrow C_3H_8 + t\text{-}C_4H_9^+$$

which presumably approximate the rate-controlling steps in competitive alkylation of these substances. Now 0.5 vol. per cent benzene in pentane, which represents an optimum concentration for suppression of side reactions according to data in Table 17, corresponds to a molar ratio of pentane to benzene of about 150; while a *weight* ratio of butane to pentane of two, required for comparable suppression of side reactions by isobutane according to data in Table 19, corresponds to a *molar* ratio of butane to pentane of about 2.5. Hence, relative to a pentane concentration of unity, it is apparent that an isobutane concentration 2.5 × 150 = 375 times that of benzene is required for comparable suppressor action, in good agreement with the relative reactivities of benzene and isobutane directly determined in competitive alkylation. The concentration of a naphthene required is intermediate between that of benzene and isobutane (Table 18); this is in accordance with the fact that methylcyclopentane was found to be several times as reactive as isobutane and isopentane in competitive hydrofluoric acid-catalyzed alkylation with isobutylene[242].

TABLE 21. EFFECT OF VARIOUS AROMATIC COMPOUNDS ON EFFICIENCY OF ISOMERIZATION OF *n*-PENTANE AT 75°[a]

	Additive[b]								
	None	Chlorobenene	*p*-Chlorotoluene	*o*-Dichlorobenzene	*p*-Dichlorobenzene	Diphenyl ether	Benzophenone	Aniline	Diphenylamine
Mole % in feed	—	0.75	1.39	0.96	1.13	1.04	0.92	2.14	0.99
Product composition, mole %									
Isobutane	54.1	3.3	25.3	50.7	49.1	1.4	43.2	43.7	49.4
n-Butane	8.1	0.6	0.9	7.7	5.4		2.2	2.3	4.7
Isopentane	19.2	62.4	58.0	19.6	26.3	53.6	23.2	26.7	25.3
n-Pentane	11.8	32.1	9.0	11.8	9.8	44.3	24.0	13.8	18.3
C_9^+	6.8	1.6	6.8	10.2	9.4	0.7	7.4	13.5	2.3
Approximate conversion, %[c]	88	68	91	88	90	56	76	86	82
Approximate efficiency, %[c]	22	92	64	22	29	96	30	31	31

[a] Based on Mavity, Pines, Wackher and Brooks[156].

[b] In each experiment, 85 g *n*-pentane, 15 g anhydrous aluminum chloride, 2.7 ± 0.4 g anhydrous hydrogen chloride, and the indicated additive were used. Duration of each experiment was six hours.

[c] These figures are only approximate since the amount of catalyst oil formed in each case was not given.

The parallelism between ease of alkylation and suppressor action is also apparent from a comparison of the effectiveness of various benzene derivatives shown in Table 21. Diphenyl ether was an effective suppressor of side reactions; but dichlorobenzenes, benzophenone, and aromatic amines, in which a "deactivating" group is attached to the aromatic nucleus, were almost without effect[156]. (The amines undoubtedly exist as substituted ammonium ions under the conditions of paraffin isomerization.) The parallelism is further demonstrated by the fact that *n*-butane is not a suppressor like its readily alkylatable isomer[247].

The fact that cyclohexane suppressed side reactions for *n*-pentane (Table 18) but not for 2,2,4-trimethylpentane (Figure 6) is no anomaly but simply a consequence of relative reaction rates. Like *n*-butane, cyclohexane has no tertiary hydrogen and would not be expected to be an active suppressor. Furthermore, its rate of isomerization to methylcyclopentane, which is an active suppressor, is much slower than the rate of conversion of 2,2,4-trimethylpentane. (In experiments in which 2,2,4-trimethylpentane and methylcyclopentane were treated together at 26°, the methylcyclopentane was isomerized to cyclohexane about $\frac{1}{7}$ as rapidly as the 2,2,4-trimethylpentane was converted to all products[41]; and since the equilibrium constant for isomerization of methylcyclopentane to cyclohexane at 26° is about 8 (page 161), the isomerization of cyclohexane must be about $\frac{1}{56}$ as rapid as the conversion of 2,2,4-trimethylpentane.) Hence cyclohexane remains inactive when used with 2,2,4-trimethylpentane at 26°. Now although no supporting data are available, it seems probable that isomerization of cyclohexane is faster than that of *n*-pentane. Therefore, cyclohexane becomes an active promoter when used with *n*-pentane. *n*-Butane remains inactive when used with *n*-pentane[247], since butane isomerization is much slower than pentane isomerization (data in Table 19).

In further support of the idea that suppressor action by an organic compound depends on its ability to be alkylated, there may be cited the fact that products of alkylation of the suppressor have been isolated[41, 156]. However, it should be pointed out that, according to the mechanism of suppressor action developed here, the consumption of a suppressor need not be large. Since the by-products of isomerization are visualized as coming from a molecular chain reaction that regenerates olefin, only a small amount of olefin may be parent to a great deal of by-product, provided only that the alkylation-dealkylation chain reaction is fast relative to the isomerization chain reaction. Hence only a small amount of suppressor need be consumed in inhibiting a great deal of side reaction. Thus it is that only a trace of an effective promoter like benzene is needed and the data in Table 19 show almost no consumption of isobutane. Indeed, extensive consumption of the suppressor would be synonymous with a poor isomerization efficiency since alkylation of the suppressor would make use of the paraffin being isomerized.

With molecular hydrogen as a suppressor, the following equilibria may play a part in keeping the olefin concentration low:

$$R^+ + H_2 \rightleftharpoons RH + H^+ \qquad \text{(XXIX)}$$

$$H^+ + \text{olefin} \rightleftharpoons R^+ \qquad \text{(XXX)}$$

where R^+ is a carbonium ion. Reaction (XXIX) is essentially the reverse of (IX) on page 66, which was proposed as a reaction-initiating step in the action of pure aluminum chloride-hydrogen chloride on a saturated hydrocarbon at elevated temperature. The reaction therefore fills a need; and it seems plausible that an increase in hydrogen pressure would be accompanied by an increase in proton activity in this system just as in aqueous systems. The hydrogenolysis of *n*-pentane (Table 15) and its higher homologs[114, 125] that occurs in the presence of aluminum chloride-hydrogen chloride may be a consequence of this increased proton activity through the *proton penetration* process (X) also described on pages 62–68. Regardless of the mechanism, there is no doubt that hydrogenation of olefins does occur in the presence of isomerization catalysts, for when complexes of aluminum chloride with unsaturated hydrocarbons were heated at 150 to 175° with hydrogen under pressure, aluminum chloride was liberated and paraffins were produced[114].

If (XXIX) be admitted, a comparison of the reactions of a carbonium ion with the several types of side reaction suppressors reveals important differences between hydrogen and an aromatic compound on the one hand, and a naphthene and isobutane on the other. The several reactions are:

$$R^+ + H_2 \rightarrow RH + H^+ \qquad \text{(XXIX)}$$

$$R^+ + ArH \rightarrow RAr + H^+ \qquad \text{(XXXI)}$$

$$R^+ + C_nH_m \rightarrow RH + C_nH_{m-1}^+ \qquad \text{(XXXII)}$$

$$R^+ + i\text{-}C_4H_{10} \rightarrow RH + t\text{-}C_4H_9^+ \qquad \text{(XXXIII)}$$

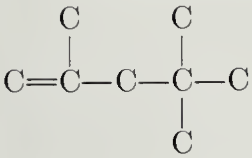
It is apparent that (XXIX) and (XXXI) consume a carbonium ion, whereas (XXXII) and (XXXIII) do not. For a carbonium ion chain reaction, naphthenes and isobutane are "chain-transfer" agents, whereas hydrogen and aromatic compounds are chain stoppers. Thus it is that hydrogen and aromatic compounds[252] inhibit isomerization as well as side reactions (data in Tables 17, 21, 25 and 29) whereas naphthenes and isobutane do not.

Isomerization of Olefins

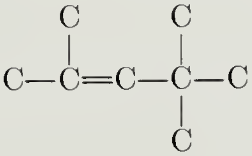
Phenomenological Aspects. Five types of olefin isomerization, differing in ease of accomplishment, may be distinguished. In order of increasing difficulty, these are: (1) *cis-trans* isomerization[226]; (2) double bond shift at a chain branch; (3) double bond shift in a branchless chain; (4) skeletal isomerization without change in maximum chain length; (5) skeletal isomerization with change in maximum chain length. By suitable choice of catalyst and conditions, any one of these may be accomplished without accompaniment by one more "difficult," but not without accompaniment by one less difficult. This is illustrated by the examples discussed below.

cis-trans Isomerization. *cis*-2-Butene was slowly isomerized to *trans*-2-butene without formation of 1-butene in the presence of activated charcoal at −80°[273]. This transformation also takes place without a catalyst at 347 to 420°[124] and is one of the very few types of hydrocarbon isomerization that can be accomplished thermally *without* accompanying decomposition (page 43).

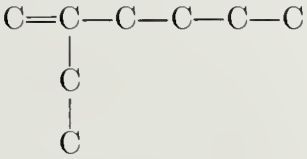
Double Bond Shift at a Chain Branch. The 2,4,4-trimethylpentenes (O and P below) were interconverted, and 2-ethyl-1-hexene (Q) was isomerized, on silica gel (containing adsorbed mineral acid[297]?) at 25°; but 1-hexene was not isomerized under similar conditions[74].


$C{=}C(C)-C-C(C)_2-C$

(O)

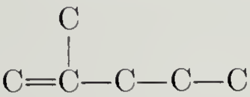

$C-C(C){=}C-C(C)_2-C$

(P)

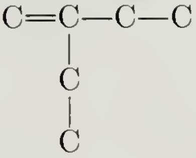

$C{=}C(C_2)-C-C-C-C$

(Q)

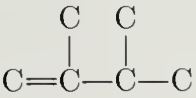
Also with silica at room temperature, 2-methyl-1- and -2-pentene (R and S below) were interconverted, the 2,3-dimethylbutenes (Y and Z) were interconverted, and 2-ethyl-1-butene (V) and 3-methyl-2-pentene (W) were interconverted; but 2-methyl-3-pentene (T), 4-methyl-1-pentene (U), and 3,3-dimethyl-1-butene (AA) were unchanged[127].


$C{=}C(C)-C-C-C$

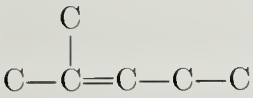
(R)


$C{=}C(C-C)-C-C$

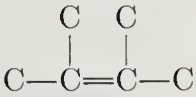
(V)


$C{=}C(C)-C(C)-C$

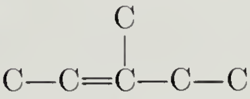
(Y)


$C-C(C){=}C-C-C$

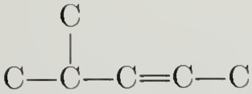
(S)


$C-C(C){=}C(C)-C$

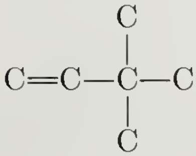
(Z)


$C-C{=}C(C)-C-C$

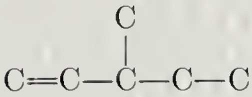
(W)


$C-C(C)-C{=}C-C$

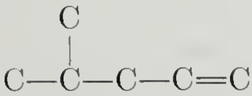
(T)


$C{=}C-C(C)_2-C$

(AA)


$C{=}C-C(C)-C-C$

(X)


$C-C(C)-C-C{=}C$

(U)

The 2,3-dimethylbutenes (Y and Z) were interconverted with a cobalt-containing "synthesis" catalyst at 190° without production of 3,3-dimethyl-1-butene (AA) or other hexenes[127].

Double Bond Shift in a Branchless Chain. 1-Butene has been converted to 2-butenes without production of appreciable amounts of the thermodynamically favored isobutylene with a variety of catalysts from room temperature to 450°[113, 159, 273, 320]. 1-Dodecene was isomerized to a mixture of 1-, 2-, 3-, 4-, and 5-dodecenes by magnesium bromide in anhydrous ether at about 35°[5]. The various 2-methylpentenes (R, S, T, and U) were equilibrated with a cobalt-containing "synthesis" catalyst at 190° without production of 3-methylpentenes (V, W, and X)[127].

Skeletal Isomerization without Change in Maximum Chain Length. The three dimethylbutenes (Y, Z, and AA) are interconverted with aluminum sulfate, alumina, or phosphorus pentoxide on silica gel at 275 to 330° without production of less highly branched isomers[25, 47, 127, 133, 301]. The various 2- and 3-methylpentenes (R, S, T, U, V, W, and X) are interconverted with alumina at 200° without formation of more or less highly branched isomers[127].

Skeletal Isomerization with Change in Maximum Chain Length. Conversion of straight-chain olefins to branched-chain isomers has been accomplished with various forms of alumina[17, 18, 79, 97, 175, 188], with aluminum sulfate[73, 97], with supported phosphoric acid[18, 73, 97, 175, 198, 200, 204-5] and with zinc chloride on pumice[33, 198-9] at temperatures above about 260°, with permutite[245] at 400°, with thoria[79] above about 400°, and with beryllia[314] at 450°. These are typical of the conditions of temperature and catalyst acidity required for this type of isomerization. It takes place at lower temperatures with stronger acids, but not without polymerization and hydrogen transfer. (For example, 2-butene gave iso-butane and polymers with 96 per cent sulfuric acid at 0°[32]).

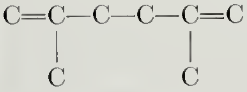
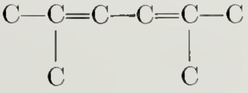
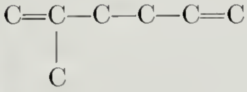
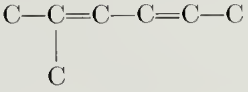
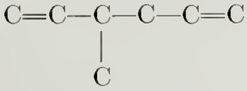
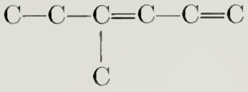
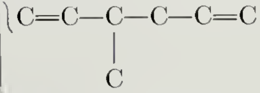
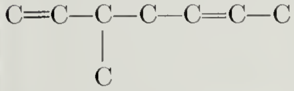
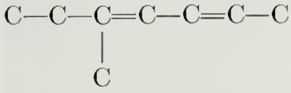
Similar conditions are required for alteration of ring size in cycloalkenes, for example, the interconversion of cyclohexene and methylcyclopentenes[1, 3, 4, 224, 245, 251, 312-3].

These examples indicate that the five types of olefin isomerization are separated by differences in activation energy that may in some cases be quite large.

Similar differences in ease of isomerization were apparent in results obtained with diolefins shown in Table 22. As with monoölefins, double bond shifting is facilitated by the presence of a chain branch. (Compare Experiments 1, 2, and 3; and note that 3-methyl-1,5-hexadiene gave "3-methyl-3,5-hexadiene" and that 3-methyl-1,5-heptadiene gave "3-methyl-3,5-heptadiene," both involving migration of a double bond past a chain branch.) These data also show that terminal double bonds are shifted more readily than those buried in the chain. (Compare Experiments 1, 5, and 7 and Experiments 4 and 6; and note that 1,5-hexadiene gave more 2,4-hexadiene than 1,3-hexadiene.)

Mechanism of Isomerization with Acidic Catalysts. The examples of olefin isomerization mentioned above, except possibly those with activated charcoal and the cobalt-containing "synthesis" catalyst, have been with catalysts that are commonly regarded as *acidic*. The isomerization of olefins with *acidic* catalysts can generally be interpreted by means of a carbonium ion mechanism[84, 188, 272, 298] with the following steps: (1) Addition of a proton from the catalyst to the olefin to produce a carbonium ion. (2) Rearrangement of the carbonium ion. (3) Transfer of a proton from the new carbonium ion to the catalyst to regenerate an olefin with a new structure. The fact that the rate of exchange of tritium between 1-butene and phosphoric acid, when corrected for isotope effects, was the same as the rate of isomerization of 1-butene to 2-butene[273] is in accordance with such a carbonium ion mechanism.

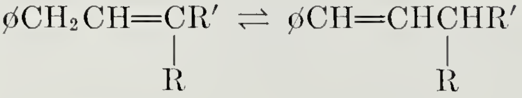
TABLE 22. ISOMERIZATION OF DIOLEFINS WITH ACTIVATED ALUMINA AT 365°[a]

Experiment	Diolefin charged	Total conversion (%)[b]	Product	Yield (%)
1	C=C—C—C—C=C	56	C—C=C—C=C—C C=C—C=C—C—C	39 3
2	 $\mathrm{C{=}\underset{\overset{\mid}{C}}{C}{-}C{-}C{-}\underset{\overset{\mid}{C}}{C}{=}C}$	99	 $\mathrm{C{-}\underset{\overset{\mid}{C}}{C}{=}C{-}C{=}\underset{\overset{\mid}{C}}{C}{-}C}$	81
3	 $\mathrm{C{=}\underset{\overset{\mid}{C}}{C}{-}C{-}C{-}C{=}C}$	100	 $\mathrm{C{-}\underset{\overset{\mid}{C}}{C}{=}C{-}C{=}C{-}C}$	58
4	 $\mathrm{C{=}C{-}\underset{\overset{\mid}{C}}{C}{-}C{-}C{=}C}$	100	 $\mathrm{C{-}C{-}\underset{\overset{\mid}{C}}{C}{=}C{-}C{=}C}$	14
5	C=C—C—C—C=C—C	42	C—C=C—C=C—C—C  $\mathrm{C{=}C{-}\underset{\overset{\mid}{C}}{C}{-}C{-}C{=}C}$	6 8
6	 $\mathrm{C{=}C{-}\underset{\overset{\mid}{C}}{C}{-}C{-}C{=}C{-}C}$	30	 $\mathrm{C{-}C{-}\underset{\overset{\mid}{C}}{C}{=}C{-}C{=}C{-}C}$	4
7	C—C=C—C—C—C=C—C	28	C—C—C=C—C=C—C—C	0.5

[a] From Henne and Turk[101].

[b] Some cracking occurred in each case.

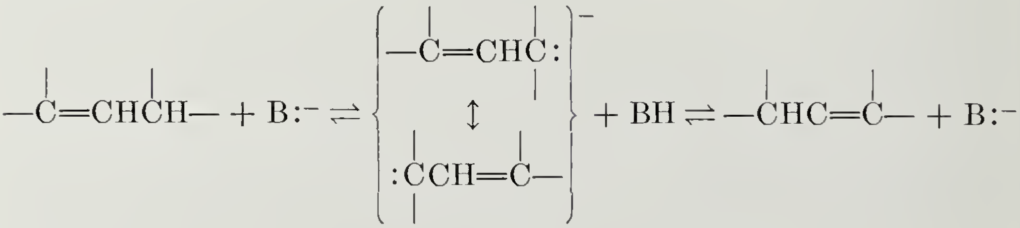
Isomerization with Basic Catalysts. 1-Alkenes have been isomerized by a shift of the double bond toward the center of the molecule by means of potassium amide in liquid ammonia at 25°; and 1,5-hexadiene was converted to its conjugated isomer, 2,4-hexadiene, under the same conditions[250]. Calcium amide is effective for isomerizing 2- and 3-methyl-1-butene to 2-methyl-2-butene and 2,5-dimethyl-1,5-hexadiene to its conjugated isomer, 2,5-dimethyl-2,4-hexadiene[82a]. The temperature used in each case was the boiling point of the hydrocarbon. Calcium and barium hydrides are effective at 150 to 475° for isomerizing 1-pentene to *cis*- and *trans*-2-pentenes[309a]. Certain 3-phenylpropenes (BB) have been isomerized to equilibrium mixtures with 1-phenylpropenes (CC) by means of alcoholic alkali at 165°[12, 13] (page 44).



$$\phi CH_2CH{=}\underset{\underset{\displaystyle R}{|}}{C}R' \rightleftharpoons \phi CH{=}CH\underset{\underset{\displaystyle R}{|}}{C}HR'$$

(BB) (CC)

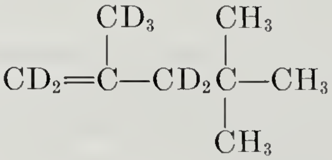
Olefin isomerization with basic catalysts appears to be limited to such shifting of the position of the double bond as is illustrated by the above-mentioned examples. Thus calcium and barium hydrides were not effective for interconversion of cyclohexene and 1-methylcyclohexene at 300 to 475°[309a]. The mechanism presumably involves the formation of a resonance-stabilized carbanion (DD):



$$-\overset{|}{C}{=}CH\overset{|}{C}H- + B:^- \rightleftharpoons \left\{\begin{matrix} -\overset{|}{C}{=}CH\underset{|}{\overset{|}{C}}: \\ \updownarrow \\ :\underset{|}{\overset{|}{C}}CH{=}\overset{|}{C}- \end{matrix}\right\}^- + BH \rightleftharpoons -\overset{|}{C}HC{=}\overset{|}{C}- + B:^-$$

(DD)

Because of the stabilization by resonance, hydrogen on *alpha* carbons is much more reactive than that in other parts of the molecule. This is demonstrated by the fact that 2,4,4-trimethyl-1-pentene gave 2-(methyl-d_3)-4,4-dimethyl-1-pentene-1,1,3,3-d_4 (EE below) when treated with potassium amide and ammonia-d_3 at 120°[250].



$$CD_2{=}\overset{\displaystyle CD_3}{\overset{|}{C}}-CD_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH_3$$

(EE)

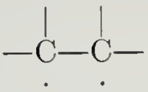
Metallic sodium, promoted with organic compounds such as *o*-chlorotoluene and anthracene, which are capable of reacting with the sodium to form organosodium compounds, is also an effective catalyst for double bond migration in olefins. Thus 1-butene was isomerized to a near-equilibrium mixture with 2-butene by means of sodium promoted with *o*-chlorotoluene and in benzene or cyclohexane as solvent in 3.5 to 4.0 hours at 150°. Similarly 1-decene was 99 per cent isomerized to a mixture of *cis*- and *trans*-decenes with the general formula RCH═CHR′ in 20 hours at the boiling point (165 to 170°). Isomerization proceeded without extensive side reactions; and no skeletal isomerization of the butenes was observed. A mechanism similar to that described above was proposed with an organosodium compound, formed by reaction of the sodium with the promoter, acting as a base[217b].

Isomerization with Electronic-type Catalysts. The *cis-trans* isomerization of 2-butene with activated charcoal mentioned above[273] and the double bond shifting that occurs in the presence of cobalt[127], nickel[270, 273, 290], palladium[315], or platinum[137, 144] involve catalysts with which acidic properties are not ordinarily associated. A carbonium ion mechanism is not ruled out with these catalysts (activation by alternate heating in oxygen and hydrogen or by reduction of an oxide may leave oxygen and protons on the surface) but it does not seem likely because of the absence of skeletal isomerization. Moreover, these substances are primarily hydrogenation catalysts; and since they are transition elements, this catalytic activity is probably a consequence of their having unfilled *d* orbitals. This gives them the ability to accept electrons one at a time, and thus to promote reaction by an atomic-free radical mechanism. For this reason, they may be described as *mono*-electronic (pages 51, 74).

Nickel, for example, may be given the electronic structure:

$$\text{Ni (At. no. 28) } 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \underset{(3d\quad\text{subshell})}{(:)(:)(:)(.)(.)}\quad \underset{4s}{(:)}$$

Adsorption of a hydrogen *atom* or organic radical may result in filling one of the *d* orbitals. Olefins may be adsorbed at one or both of the doubly bonded carbons as a di-radical:

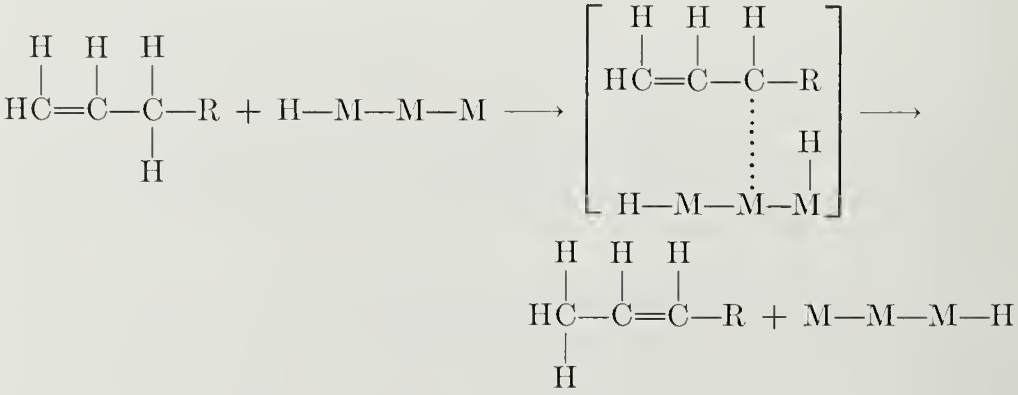


$$-\underset{\cdot}{\overset{|}{\mathrm{C}}}-\underset{\cdot}{\overset{|}{\mathrm{C}}}-$$

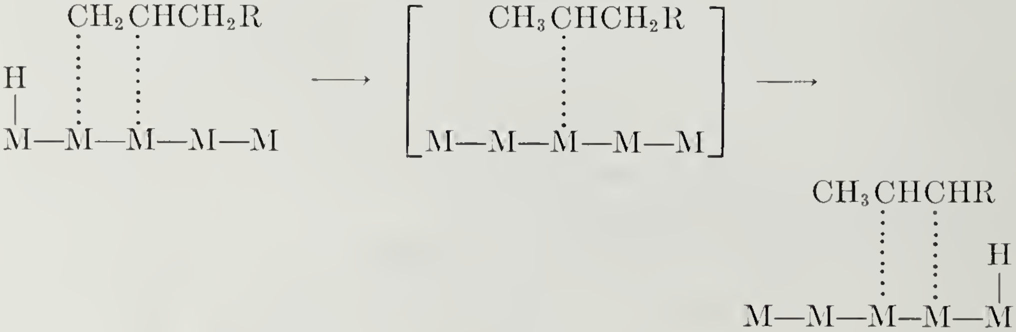
At any rate, it seems probable that the *oxidation state* of the organic fragment in reactions with these catalysts is that of a *free radical* rather than that of a carbonium ion or carbanion (cf. pages 57–58).

Accordingly, double bond migration may take place on the surface of such a metal (M) by one of the following mechanisms[270].

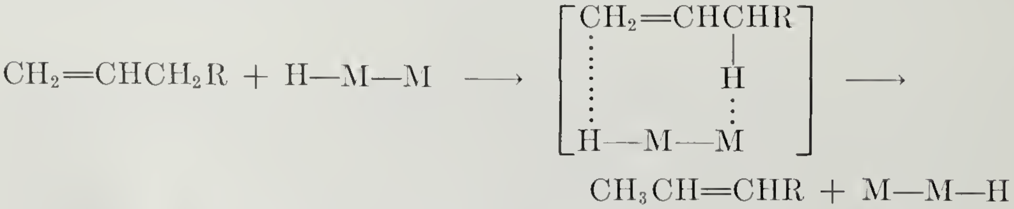
(*1*) *The "dissociative" mechanism*[62]. Adsorption of the olefin occurs at an *alpha* carbon by a dissociative process giving M—H and a carbon-metal bond. A hydrogen atom already adsorbed on the surface then adds to the opposite end of the double bond:



(*2*) *The "associative" mechanism*[290]. The olefin is adsorbed at the double bond. A hydrogen atom already on the surface adds to one end of the double bond while a hydrogen from the *alpha* carbon at the other end is adsorbed at another site:



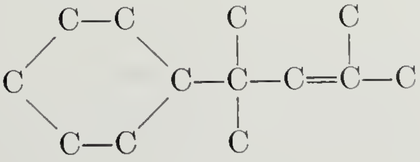
(*3*) *The "hydrogen-switch" mechanism*[273]. This mechanism, in contrast to the "dissociative" and "associative" mechanisms, does not involve carbon-to-metal bonds[270]. A hydrogen atom already on the surface of the metal is added to one end of the double bond while a hydrogen from the *alpha* carbon at the other end is simultaneously adsorbed at another site[270]:



Available experimental data do not permit an unequivocal choice between these three points of view[270]. In accordance with any one of them, each molecule isomerized will have acquired one new hydrogen atom from the catalyst. This has been found to be so by a comparison of the rates of isomerization of 1-butene to 2-butenes and of deuterium-hydrogen exchange between 1-butene and deuterium in the presence of nickel[270]. Such studies were complicated by the fact that in the presence of hydrogen at 100°, the isomerization rate was ten times that in the presence of deuterium. When this difference was taken into account, the rates and activation energies of isomerization and exchange were found to be practically the same[270]. Furthermore, the rate constant for introduction of a second deuterium at 100° was about $\frac{1}{15}$ that for the first deuterium. The above mechanisms indicate that, with 1-butene as the substrate, the introduction of a second deuterium would be accompanied largely by reversion of 2-butene-1-*d* to 1-butene-d_2, either $CHD{=}CHCHDCH_3$ or $CH_3DCHDCH{=}CH_2$. Inasmuch as the equilibrium content of 2-butene is about 94 per cent at 100° (pages 166–167), the rate of reversion would be $\frac{6}{94}$ the rate of isomerization of 1-butene, which is in good agreement with the ratio of $\frac{1}{15}$ for the rate of introduction of a second deuterium.

Although hydrogen has been found to be necessary for double bond migration on nickel at 60 to 135°[270, 290], which is in accordance with the above mechanisms, carbon dioxide was a suitable carrier gas for the conversion of 2,7-dimethyl-1-octene to 2,7-dimethyl-2-octene on palladium at 200°[315]. Therefore, some other mechanism is indicated under these conditions.

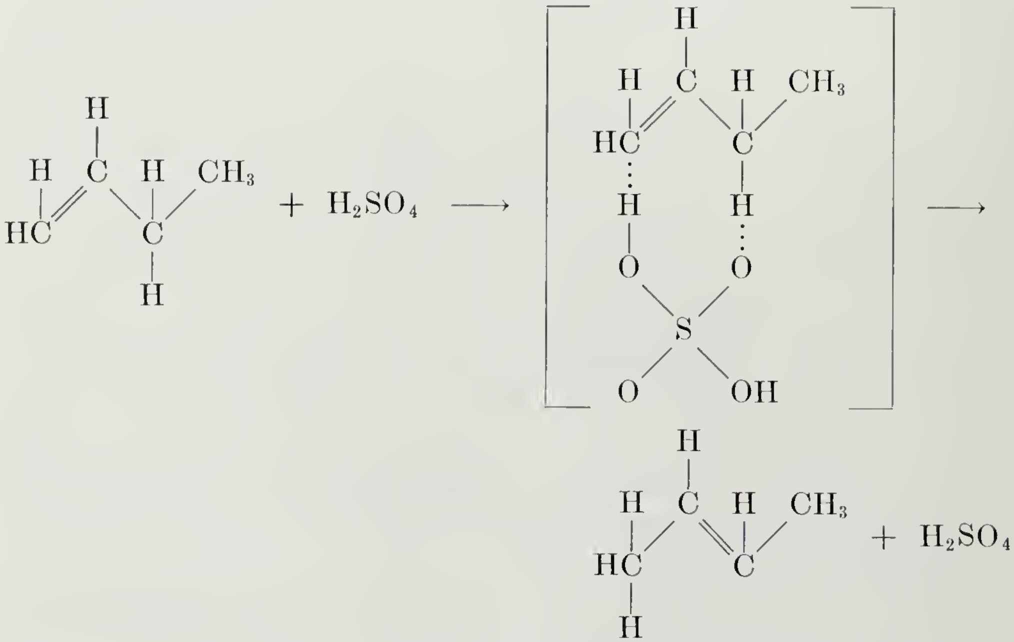
In accordance with the stepwise picture of double-bond migration furnished by the above mechanisms, the compound with a quaternary carbon,



(FF)

4-cyclohexyl-2,4-dimethyl-2-pentene (FF) was not isomerized (to a cyclohexene derivative) in the presence of platinum[137] at 200°.

According to the "hydrogen-switch" mechanism, "the critical demand on the catalyst is that it be able to furnish a hydrogen and accept a hydrogen at a distance of approximately 3.5 Å"[273], this being the minimum distance between C_1 of an olefin and a hydrogen on C_3. This demand is met by a number of substances in addition to nickel (3.52 Å), including sulfuric acid (3.45 Å), silicic acid (3.50 Å), phosphoric acid (3.46 Å), perchloric acid (3.41 Å), "$HAlCl_4$" (3.46 Å), and "$HAlBr_4$" (3.58 Å), which are known to catalyze olefin isomerization. In these geometric terms, the isomerization of 1-butene by sulfuric acid, for example, can be represented as follows:



Although these geometric considerations support the "hydrogen-switch" mechanism, no quantitative correlations of catalyst activity with interatomic distances, which is the least one might expect of such a detailed theory, have appeared. Furthermore, it is not unlikely that many substances could be named which have the required geometry but which are not active catalysts.

Isomerization of Aromatic Hydrocarbons

Phenomenological Aspects. Several types of isomerization peculiar to aromatic hydrocarbons are conceivable. Some of these are:

(1) A shift in the position of an alkyl group attached to an aromatic ring, as in the interconversion of isomeric xylenes.

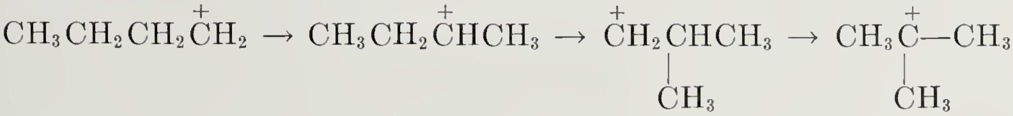
(2) Isomerization within an alkyl group or nonaromatic side chain attached to an aromatic ring, as in the conversion of *n*-propylbenzene to *iso*propylbenzene.

(3) Isomerization involving changes in the carbon content of alkyl groups or nonaromatic side chains attached to an aromatic ring; the simplest example is the interconversion of a xylene and ethylbenzene.

(4) Interconversions of polynuclear aromatic hydrocarbons; for example, anthracene and phenanthrene.

Other types of isomerization and various combinations of the several types are conceivable and have been observed[55].

Mechanisms. The isomerization of a polyalkylbenzene by the shift of an alkyl group (type 1 above) is sometimes accompanied by disproportionation to products having more or fewer alkyl groups attached to the same aromatic nucleus. This fact has led to the view that such isomerizations comprise dealkylation and realkylation and are not truly intramolecular. This point of view was strengthened by early reports, now regarded as incorrect, that isomerization of various 1,3-dimethyl-4-alkylbenzenes was accompanied by rearrangement of the migrating alkyl group. Thus 1,3-dimethyl-4-*n*-butylbenzene was reported to give 1,3-dimethyl-5-*sec*-butylbenzene, and 1,3-dimethyl-4-*sec*-butylbenzene was reported to give 1,3-dimethyl-5-*tert*-butylbenzene, when heated with aluminum chloride at 100°[178, 263]. In order to account for these observations, it was supposed that butyl positive ions were formed and rearranged in accordance with Whitmore's generalization (I, page 58) before rejoining the aromatic nucleus[178]:



$$\mathrm{CH_3CH_2CH_2\overset{+}{C}H_2} \longrightarrow \mathrm{CH_3CH_2\overset{+}{C}HCH_3} \longrightarrow \mathrm{\overset{+}{C}H_2\underset{\displaystyle CH_3}{CH}CH_3} \longrightarrow \mathrm{CH_3\underset{\displaystyle CH_3}{\overset{+}{C}}{—}CH_3}$$

This work raised the question, "If a *sec*-butyl ion is formed from an *n*-butyl ion why is it not further isomerized to yield finally a *tert*-butyl ion[178]?" However, a recent repetition of these isomerizations, supplemented by infrared spectroscopic examination of the products, has established that migration of butyl groups occurs chiefly without rearrangement: 1,3-dimethyl-4-*n*-butylbenzene gave 1,3-dimethyl-5-*n*-butylbenzene; 1,3-dimethyl-4-*sec*-butylbenzene gave 1,3-dimethyl-5-*sec*-butylbenzene; and 1,3-dimethyl-4-isobutylbenzene gave 1,3-dimethyl-5-isobutylbenzene as the principal rearrangement product in each case[177a]. These results are concordant with observations that *n*-butylbenzene gave some *m*-di-*n*-butylbenzene when heated with aluminum chloride at 100°[121a] and that no rearrangement of migrating *n*- or *sec*-butyl groups occurred during disproportionation of *n*- or *sec*-butylbenzene with hydrogen fluoride-boron fluoride at room temperature[161].

The *n*-propyl group also undergoes migration without rearrangement. Thus, 1,2,4-tri-*n*-propylbenzene gave 1,3,5-tri-*n*-propylbenzene on isomerization with aluminum chloride at 100°[10]. Disproportionation of *n*-propylbenzene under similar conditions gave benzene and di-*n*-propylbenzenes[10]. Furthermore, an early report that 1,3-dimethyl-4-*n*-propylbenzene gave only 1,3-dimethyl-5-isopropylbenzene on treatment with aluminum chloride at 100°[177] has been shown to be incorrect. The major rearrangement product was 1,3-dimethyl-5-*n*-propylbenzene, although the spectroscopic and chemical evidence did not exclude the possible presence of 10 to 15 per cent of 1,3-dimethyl-5-isopropylbenzene[177b].

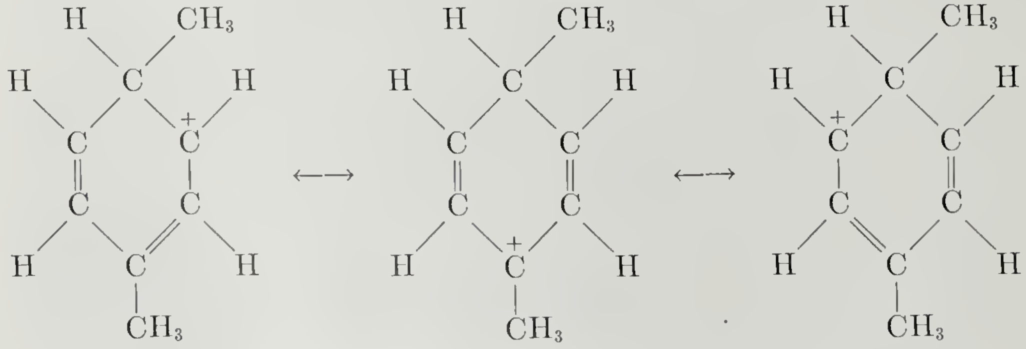
In experiments designed to detect small amounts of isomerization by means of the powerful isotopic tracer techniques, *n*-propylbenzene labeled with C^{14} in the β-position was contacted with aluminum chloride, monopropyl- and dipropylbenzene fractions from the product were oxidized to benzoic and phthalic acids, and the C^{14} content of these was determined by combustion. Data and results are presented in Table 22a. Comparison of Experiments 1 and 2 indicates the reaction is complete in 6.5 hours under the conditions selected. Experiment 3 indicates that the extent of rearrangement depends on the proportion of catalyst[233a].

Intermolecular transfer of alkyl groups, which must occur during disproportionation of an alkylbenzene, may lead eventually to an isomer of the starting material. However, the occurrence of isomerization with very little accompanying disproportionation indicates isomerization may take place by an intramolecular mechanism. Thus, *p*-xylene has been converted to near-equilibrium mixtures of xylenes without appreciable disproportionation by means of aluminum bromide-hydrogen bromide at room temperature[9], with hydrogen fluoride-boron fluoride in the temperature range 3 to 121°[160], and even with silica-alumina at 515° (Table 23)[24]. In such an event, the first step appears to be addition of a proton from the catalyst to the alkylbenzene to form a carbonium ion, very likely a resonance hybrid of forms such as the following in the case of *p*-xylene:

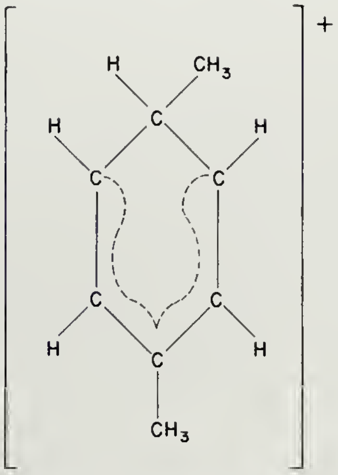
TABLE 22a. REARRANGEMENT OF *n*-PROPYL GROUPS DURING DISPROPORTIONATION[a]
(Temperature = 100°)

Experiment	1	2	3
n-[β-C^{14}]Propylbenzene, g	13.8	13.8	13.8
Aluminum chloride, g	2.5	2.5	5.0
Time of heating, hr	6.5	24	6.5
Rearrangement, % calculated from			
Benzoic acid	12.6	12.4	31.2
Phthalic acid	13.1	12.5	31.2

[a] From Roberts and Brandenberger[233a].

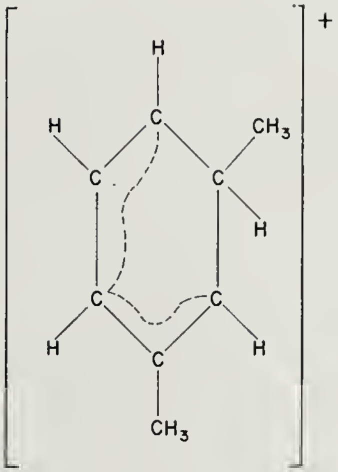


which may be represented more simply as follows[160]:



(GG)

The next step is rearrangement to another resonance-stabilized cation:

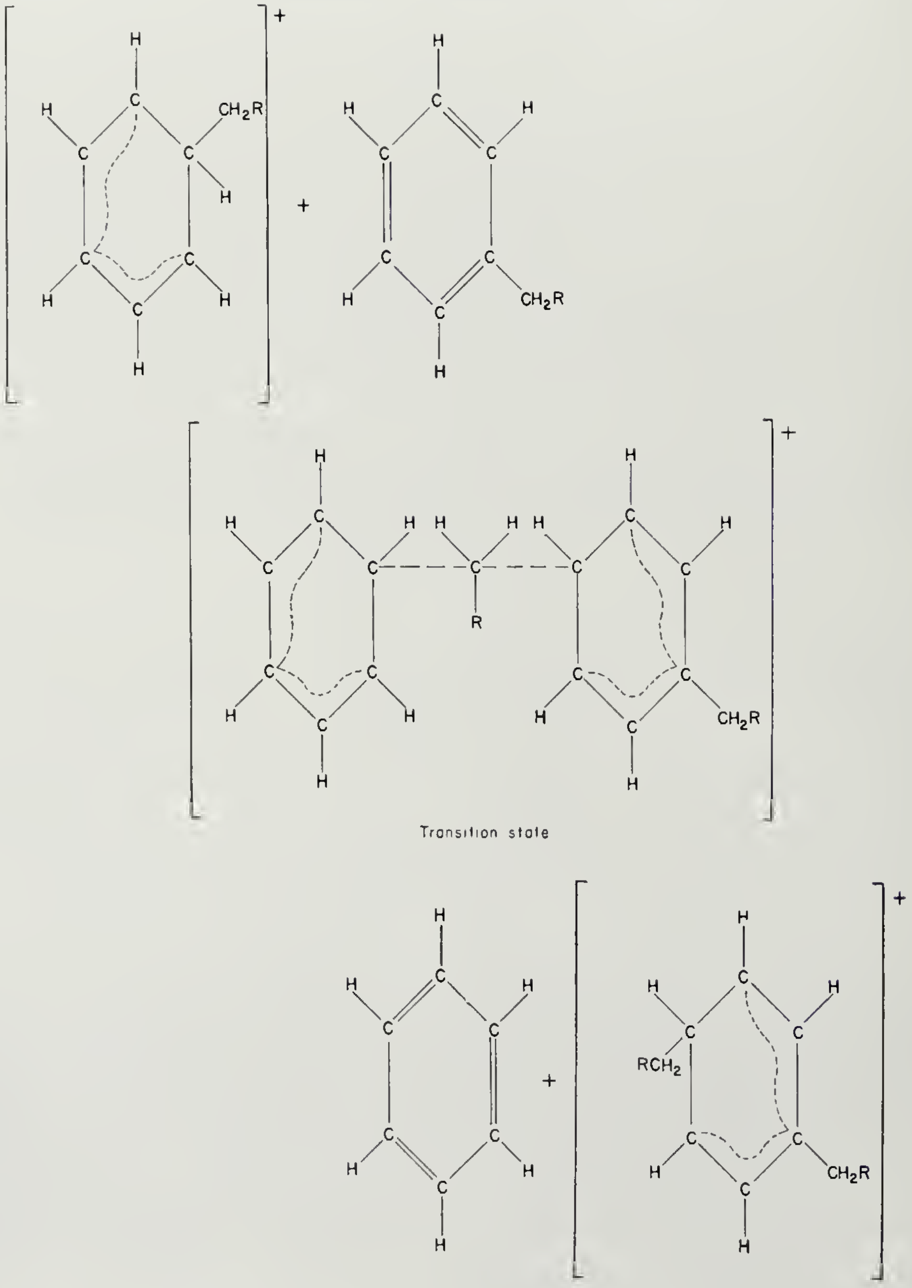


(HH)

Finally, return of a proton by the cation (HH) to the catalyst gives the rearranged product[9, 160].

In further support of this mechanism may be cited the observation that, in the absence of hydrogen bromide, *p*-xylene remained unchanged after contact with aluminum bromide at room temperature for a day[9]. The rate of isomerization increased with the concentration of hydrogen bromide. Thus it appears that a proton source is essential, as required by the first step in the mechanism outlined above.

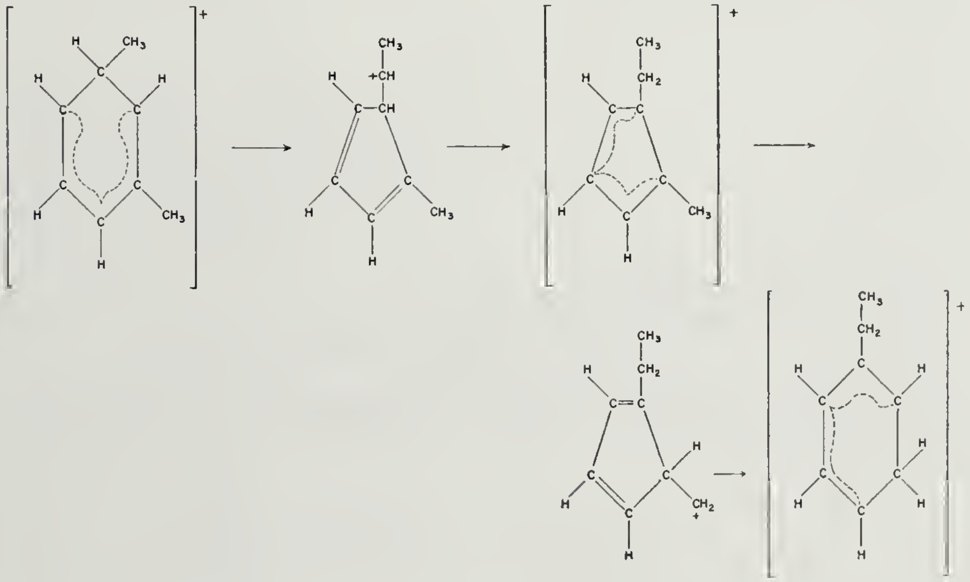
By this mechanism, a *n*-propyl group, for example, could migrate without undergoing isomerization, since it need never be free as an alkyl positive ion. A companion mechanism for disproportionation, in which the structure of the alkyl group is preserved, involves a bimolecular displacement of one aromatic hydrocarbon by another on the *alpha* carbon of the positive ion[161]:



In support of this mechanism, the disproportionation of *m*-xylene in the presence of hydrogen fluoride-boron fluoride was found to be second order in xylene with an activation energy about 10 kcal higher than the isomerization of *p*-xylene[153, 161].

The second order nature of the disproportionation is also illustrated by the effect of pressure on the course of isomerization of xylenes over a silica-alumina catalyst at 515° shown by the data in Table 23. A reduction in pressure resulted in a decrease in the fraction of disproportionation as would be expected if the disproportionation were of higher order than the isomerization. "In the disproportionation reaction, two molecules of xylene apparently are adsorbed on sites which are located sufficiently close to each other to allow a shift of a methyl group, thereby forming toluene and a C_9-aromatic. If the operating pressure is reduced so that the catalyst surface is more sparsely covered, the isomerization reaction proceeds to the exclusion of the disproportionation reaction."[24]

The data in Table 23 also reveal isomerization of xylenes to ethylbenzene. The isomerization is undoubtedly intramolecular, in view of the high product recoveries and almost negligible disproportionation at the lower pressure. The transformation can be represented intramolecularly by means of resonance-stabilized carbonium ions as follows:



Alkyne-Alkadiene Interconversions

Isomerization with Acidic Catalysts. Isomerization of alkynes and alkadienes has been studied extensively with chromia-alumina[135, 138-40, 143, 146-9] at 225 to 300° and with Floridin[254-62], a naturally-occurring silicate, at 200 to 330°. 1-Heptyne is isomerized in the presence of pumice at 350° [88]. On these chalcide-type, probably acidic, catalysts the reaction is governed largely by thermodynamic stabilities of the several possible isomers; and since 1,3-dienes are usually less energy-rich than non-conjugated dienes and alkynes, they are often formed and then undergo polymerization. An interesting exception appears to be 2,4-dimethyl-1,3-pentadiene (II), which is said to be isomerized on Floridin to 2,4-dimethyl-2,3-pentadiene (JJ)[256].

$$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 \longrightarrow CH_3\overset{CH_3}{\overset{|}{C}}{=}C{=}\overset{CH_3}{\overset{|}{C}}CH_3$$

(II) (JJ)

Skeletal isomerization has also been observed, as in the isomerization of 4,4-dimethyl-1,2-pentadiene (KK) to 2,4-dimethyl-2,3-pentadiene (JJ) on Floridin at 230°[258].

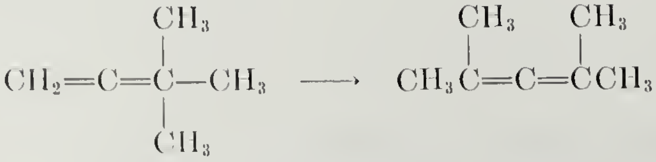
Table 23. Effect of Pressure on Isomerization and Disproportionation of Xylenes with Silica-Alumina at 515°[a]

Experiment	0[b]	1	2	3
Pressure, atm.	—	1	0.12	0.12
Liquid space velocity, hr^{-1}	—	0.7	0.6	1.2
Product composition, mole %[c]				
Benzene	—	1.2	—	—
Toluene	—	13.0	1.1	1.0
m-Xylene	84.0	32.3	59.8	60.3
p-Xylene	9.0	18.9	18.1	20.6
o-Xylene	5.0	13.0	9.2	7.0
Ethylbenzene	2.0	5.1	11.5	11.1
C_9 Aromatics	—	16.5	0.3	—

[a] From Boedeker and Erner[24].

[b] Charge composition given in this column.

[c] No loss basis. Liquid recoveries were above 98 per cent in all cases.



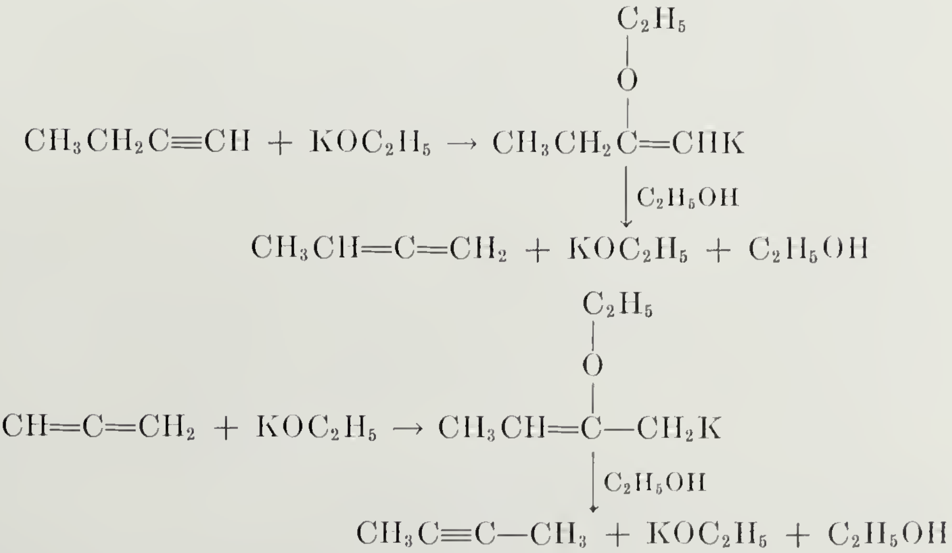
$$CH_2{=}C{=}\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3 \longrightarrow CH_3\overset{CH_3}{\overset{|}{C}}{=}C{=}\overset{CH_3}{\overset{|}{C}}CH_3$$

(KK) (JJ)

In view of the above-mentioned characteristics of the isomerization of alkynes and alkadienes on chalcide-type catalysts, it seems probable that intermediates formed by addition of a proton from the catalyst to the substrate are involved.

Isomerization with Basic Catalysts. In addition to acidic catalysts of the type mentioned above, basic catalysts can be used to effect certain alkyne-alkadiene isomerizations. For example, in 1887, Favorskii[63] reported the isomerization of 1-butyne and 1-pentyne to the corresponding

2-alkynes by means of alcoholic alkali at 170°. He thought the alcohol was essential and that alkoxyalkenes were formed as intermediates:



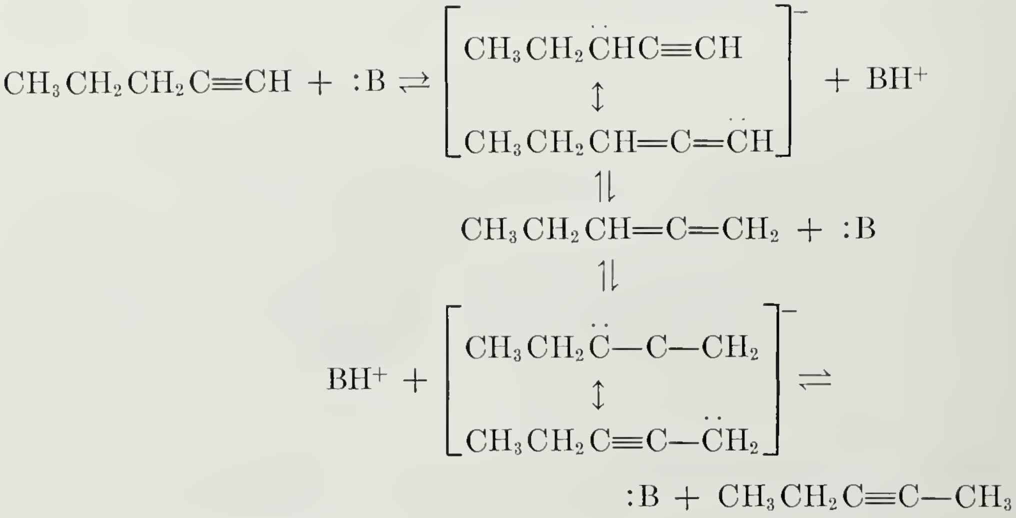
$$
\begin{aligned}
&CH_3CH_2C{\equiv}CH + KOC_2H_5 \rightarrow CH_3CH_2\overset{\substack{C_2H_5\\ |\\ O\\ |}}{C}{=}CHK\\
&\qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow C_2H_5OH\\
&\qquad\qquad CH_3CH{=}C{=}CH_2 + KOC_2H_5 + C_2H_5OH\\
&CH_3CH{=}C{=}CH_2 + KOC_2H_5 \rightarrow CH_3CH{=}\overset{\substack{C_2H_5\\ |\\ O\\ |}}{C}{-}CH_2K\\
&\qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow C_2H_5OH\\
&\qquad\qquad CH_3C{\equiv}C{-}CH_3 + KOC_2H_5 + C_2H_5OH
\end{aligned}
$$

Conclusive evidence against this mechanism is provided by the fact that 2-ethoxy-1-pentene is unchanged by alcoholic potassium hydroxide under conditions leading to equilibration of 1-pentyne, 2-pentyne, and 1,2-pentadiene[115]. Furthermore, 1-heptyne has been isomerized with alkaline catalysts in the absence of alcohol, as with soda lime at 380°, and is produced from isomeric heptynes by means of sodamide in mineral oil at 160°[88].

With these alkaline catalysts, isomerization appears to be limited to interconversions of 1- and 2-alkynes and 1,2-alkadienes. The formation of 1,3-alkadienes and skeletal isomerization have not been observed. The absence of 1,3-alkadienes cannot be attributed to their ease of polymerization, for 1,3-pentadiene survived treatment by alcoholic potassium hydroxide under conditions leading to equilibrium between 1-pentyne, 2-pentyne and 1,2-pentadiene[115].

The nature of the product is therefore governed by thermodynamic relationships between 1-alkyne, 2-alkyne, and 1,2-alkadiene. Of these, the 2-alkyne is usually the most stable. The others, being present in only small amounts at equilibrium, have often escaped detection. The isomerization of high molecular weight 2-alkynes to 1-alkynes takes place in the presence of sodium at 200 to 215°, in apparent violation of the probable thermodynamic requirements[131]. This reaction may not be a true isomerization, however, but may involve the formation of a sodium 1-alkynide as the product, which would displace the equilibrium toward the 1-alkyne.

The interconversion of 1-alkynes, 2-alkynes, and 1,2-alkadienes in the presence of alkali probably involves resonance-stabilized *carbanions*, the mechanism being illustrated with 1-pentyne[115] as follows:



$$CH_3CH_2CH_2C{\equiv}CH + :B \rightleftharpoons \left[\begin{array}{c} CH_3CH_2\ddot{C}HC{\equiv}CH \\ \updownarrow \\ CH_3CH_2CH{=}C{=}\ddot{C}H \end{array}\right]^- + BH^+$$

$$\rightleftharpoons$$

$$CH_3CH_2CH{=}C{=}CH_2 + :B$$

$$\rightleftharpoons$$

$$BH^+ + \left[\begin{array}{c} CH_3CH_2\ddot{C}{-}C{-}CH_2 \\ \updownarrow \\ CH_3CH_2C{\equiv}C{-}\ddot{C}H_2 \end{array}\right]^- \rightleftharpoons$$

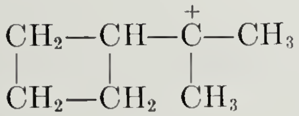
$$:B + CH_3CH_2C{\equiv}C{-}CH_3$$

Further Aspects of Carbonium Ion Theory

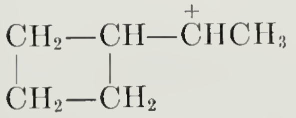
It will be apparent from much of the foregoing that the carbonium ion theory plays a large part in the interpretation of isomerization of hydrocarbons in the presence of acidic catalysts. It is of course futile to debate the "correctness" of the carbonium ion mechanisms vis-a-vis alternative mechanisms. "Correctness" of any scientific theory is to be gauged largely in terms of its utility. Carbonium ion theory has a utility and a generality that cannot be claimed by its alternatives. With its aid, a great body of information is given a unity that would otherwise be lacking. This mass of information cannot be reviewed here, since it pertains not only to catalytic isomerization, but also to many other reactions, both catalytic and noncatalytic, such as alkylation and cracking, polymerization and depolymerization, hydration and dehydration, and displacement reactions. In view of this widespread applicability, it is inevitable that viewpoints developed in the application of carbonium ion theory to observations in one field should find utility in interpreting phenomena observed in another. Indeed it is mandatory, if carbonium ion theory is to maintain its self-consistency, that viewpoints do not remain too long divergent. Some important aspects of carbonium ion theory, arising chiefly out of studies in fields other than hydrocarbon isomerization, but having applicability to isomerization, are discussed here.

Relative Stability of Carbonium Ions. Perhaps the strongest thread in the fabric of carbonium ion theory is the concept that tertiary ions are much more stable than secondary ions and secondary ions are in turn more stable than primary ions. The concept is suggested qualitatively by Markownikov's Rule; but perhaps the earliest quantitative support was provided by the rate constants of homogeneous solvolytic reactions, such as those given in Table 5. These particular values (Table 5) show that a tertiary bromide reacts about 10^6 times as readily as a secondary bromide, which is in turn about 20 times as reactive as a primary bromide, in reactions for which the rate-controlling step is conceivably dissociation into a carbonium ion. The difference in rates for *tert*-butyl and iso-propyl corresponds to an activation energy difference of about 11 kcals, which is of the same order of magnitude as the 10 to 15 kcals difference in stability of tertiary and secondary carbonium ions reportedly calculated from energy data[267].

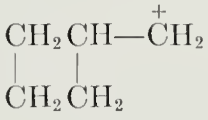
Irrespective of these quantitative considerations, innumerable observations have been correlated qualitatively with the concept of differing carbonium ion stability. Many of these have been mentioned in the preceding pages. One other that is of particular interest is the difference in behavior of various alkylcyclobutanes toward aluminum halide isomerization catalysts near room temperature. Methylcyclobutane polymerized with no detectable isomerization. Ethylcyclobutane isomerized to methylcyclopentane and cyclohexane; but the isomerization was accompanied by over 50 per cent of polymerization. With isopropylcyclobutane, however, extensive isomerization to methylcyclohexane and dimethylcyclopentanes occurred with very little polymerization. The striking difference in the tendency of these compounds to isomerize was attributed to decreasing ease of formation of the ions (LL), (MM), and (NN)[212]:



(LL)



(MM)

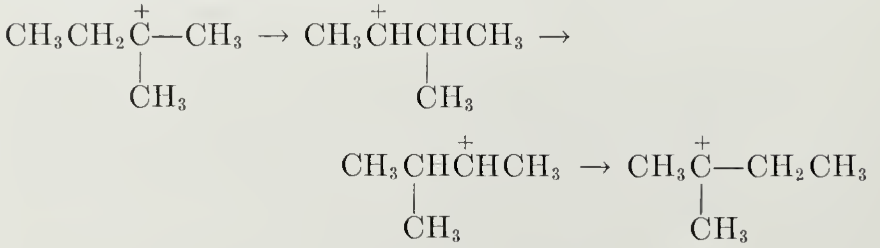


(NN)

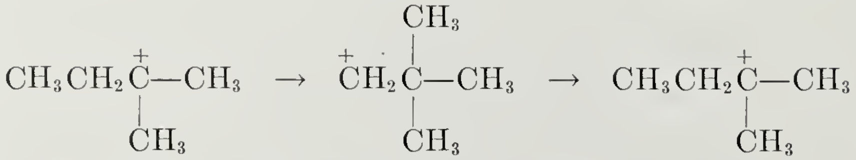
In each case, formation of the ion is essential to isomerization with ring enlargement and is in competition with a protolytic opening of the cyclobutane ring.

Alternative Routes in Carbonium Ion Rearrangements. Paradoxically, perhaps the greatest weakness of carbonium ion theory is its adaptability. Almost any conceivable rearrangement can be represented by means of a series of 1,2-shifts of alkyl groups or hydrogen in carbonium ion intermediates, however bizarre it may need to be. Even in simple cases, the over-all result can often be given more than one route. Then the theory is most dissatisfying, since there is no certainty that the route chosen represents the truth. The only way to learn which route has actually been taken is by means of isotopic tracers; and somehow the reward to be gotten seldom seems worth the labor. Isotopic tracer studies have been made in a couple of instances to gauge the relative importance of alternatives routes in carbonium ion rearrangements, and these are described here.

For 2-methylbutane, interchange of C-1 and C-4 may occur by either one of the following routes[233]:

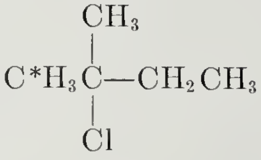


$$CH_3CH_2\overset{+}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_3 \rightarrow CH_3\overset{+}{C}H\underset{\substack{|\\ CH_3}}{C}HCH_3 \rightarrow CH_3\underset{\substack{|\\ CH_3}}{C}H\overset{+}{C}HCH_3 \rightarrow CH_3\overset{+}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_2CH_3 \qquad \text{(XXXI)}$$



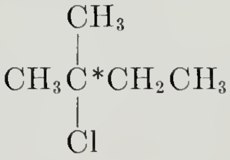
$$CH_3CH_2\overset{+}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_3 \rightarrow \overset{+}{C}H_2\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_3 \rightarrow CH_3CH_2\overset{+}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_3 \qquad \text{(XXXII)}$$

These routes can be distinguished by the use of isotopic tracers since every molecule which isomerizes by path (XXXI) exchanges not only C-1 and C-4 but C-2 and C-3 as well; isomerization by (XXXII) results in exchange between C-1 and C-4 only. An estimate of the relative rates of routes (XXXI) and (XXXII) *during rearrangement of tert-amyl chloride with aluminum chloride at 0°* was obtained by using a mixture of 2-chloro-2-methylbutane-1-C^{14} (OO) and 2-chloro-2-methylbutane-2-C^{14} (PP) (C^{14} designated by an asterisk).



$$C^*H_3\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Cl}}{C}}{-}CH_2CH_3$$

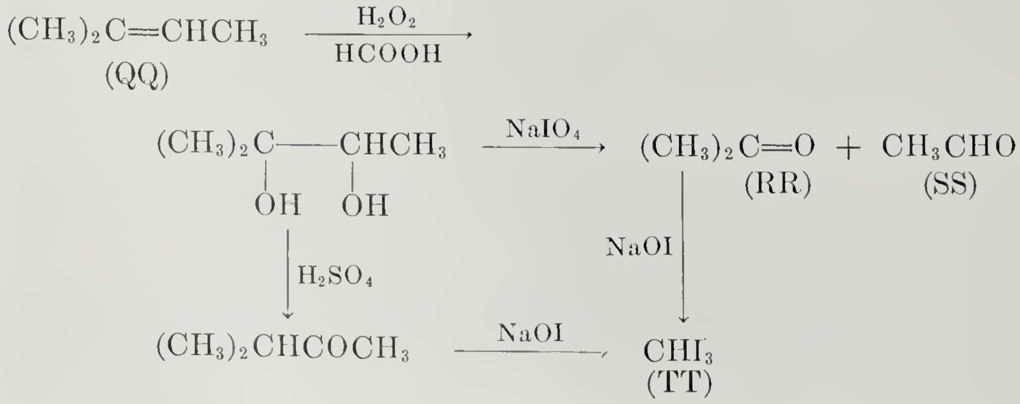
(OO)



$$CH_3\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Cl}}{C}}{}^*CH_2CH_3$$

(PP)

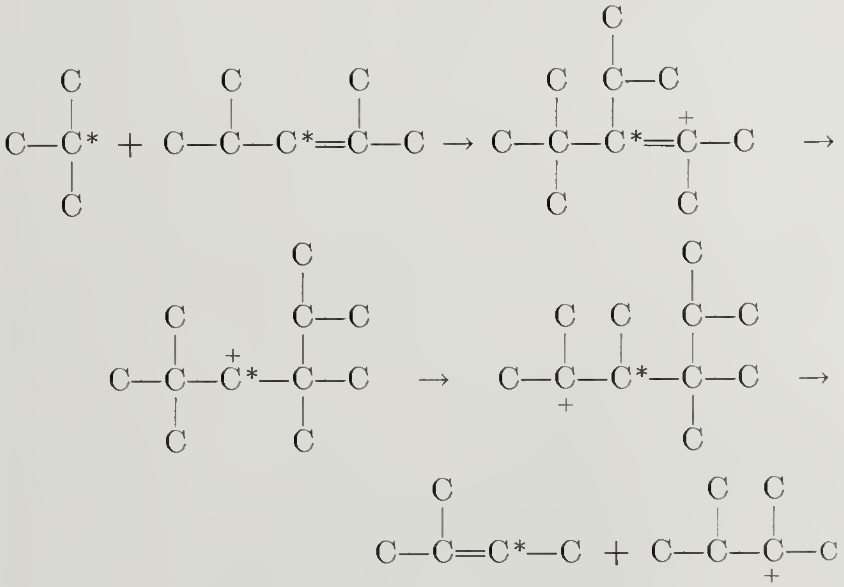
The mixture of isotopically labeled *tert*-amyl chlorides, after brief treatment with aluminum chloride at 0°, was converted to trimethylethylene (QQ) by boiling with water; and the trimethylethylene was degraded according to the following scheme[233].



$$\begin{tikzcd}
\underset{\text{(QQ)}}{(CH_3)_2C{=}CHCH_3} \arrow[r, "H_2O_2"', "HCOOH"'] & {} \\
\underset{\substack{|\qquad\quad |\\ OH\qquad OH}}{(CH_3)_2C{-}CHCH_3} \arrow[r, "NaIO_4"] \arrow[d, "H_2SO_4"] & \underset{\text{(RR)}}{(CH_3)_2C{=}O} + \underset{\text{(SS)}}{CH_3CHO} \arrow[d, "NaOI"'] \\
(CH_3)_2CHCOCH_3 \arrow[r, "NaOI"] & \underset{\text{(TT)}}{CHI_3}
\end{tikzcd}$$

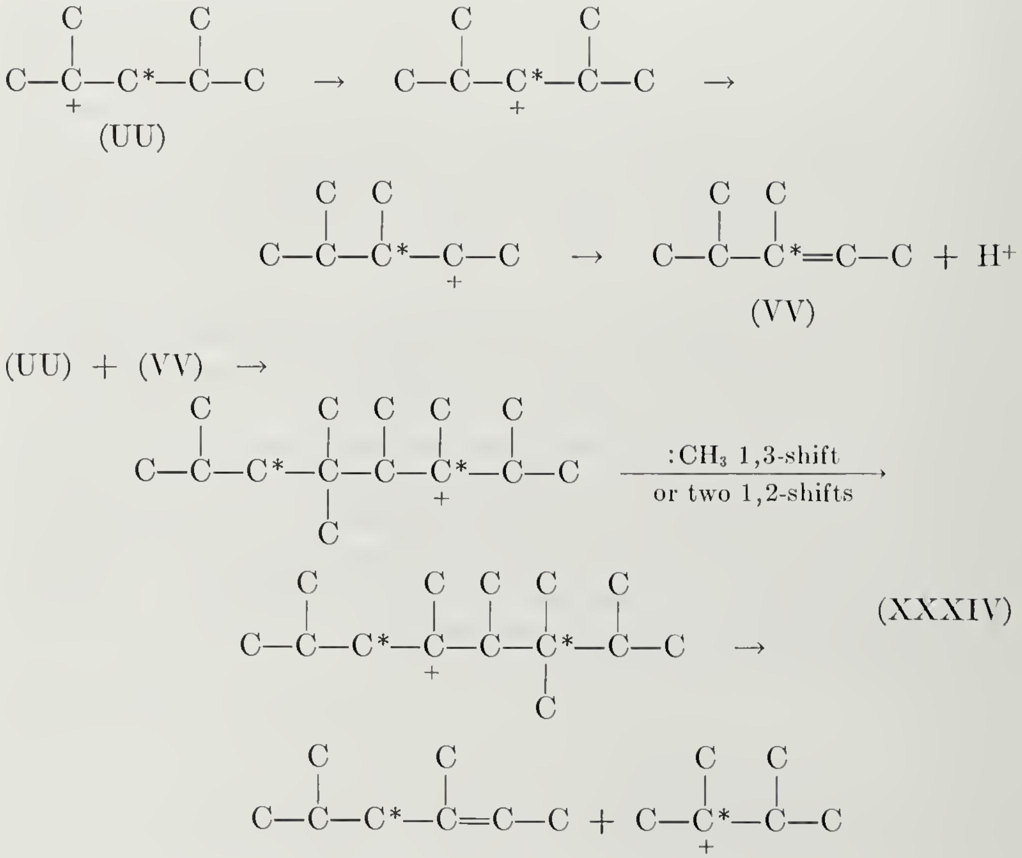
The radioactivity was determined in the iodoform (TT) (from two sources), in the acetone (RR) (as the 2,4-dinitrophenylhydrazone), and in the acetaldehyde (SS) (as the dimethone derivative) in order to measure the relative amounts of isomers with C^{14} at C-1, C-2, C-3, and C-4. From these data, the relative rates of (XXXI) and (XXXII) were computed by the use of suitable kinetic equations. The result was 87 ± 5 per cent reaction by path (XXXI). As would be expected, sequence (XXXI) involving only secondary carbonium ion intermediates was considerably more favored than sequence (XXXII) involving a primary carbonium ion. That the difference in rates was not larger may indicate some favoring of the path with the fewer steps[233].

Another case somewhat more complex than the foregoing dealt with the isomerization and disproportionation of 2,4-dimethylpentane induced by boron fluoride and *tert*-butyl fluoride in *iso*-butane as a solvent at 30°. The 2,4-dimethylpentane was about 23 per cent isomerized (mainly to 2,3-dimethylpentane) and about 23 per cent converted to products of disproportionation and alkylation. The major by-product was 2,3-dimethylbutane. In order to account for the 2,3-dimethylbutane, the mechanism given below was proposed[243] and tested[70] using 2,4-dimethylpentane with C^{14} in the "3" position (designated by an asterisk).



(XXXIII)

Examination of the mechanism shows that the 2,3-dimethylbutane from an experiment using 2,4-dimethylpentane tagged in the "3" position should be devoid of radioactivity. In the tracer experiment[70], it was found that 24 per cent of the 2,3-dimethylbutane was radioactive. Thus 76 per cent of the 2,3-dimethylbutane could have been formed by the sequence (XXXIII) above; but 24 per cent must have been formed by another route. The following was proposed to account for the formation of radioactive 2,3-dimethylbutane[70]:



$$\underset{\text{(UU)}}{\mathrm{C{-}\underset{+}{\overset{C}{C}}{-}C^*{-}\overset{C}{C}{-}C}} \rightarrow \mathrm{C{-}\overset{C}{C}{-}\underset{+}{C^*}{-}\overset{C}{C}{-}C} \rightarrow$$

$$\mathrm{C{-}\overset{C}{C}{-}\overset{C}{C^*}{-}\underset{+}{C}{-}C} \rightarrow \underset{\text{(VV)}}{\mathrm{C{-}\overset{C}{C}{-}\overset{C}{C^*}{=}C{-}C}} + \mathrm{H^+}$$

$$\text{(UU)} + \text{(VV)} \rightarrow$$

$$\mathrm{C{-}\overset{C}{C}{-}C^*{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{\overset{C}{C^*}}{-}\overset{C}{C}{-}C} \xrightarrow[\text{or two 1,2-shifts}]{:\mathrm{CH_3}\ \text{1,3-shift}}$$

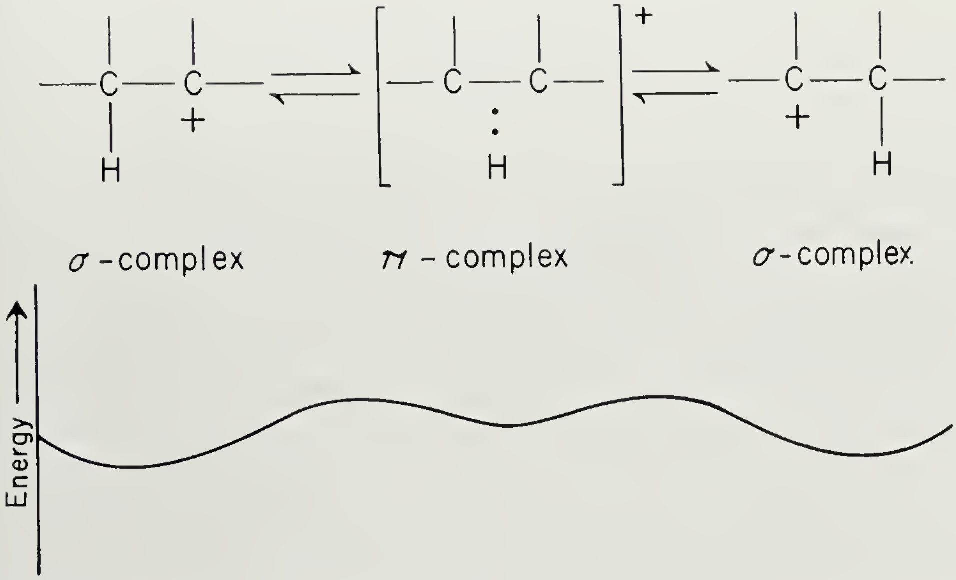
$$\mathrm{C{-}\overset{C}{C}{-}C^*{-}\underset{+}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{C}{\overset{C}{C^*}}{-}\overset{C}{C}{-}C} \rightarrow$$

$$\mathrm{C{-}\overset{C}{C}{-}C^*{-}\overset{C}{C}{=}C{-}C} + \mathrm{C{-}\underset{+}{\overset{C}{C^*}}{-}\overset{C}{C}{-}C}$$

(XXXIV)

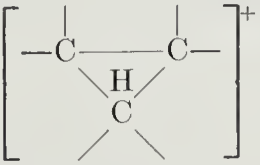
The observations discussed here point up the problems associated with trying to predict the course of a reaction by means of the carbonium ion theory. They indicate not only that more than one route may be available for the formation of rearrangement and disproportionation products but also that shifts of alkyl groups other than methyl must be considered, especially in highly branched carbonium ions of high molecular weight (reaction sequence XXXIII)[241, 243].

pi-Complex Theory and Applications. Theoretical considerations based on quantum mechanics indicate that two forms of carbonium ion may be stable[50], one the classical form in which a carbon has an "open sextet" of electrons, now called a "*sigma*-complex"[26], the other form being that of an olefin with a proton occupying a position essentially midway between the double bonded carbons and called a "*pi*-complex"[26]. Furthermore, an activation energy may be required for interconversion of the two forms. The two forms and the energy relationships between them may be indicated as follows:



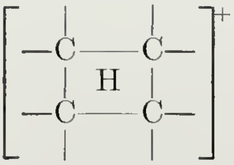
A *pi*-complex such as this has been said to have a "protonated double bond"[221]. Rearrangements involving a 1,2-shift of hydrogen may go through such an intermediate form. The possibility of two stable forms for a carbonium ion separated by a small energy of activation has been helpful in interpreting certain aspects of acid-catalyzed hydration of olefins[268].

In an extension of this viewpoint, a methyl or other alkyl group takes the place of the proton in the *pi*-complex[160, 267, 309]. The resulting structure has been represented in a number of different ways[308]; but by analogy with the *pi*-complex having a protonated double bond, it may be regarded as a protonated cyclopropane and depicted as follows:



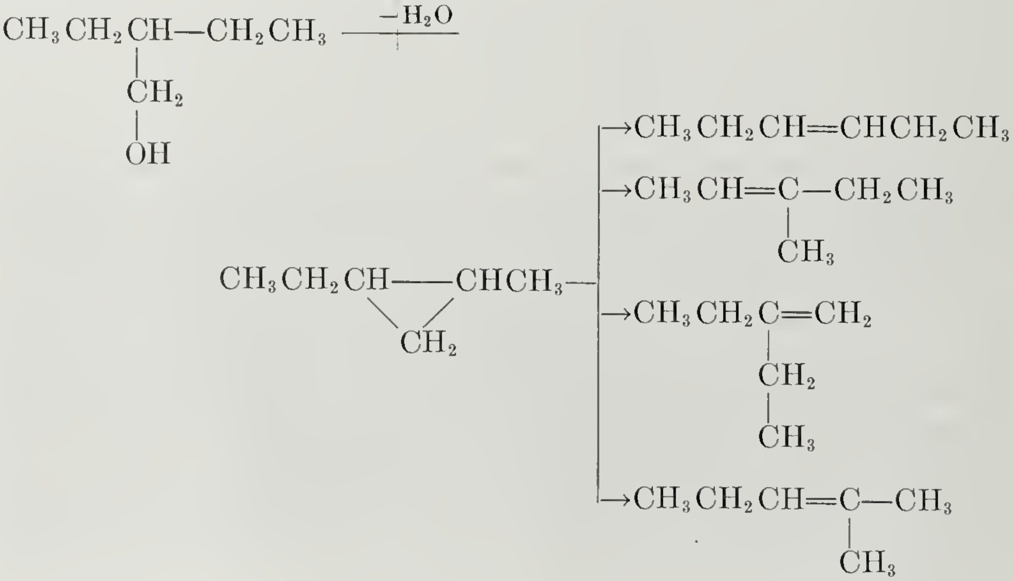
This type of *pi*-complex may go over into a classical carbonium ion, or *sigma* complex, by attachment of the proton to any one of the three carbons of the cyclopropane ring. Rearrangements involving a 1,2-shift of an alkyl group may go through such an intermediate stage. But the symmetry of such an intermediate and the possibility of the proton's becoming attached to any one of the three carbons are important new dimensions not possessed by the representation of such rearrangements in terms of classical carbonium ions alone. Such a structure has been helpful in accounting for the stereochemistry of certain displacement reactions[232a, 309].

An obvious extension of the protonated cyclopropane structure is a protonated cyclobutane:



The protonated cyclopropane and protonated cyclobutane, which are analogous to structures having a protonated double bond, are suggested by the well-known similarities in the chemical behavior of olefins, cyclopropanes, and cyclobutanes. The reactivity of such molecules, formerly attributed to strain, is now attributed to less efficient hybridization of *s*- and *p*-type atomic orbitals, occasioned by the geometry of the molecules, the carbon-carbon bonds thus retaining more *p*-type character than a tetrahedral, fully hybridized, sp^3 bond[46]. Such molecules are therefore susceptible to protonation to a degree not possessed by larger-ring compounds in which the sp^3 hybridization is complete. An atomic orbital representation of a protonated cyclopropane has been given[232a]. In addition, it should be borne in mind that the factors contributing to stability of a protonated cyclopropane or protonated cyclobutane are probably the same as those contributing to stability of cyclopropanes and cyclobutanes themselves; and one of these factors is an accumulation of alkyl groups on the ring carbons[108].

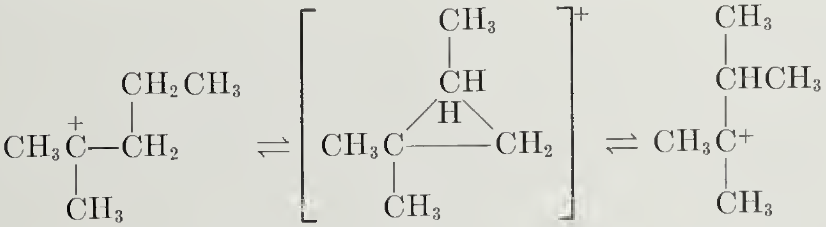
In a study of catalytic dehydration of alcohols and isomerization of olefins with alumina and thoria at about 400°, Goldwasser and Taylor[79] concluded the products resulted from intermediate cyclopropanes (less often, cyclobutanes). Rupture of any bond in the ring gave a free radical intermediate which then satisfied its valence requirements by intramolecular shift of a hydrogen. For example,



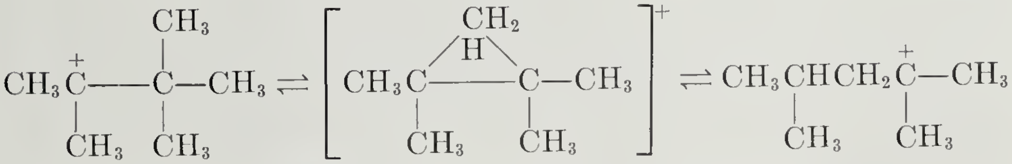
This mechanism accounted well for the products observed. The chief criticism has been that it did not indicate the part played by the catalyst. The present view is that a *catalyst-complexed* cyclopropane (or cyclobutane), rather than a small ring *molecule*, is formed as an intermediate, the two being separated by a rather high activation energy barrier. The ring opening, however, takes the same course as was considered necessary by Goldwasser and Taylor to account for the observed products.

As with the carbonium ion theory itself, the "correctness" of these new concepts can only be gauged by their utility; and this is bound to increase as more scientists realize their value and as more intimate knowledge becomes available regarding reactions susceptible to a carbonium ion interpretation. Some applications to hydrocarbon isomerization are considered in the following paragraphs.

(1) According to classical carbonium ion theory, isomerization of 2- or 3-methylpentane to 2,3-dimethylbutane necessitates formation of intermediate primary and secondary carbonium ions; and saddled with this viewpoint, it is difficult to explain the lack of isomerization of isobutane or isopentane to the normal isomers via similar routes in the presence of sulfuric acid (pages 68–72). In terms of a protonated cyclopropane intermediate, however, isomerization of 2- or 3-methylpentane to 2,3-dimethylbutane can occur without the formation of high energy primary or secondary carbonium ions:



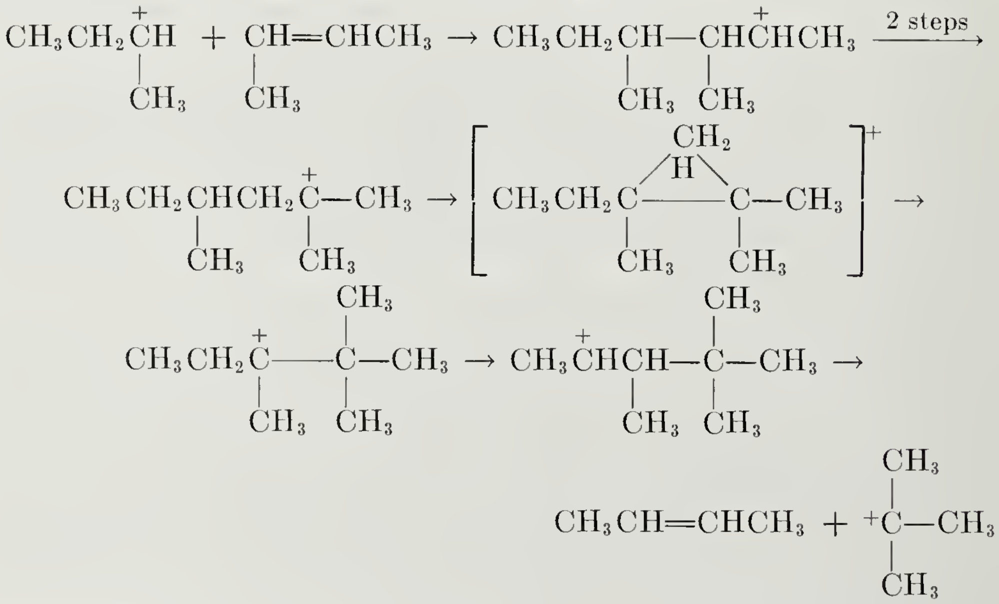
The isomerization of 2,2,3-trimethylbutane to dimethylpentanes may similarly be represented[267]:



Only comparatively stable tertiary carbonium ions and protonated cyclopropanes need be involved, therefore, in these isomerizations.

(2) As has been pointed out, it is difficult to reconcile the facts that isobutane is produced from straight chain butenes, and isopentane is produced from 2-pentene, in sulfuric acid-catalyzed alkylation of methylcyclopentane[214] with the complete lack of isomerization of isobutane and isopentane by sulfuric acid, inasmuch as carbonium ion forma-

tion from the latter is demonstrated by D-H exchange[192]. By means of the *pi*-complex theory, however, and bearing in mind that an accumulation of alkyl groups on the ring carbons probably stabilizes small-ring structures, a preferred (low-energy) route for the formation of rearranged alkanes from straight-chain alkenes can be set up as follows:



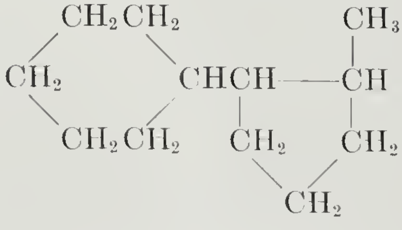
$$CH_3CH_2\underset{\displaystyle CH_3}{\overset{+}{C}H} + \underset{\displaystyle CH_3}{CH}{=}CHCH_3 \rightarrow CH_3CH_2\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CH_3}{CH}\overset{+}{C}HCH_3 \xrightarrow{\text{2 steps}}$$

$$CH_3CH_2\underset{\displaystyle CH_3}{CH}CH_2\underset{\displaystyle CH_3}{\overset{+}{C}}-CH_3 \rightarrow \left[CH_3CH_2\underset{\displaystyle CH_3}{C}\overset{\displaystyle CH_2}{\overset{H}{\text{———}}}\underset{\displaystyle CH_3}{C}-CH_3 \right]^+ \rightarrow$$

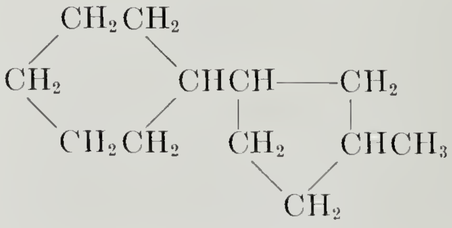
$$CH_3CH_2\underset{\displaystyle CH_3}{\overset{+}{C}}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_3 \rightarrow CH_3\overset{+}{C}H\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_3 \rightarrow$$

$$CH_3CH{=}CHCH_3 + {}^{+}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_3$$

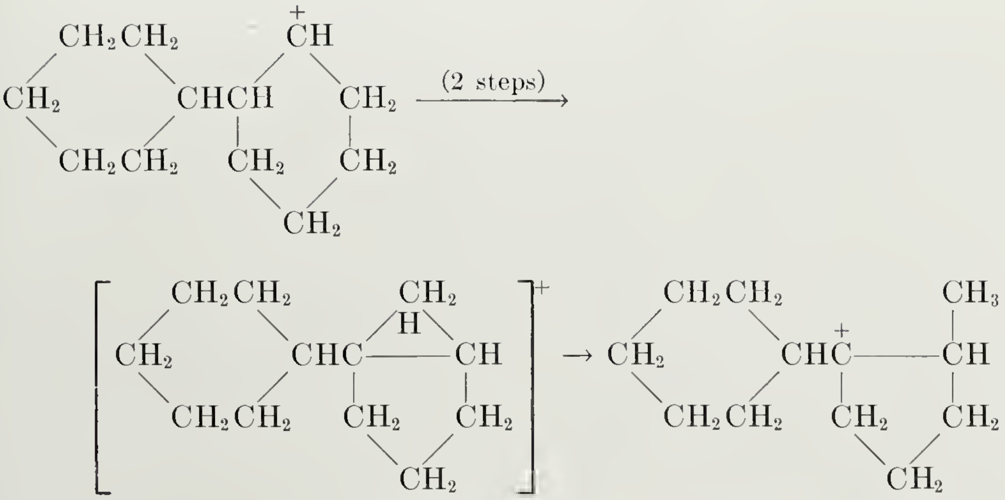
Some support for this mechanism comes from the related observation that 2-butene gave isobutane when treated alone with 96 per cent sulfuric acid at 0°; but the production of isobutane was preceded by an induction period, presumably required for the formation of polymer[32]. In the case of cyclohexene and 97 per cent sulfuric acid at 0°, 1-cyclohexyl-2-methylcyclopentane (WW) and 1-cyclohexyl-3-methylcyclopentane (XX)[264] were produced. This observation can similarly be reconciled with the lack of isomerization of methylcyclopentane with sulfuric acid by means of the *pi*-complex theory, the rearrangement taking place within the highly branched dimer carbonium ion rather than within the relatively simple carbonium ion derived from cyclohexene (see below). Such routes involving the carbonium ion derived from the dimer are undoubtedly also favored by the high olefin concentration present under the conditions of the experiments under consideration.



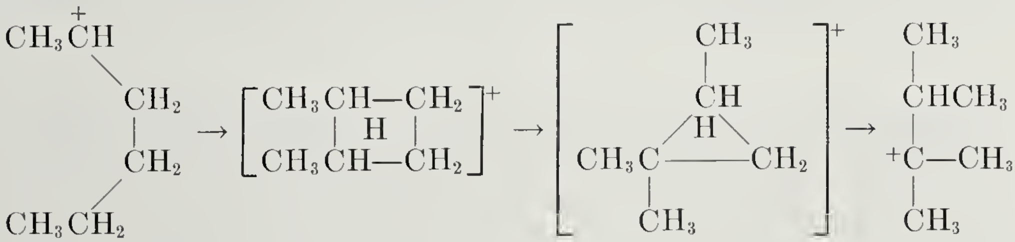
(WW)



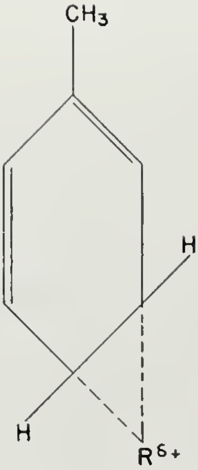
(XX)



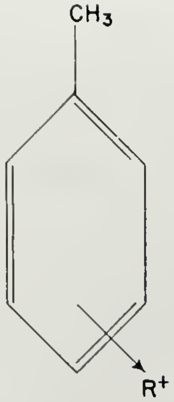
(3) Evidence has been presented that 2,3-dimethylbutane is a *primary* product of the isomerization of *n*-hexane with aluminum chloride at 100° [59]. This finding is difficult to understand in terms of the classical carbonium ion theory, which would suggest that the methylpentanes would be necessary intermediates. However, the concept of a protonated cyclobutane provides a direct route from *n*-hexane to 2,3-dimethylbutane:



(4) The relative migration aptitudes of methyl, ethyl, and isopropyl groups attached to an aromatic nucleus have been determined by comparison of the rates of isomerization of *p*-xylene, *p*-ethyltoluene, and *p*-isopropyltoluene. In each case the *meta* isomer was the chief product. The isomerizations were carried out in toluene solution with one mole of hydrogen bromide and one mole of aluminum bromide (as Al_2Br_6) per mole of alkyltoluene. The rates of isomerization were found to increase markedly in the series: *p*-xylene, *p*-ethyltoluene, and *p*-isopropyltoluene. Thus the order of ease of migration of alkyl groups under these conditions was established as methyl < ethyl < isopropyl, with *tert*-butyl presumably faster still. Inasmuch as this is also the order of ability of the alkyl groups to accommodate a positive charge as a carbonium ion, the results were taken to indicate a transition state (YY) or *pi*-complex intermediate (ZZ) in which the alkyl group R carries a positive charge[26a].

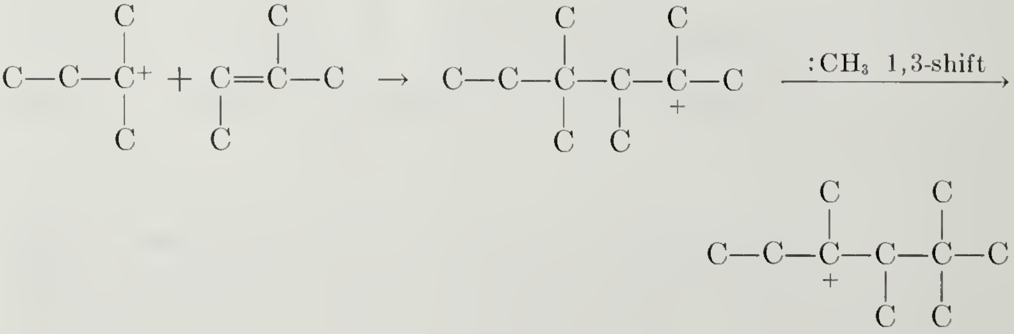


(YY)



(ZZ)

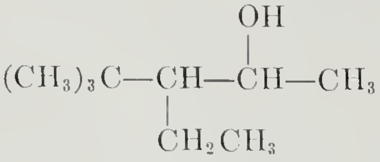
The 1,3-rearrangement. Although rearrangements of great complexity can be considered the result of a series of 1,2-shifts of alkyl groups or hydrogen within carbonium ions, a number of rearrangements were observed in studies of olefin polymerization and depolymerization which indicated a 1,3-shift of a methyl group. For example, the dehydropolymerization of 3-methyl-2-butanol by hot 75 per cent sulfuric acid gave a large amount of 3,4,5,5-tetramethyl-2-hexene which could have arisen either by two 1,2-shifts[294] or more simply by a 1,3-shift of a methyl[53] (*cf.* XXVII, page 92):



$$\begin{array}{cccccccccccccccccccccccc}
 & & & & \mathrm{C} & & & & \mathrm{C} & & & & & & & & \mathrm{C} & & & & \mathrm{C} & & & \\
 & & & & | & & & & | & & & & & & & & | & & & & | & & & \\
\mathrm{C} & — & \mathrm{C} & — & \mathrm{C}^+ & + & \mathrm{C} & = & \mathrm{C} & — & \mathrm{C} & \rightarrow & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & \xrightarrow{:\mathrm{CH_3}\ \ 1,3\text{-shift}} \\
 & & & & | & & | & & & & & & & & & & | & & | & & + & & & \\
 & & & & \mathrm{C} & & \mathrm{C} & & & & & & & & & & \mathrm{C} & & \mathrm{C} & & & & &
\end{array}$$

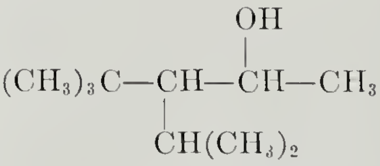
$$\begin{array}{ccccccccccc}
 & & & & \mathrm{C} & & & & \mathrm{C} & & \\
 & & & & | & & & & | & & \\
\mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} \\
 & & & & + & & | & & | & & \\
 & & & & & & \mathrm{C} & & \mathrm{C} & &
\end{array}$$

In order to detect a 1,3-shift of a methyl without the obscuring possibility of two successive 1,2-shifts, the highly branched alcohols, 4,4-dimethyl-3-ethyl-2-pentanol (AAA)[174] and 4,4-dimethyl-3-isopropyl-2-pentanol (BBB)[45] were prepared and dehydrated.



$$\begin{array}{ccccccc}
 & & & & \mathrm{OH} & & \\
 & & & & | & & \\
\mathrm{(CH_3)_3C} & — & \mathrm{CH} & — & \mathrm{CH} & — & \mathrm{CH_3} \\
 & & | & & & & \\
 & & \mathrm{CH_2CH_3} & & & &
\end{array}$$

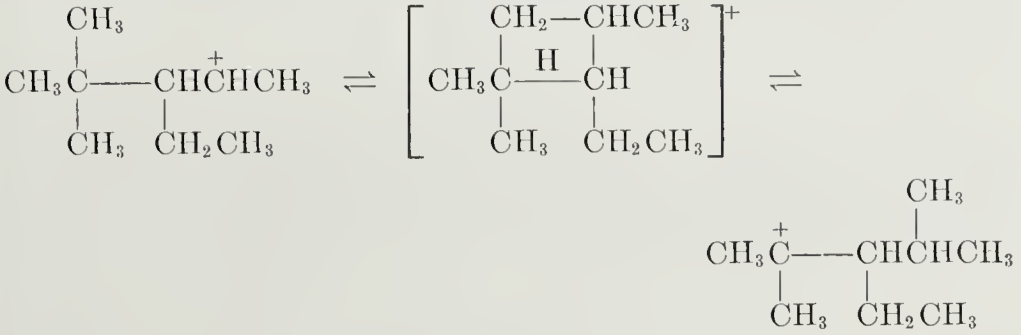
(AAA)



$$\begin{array}{ccccccc}
 & & & & \mathrm{OH} & & \\
 & & & & | & & \\
\mathrm{(CH_3)_3C} & — & \mathrm{CH} & — & \mathrm{CH} & — & \mathrm{CH_3} \\
 & & | & & & & \\
 & & \mathrm{CH(CH_3)_2} & & & &
\end{array}$$

(BBB)

In the case of (BBB), no evidence could be found for formation of the expected 1,3-rearrangement product, 2,4-dimethyl-3-isopropyl-2-pentene[45]; but in the case of (AAA), the major product was that of a 1,3-rearrangement, namely, 2,4-dimethyl-3-ethyl-2-pentene[174]. The 1,3-shift may involve an intermediate protonated cyclobutane:



The structure of the alcohol (AAA) makes it impossible to represent the migration of the methyl by any reasonable series of 1,2-shifts.

Although the conditions under which a 1,3-rearrangement may occur are not yet clearly defined, it would seem to be one more possibility during acid-catalyzed hydrocarbon isomerization. It has been suggested that formation of the required intermediate four-membered ring would be favored by accumulation of alkyl groups on the ring carbons[302].

KINETICS

A study of the kinetics of a reaction has often given much insight into its mechanism. However, this has not been so for catalytic isomerization of hydrocarbons, for here the rate of reaction depends on many hard-to-control parameters. The system is often heterogeneous and the rate of reaction may depend on rate of stirring, particle size and surface area of the catalyst, and other factors influencing the nature of contact between catalyst and substrate. Traces of impurities have a profound effect, as already described on pages 61–64, and their concentration and therefore the magnitude of their effect often changes with time. Catalyst activity is sometimes hard to duplicate in separate preparations and often declines with use. These many hard-to-control factors must be demonstrated or assumed to be constant, or must be corrected for, before an observed variation in rate can be attributed to a controllable parameter under investigation.

The dependence of rate of isomerization on such controllable parameters as the initial quantity of catalyst, the temperature, the pressure, and the nature of the hydrocarbon will be considered here. Interpretation of these observations is incomplete; but certain regularities are apparent from which directions for further work may be indicated.

Reaction Order

The catalytic isomerization is generally regarded to be first order with respect to a hydrocarbon. Therefore, when the equilibrium constant is very large, or when the conversion of substrate is so low that the reverse reaction may be neglected, the simple form of the first order law may be used to evaluate a rate constant, k_1. That is,

$$k_1 = \frac{1}{t} \ln a/c \tag{1}$$

where a is the initial concentration and c is the concentration after time, t. More generally, however, the reverse reaction must be taken into account by use of an equation of the form

$$k_1 = \frac{x_e}{at} \ln \frac{x_e}{x_c - x} \tag{2}$$

where x_e is the equilibrium concentration of *product*, x is its concentration after time, t, and a is the initial concentration of starting material[132].

The rate constant, k_1, depends on many factors. By varying one of these factors and keeping all others constant or correcting for simultaneous variations in others, information can be obtained from which k_1 can be expressed as a function of the parameter varied.

The first order nature of catalytic isomerization of hydrocarbons is illustrated by the data in Table 24 pertaining to the isomerization of *cis*-decahydronaphthalene with aluminum chloride as catalyst. In this study, no solvent was used and the mole fraction of *cis*-decahydronaphthalene in the catalyst-free reaction mixture was determined by measurement of the refractive index on the assumption that *trans*-decahydronaphthalene was the sole product[249]. The rate constants were calculated by use of Eq. (2), the mole fraction of *trans*-decahydronaphthalene at equilibrium being evaluated with the aid of available thermodynamic data[194] as approximately 0.98 in the temperature range 0 to 45°[42]. The near constancy of k_1 over a wide range of conversion for a given set of reaction conditions in Parts a, b, and c of the table indicates the isomerization is indeed first order in *cis*-decahydronaphthalene. The dependency of k_1 on the quantity of catalyst and on the temperature (Part d of the Table) is considered below.

In the foregoing example, reaction mixtures were heterogeneous, for aluminum chloride is not appreciably soluble in saturated hydrocarbons. Homogeneous liquid phase isomerizations of *o*- and *p*-xylene have been carried out under two sets of conditions. In one study, a large excess of anhydrous hydrofluoric acid was used as the solvent and more than enough boron fluroide was used to form a soluble complex with the xylene. The isomerization of *o*- or *p*-xylene to *m*-xylene was first order[160]. In another study, toluene was the solvent and the catalyst comprised one mole of aluminum bromide (as Al_2Br_6) and one mole of hydrogen bromide per

TABLE 24. KINETICS OF ISOMERIZATION OF *cis*-DECAHYDRONAPHTHALENE[a]

Time (hr)	*cis*-Dec. mole fraction	10^2k_1, hr^{-1}	Time (hr)	*cis*-Dec. mole fraction	10^2k_1, hr^{-1}
Part a. 25°; 0.222 mole $AlCl_3$/mole Dec.					
0	1.0	—	31	0.260	4.4
1	0.917	(8.6)[b]	36	0.215	4.4
2	0.855	(7.8)[b]	42	0.164	4.4
3	0.833	6.1	48	0.122	4.5
4	0.793	5.8	55	0.097	4.5
5	0.733	6.3	62	0.067	4.7
13	0.501	5.4	66	0.054	4.9
16	0.432	5.3	70	0.035	5.6
26	0.313	4.5	Average k_1 : 0.051 ± 0.006		
Part b. 25°; 0.444 mole $AlCl_3$/mole Dec.					
4	0.368	25.4	10	0.037	(38)[b]
8	0.139	25.7	Average k_1 : 0.256 ± 0.002		
Part c. 25°; 0.958 mole $AlCl_3$/mole Dec.					
2	0.594	26.2	8	0.190	(20.3)[b]
4	0.374	25.0	Average k_1 : 0.256 ± 0.006		

Part d. 0.222 mole $AlCl_3$/mole Dec.

Temp. (°C)	Time (hr)	*cis*-Dec. mole fraction	10^2k_1, hr^{-1}
0	140	0.170[c]	1.3
10	60	0.224[c]	2.5
25	42	0.159[c]	4.5
35	20	0.145[c]	10.0
45	9	0.063[c]	34

[a] Based on Seyer and Yip[249].

[b] Values in parentheses omitted from average.

[c] Data taken from a graph of Seyer and Yip[249].

mole of xylene. The isomerization to *m*-xylene appeared to be second order in *o*- or *p*-xylene; but this result was interpreted as first order in *o*- or *p*-xylene and first order in hydrogen bromide-aluminum bromide, which was presumably removed as isomerization progressed through formation of a stable complex with the more basic *m*-xylene produced[26a].

Dependence of Rate on Catalyst and Other Substances

Isomerization with Aluminum Halides. The data in Parts a, b, and c of Table 24 show that a two-fold increase in the amount of aluminum chloride (from 0.222 to 0.444 mole/mole substrate) resulted in a five-fold increase in the rate of isomerization of *cis*-decahydronaphthalene; but a further increase in the amount of catalyst (from 0.444 to 0.958 mole/mole substrate) did not further increase the rate. The full meaning of these results is not clear. However, inasmuch as the solubility of aluminum chloride in the hydrocarbon is so low that the concentration of *dissolved* aluminum chloride can be assumed to have been the same in all the experiments, the increase in rate brought about by increasing the amount of catalyst from 0.222 to 0.444 mole/mole substrate indicates that the undissolved aluminum chloride serves as a catalyst; that is, the isomerization is at least partly heterogeneous[249]. The same conclusion has been reached regarding the aluminum chloride-catalyzed isomerization of cyclohexane[152, 265].

The five-fold increase in rate brought about by a two-fold (1.7-fold in mole fraction units) increase in the amount of aluminum chloride, observed above with *cis*-decahydronaphthalene, indicates a greater-than-first order dependence of rate on the quantity of catalyst. However, the rate of isomerization of cyclohexane with moist aluminum chloride at 27° has been reported to be directly proportional to the quantity of catalyst over a 40-fold range[265]; while data from another source presented in Table 25 indicate the rate is proportional to some fractional power of the quantity of aluminum chloride, approximately one-half. In the latter case, use of a half-order dependence on the quantity of hydrogen chloride, too, results in fairly good correlation of the rates. Inasmuch as a slow isomerization was observed in the absence of added hydrogen chloride, an empirical expression of the form

$$\text{rate} = k_1(\text{cyclohexane}) = k_1'(\text{AlCl}_3)^{1/2}(B + \text{HCl})^{1/2}(\text{cyclohexane})$$

was used[42] to correlate the data; and B was evaluated as 0.00041 (in mole fraction units) by use of the data of Experiments 5 and 6. B may represent the mole fraction of some unknown promoter.

Data in Part (b) of Table 25 show the rate is inversely dependent on the hydrogen pressure. A reason for the inhibiting effect of hydrogen has been suggested on pages 97–98.

Data for the isomerization of methylcyclopentane with aluminum bromide and hydrogen bromide and with *sec*-butyl bromide as initiator[210] have been used[42] to calculate first-order rate constants by means of Eq. (2), the equilibrium mole fraction of cyclohexane being taken as 0.81 (see page 161). The data and results of the calculations are presented in Table 26. Except for two experiments using small amounts of aluminum bromide,

Table 25. Effect of Quantity of Aluminum Chloride, Hydrogen Chloride, and Hydrogen on Rate of Isomerization of Cyclohexane[a]

Part a. 100°; 41 atm. H_2

Experiment	$AlCl_3$	HCl	k_1, hr^{-1}	k_1'[b]
	mole/mole cyclohexane			
1	0.012	0.050	0.70	29
2	0.025	0.050	1.45	44
3	0.050	0.050	2.29	50
4	0.100	0.050	3.27	3
5	0.050	0.000	0.26	59
6	0.050	0.025	1.97	59
7	0.050	0.100	3.38	55

Part b. 100°; 0.050 mole $AlCl_3$ and 0.050 mole HCl

H_2, *atm.*	k_1, hr^{-1}
0	3.22
20.5	3.02
41	2.29
68	2.00

[a] Based on Lien, D'Ouville, Evering and Grubb[152].

[b] $k_1' = k_1/(AlCl_3)^{1/2}\ (0.00041 + HCl)^{1/2}$, where (X) = mole fraction X.

Table 26. Effect of Quantity of Aluminum Bromide, Hydrogen Bromide, and *sec.*-Butyl Bromide on Rate of Isomerization of Methylcyclopentane[a]

$AlBr_3$[b]	HBr[b,c]	*sec.*-C_4H_9Br[b,d]	Cyclohexane, mole fraction[b] in 2 hr, 25°	10^2k_1, hr^{-1}	k_1'[e]
Mole/mole methylcyclopentane					
0.020	0.001	0.001	0.08	4.2	31
0.020	0.005	0.001	0.31	20	30
0.020	0.010	0.001	0.49	38	29
0.020	0.020	0.001	0.53	43	17
0.001	0.005	0.001	0.01	0.6	3.8
0.001	0.010	0.001	0.02	1.0	3.2
0.005	0.005	0.001	0.13	7.1	21
0.005	0.010	0.001	0.25	15	22
0.020	0.010	0.00025	0.15	8.3	25
0.020	0.010	0.0007	0.29	18	19
0.020	0.010	0.0025	0.69	77	24

[a] Based on Pines, Aristoff, and Ipatieff[210].

[b] Most of the data in these columns were taken from graphs, *loc. cit.*

[c] Includes HBr added as *sec*-butyl bromide.

[d] Treated as if it were C_4H_8 + HBr.

[e] $k_1' = 10^{-4}k_1/(AlBr_3)^{1/2}(HBr)(s\text{-}C_4H_9Br)$, where (X) = mole fraction X.

wherein the conversion was only 1 to 2 per cent, the data indicate approximately a half-order dependence on aluminum bromide, a first-order dependence on hydrogen bromide, and a first-order dependence on the initiator (treated as butylene) (column 6 and footnote *e* of Table 26).

Yet another type of dependence on quantity of catalyst was observed in the isomerization of butanes by aluminum bromide and hydrogen bromide[134]. Conversions were limited to less than 10 per cent so that the reverse reaction could be neglected; and fairly reproducible values for a rate constant were obtained by use of an expression of the form

$$d(i\text{-}C_4H_{10})/dt = k_2(HAlBr_4)(n\text{-}C_4H_{10}) \tag{3}$$

That is, the rate seemed to be proportional to the concentration of $HAlBr_4$, which was calculated from the stoichiometry of the equation

$$Al_2Br_6 + 2HBr \rightarrow 2HAlBr_4 \tag{XXXV}$$

on the assumption this reaction has an equilibrium constant so large that the amount of $HAlBr_4$ produced in the mixture was determined by the amount of that reagent added in limiting quantity. In separate experiments with *n*-butane at 65°, for example, the amount of aluminum bromide was varied by a factor of 36, while the amount of hydrogen bromide was varied by a factor of 8; the actual rate of isomerization then varied by a factor of 8; but by use of Eq. (3), values of k_2 were obtained that differed by a factor less than 1.6. Other rate expressions, for example

$$d(i\text{-}C_4H_{10})/dt = k_3(HBr)(Al_2Br_6)^{1/2}(n\text{-}C_4H_{10})$$

predicated on the assumption that the equilibrium constant for Eq. (XXXV) is small, gave more widely divergent values for a "constant," k_3. From these results, it would appear that the rate-controlling step involves a reaction between $HAlBr_4$ and a butane molecule. The evidence opposed to such a view has been presented on pages 55–56.

The foregoing examples indicate considerable divergence in the dependence of rate of isomerization on quantity of aluminum halide as observed by different workers. Until the reasons for these differences are known, it would appear to be risky to assume a simple first-order dependence in order to compare rates obtained with differing amounts of catalyst, especially if the amount of catalyst is varied by a large factor. It is possible, of course, that the conflicts noted are due to simultaneous variation in other parameters than those considered.

Isomerization with Sulfuric Acid and Related Substances. The rate constant for isomerization of 3-methylpentane to 2-methylpentane, evaluated by means of Eq. (2), was found to depend on the sulfuric acid concentration as shown in Table 27 (columns 1 and 3)[234]. The value of k_1

declined during each run because of degradation of the hydrocarbon and dilution of the acid by the degradation products, as shown by the following data obtained with 99.8 per cent acid:

Time, hr	0.25	0.5	1	2	3	4
k_1, hr^{-1}	0.61	0.58	0.50	0.39	0.34	0.30

The higher the initial acid concentration, the faster and greater was the decline. In order to minimize this effect, the values of k_1 recorded in Table 27 are for a uniform time of one hour.

The rate constant climbs to a sharp maximum at a sulfuric acid concentration of 99.8 per cent. Above this concentration, the rate constant falls off sharply because the decline in acid strength due to hydrocarbon degradation more than offsets any increased activity at the initial concentration. The optimum in acid concentration appeared to be independent of hydrocarbon structure, as a sharp maximum in the rate at 99.8 per cent acid was also found with 2,3-dimethylpentane, 2,4-dimethylpentane, and *cis*- and *trans*-1,4-dimethylcyclohexane[234].

Table 27. Effect of Sulfuric Acid Concentration on Rate of Isomerization of 3-Methylpentane at 25°

H_2SO_4[a] (wt. %)	$-H_0$[b]	k_1[a], hr^{-1}	Relative Energy of Activation (cals)
95.5	8.5	0.0077	2510
98.2	8.98	0.12	830
99.0	9.35	0.17	630
99.5	9.62	0.24	420
99.6	9.68	0.35	205
99.7	9.88	0.42	96
99.8	9.95	0.50	0
100.0	10.60	0.37	
100.2		0.35	
100.8		0.27	
102.1		0.20	

[a] Most of the data in these columns were taken from a graph of Roebuck and Evering[234].

[b] Values of the "acidity function" from Hammett and Deyrup[92].

It was pointed out[234] that the increase in k_1 between 95.5 and 99.8 per cent sulfuric acid paralleled the acidity function, H_0, as defined and measured by Hammett and Deyrup[92]; and values for this function are included in Table 27. The value of $-H_0$ measures the tendency of an acid to transfer a proton to a neutral base; and according to Hammett and Deyrup, "An exact parallelism between the reaction velocity and the acidity can only be expected if the velocity is proportional to the concentration of the ion formed by the addition of one hydrogen ion to one molecule of the neutral substrate, if the ratio of the concentration of this ion to the total concentration of substrate is small, and if there is no further ionization by addition of another hydrogen ion. If these conditions are fulfilled the equation

$$H_0 + \log k = \text{a constant} \tag{4}$$

where k is the velocity constant, should hold." A plot of the data in Table 27 according to Eq. (4) is presented in Figure 7. A linear relationship between $\log k_1$ and $-H_0$ is indicated. However, the slope is not unity, as required by Eq. (4), but is nearer 0.5. The rate constant does not increase as rapidly as the acidity. The reason for this may lie in the manner in which the rate constants were evaluated. As already stated, the rate constant fell off with time because of contamination of the acid with degradation products; and the decline in rate was faster the higher the initial acid concentration. The constants in Table 27 are for a uniform time of one hour. Thus they do not correspond to the maximum rates, which would probably show a dependence on $-H_0$ closer to unity.

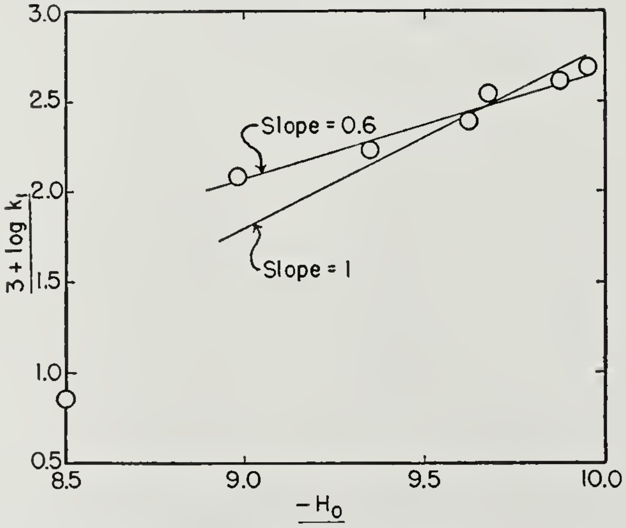


Figure 7. Relationship between rate of isomerization of 3-methylpentane and acidity function, $-H_0$, for sulfuric acid.

At any rate, the proportionality between $\log k_1$ and $-H_0$ is in qualitative concordance with the carbonium ion chain mechanism of isomerization (pages 57–68). According to this mechanism, the observed rate, R, would be proportional to the rate of the chain carrying step[192]

$$R = k_2 P X$$

where P represents the concentration of paraffin and X the concentration of carbonium ion, which is, in the words of Hammett and Deyrup, "the ion formed by the addition of one hydrogen ion to one molecule of the neutral substrate," the "neutral substrate" in this case being olefin, necessary as an initiator.

Alternatively, the differences in rates in Table 27 may be ascribed to differences in activation energy; and these differences may be calculated with the equation:

$$\log k_{1a} - \log k_{1b} = \frac{\Delta E_b^* - \Delta E_a^*}{2.303RT} \tag{5}$$

The differences, $\Delta E_a^* - \Delta E_b^*$, are presented as "relative energies of activation" in column 4 of Table 27. An analogous dependence of activation energy on "acidity" was found in the phosphoric acid-catalyzed isomerization of 1-butene to 2-butene[273]. The actual activation energies found with various P_2O_5 concentrations are presented in Table 28. Consideration of Eqs. (4) and (5) shows that

$$H_{0b} - H_{0a} = \frac{\Delta E_b^* - \Delta E_a^*}{2.303RT} \tag{6}$$

Unfortunately, values of the acidity function for phosphoric acid are not available for testing Eq. (6).

Dependence of Rate on Temperature; the Activation Energy

General Principles. The dependence of rate constant on temperature is of particular theoretical importance in catalysis. By use of the Arrhenius equation

$$k_1 = Ae^{-\Delta E^*/RT} \tag{7}$$

and values of k_1 at two or more temperatures, two important constants, the "frequency factor," A, and the activation energy, ΔE^*, may be evaluated. Alternatively, the transition state theory of reaction rates provides the equation

$$k_1 = \kappa \frac{\mathbf{k}T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \tag{8}$$

wherein **k** is the Boltzmann constant, h is Planck's constant, ΔS^* is an entropy of activation, ΔH^* is a heat of activation, and κ is a "transmission coefficient," defined as the fraction of molecules reaching the transition state which go on to reaction product[132]. The "transmission coefficient" cannot be evaluated experimentally and is usually assigned a value of unity.

Equations (7) and (8) are similar; and approximately

$$A \approx \kappa \frac{\mathbf{k}T}{h} e^{\Delta S^*/R} \tag{9}$$

TABLE 28. ACTIVATION ENERGIES OF HYDROCARBON ISOMERIZATIONS

Substrate	Product	Catalyst	Temp. Range (°C)	ΔE^* (kcals)	Ref.
n-Butane	Isobutane	$AlBr_3$-HBr	53–78.5	9.2	134
n-Butane	Isobutane	$AlCl_3$-HCl	55–100	9.55	190
3-Methylpentane	2-Methylpentane	H_2SO_4–99.8%	10–50	6.4	234
2,3-Dimethylpentane	2,4-Dimethylpentane	"	"	4.9	234
cis-Decahydronaphthalene	*trans*-Decahydronaphthalene	$AlCl_3$	0–35	9.5	249 (See text.)
(+)3-Methylhexane	*dl*-3-Methylhexane	Nickel-kieselguhr	102.7–154.2	26.0	29
Cyclohexane	Methylcyclopentane	MoS_2	370–430	35.4	154
cis-2-Butene	*trans*-2-Butene	Nickel-porcelain	65–88	4.0	273
cis-2-Butene	*trans*-2-Butene	Ni(H_2 or D_2)	75–130	5.3	270
cis-2-Butene	*trans*-2-Butene	Thermal reaction	347–420	18.0	124
trans-2-Butene	*cis*-2-Butene	Ni(H_2 or D_2)	75–130	4.8	270
1-Butene	2-Butene	Ni (H_2)	76–126	5.9	290
1-Butene	2-Butene	Ni (H_2)	60–135	5.0	270
1-Butene	2-Butene	Ni (D_2)	55–130	7.8	"
1-Butene	2-Butene	$70P_2O_5$-$30H_2O$	25–45	16.2	273
"	"	$76P_2O_5$-$24H_2O$	"	13.3	"
"	"	$80P_2O_5$-$20H_2O$	"	10.9	"
"	"	$97P_2O_5$-$3H_2O$	"	7.8	"
2-Ethyl-1-hexene	Methylheptenes	SiO_2	−24–24	9.4[a]	74
p-Xylene	*m*-Xylene	HF-BF_3	3–30	12.7	160
p-Xylene	*m*-Xylene	HBr-$AlBr_3$	0–25	21.3	26a
o-Xylene	*m*-Xylene	HBr-$AlBr_3$	0–25	22.8	"

[a] Based on reported observation of 5 per cent reaction at −24°, 65 per cent reaction at 24°.

That is, the "frequency factor," A, in the Arrhenius equation is related to the entropy of activation in the transition state theory. Actually, Eq. (7) implies a linear relationship between the logarithm of the rate constant and the reciprocal of the absolute temperature:

$$\ln k_1 = \ln A - \Delta E^*/RT$$

whereas Eq. (8) implies a linear relationship between $\ln k_1/T$ and $1/T$:

$$\ln k_1/T = \ln \kappa\mathbf{k}/h - \Delta S^*/R - \Delta H^*/RT$$

and because of the attendant differences in treatment of experimental data by Eqs. (7) and (8), ΔE^* and ΔH^* are not equal and therefore the Eq. (9) above is not a true equality. However, ΔE^* and ΔH^* seldom differ by more than 0.5 kcal; and for a narrow temperature range, $\mathbf{k}T/h$ is essentially constant, having the value 6.2×10^{12} at 300°K. Therefore, for temperatures in the neighborhood of 300°K a "frequency factor" greater than about 6.2×10^{12} corresponds to a positive entropy of activation in the transition state theory, whereas a "frequency factor" less than about 6.2×10^{12} corresponds to a negative entropy of activation, a "transmission coefficient" less than unity, or to a combination of both of these circumstances. A catalyst may increase the rate of a reaction by decreasing the activation energy, by increasing the entropy of activation, or by increasing the "transmission coefficient."

In view of the marked dependence of the rate of catalytic isomerization on many factors other than the temperature and the concentration of substrate, it is pertinent to inquire whether the "frequency factor" (or related entropy of activation) and the activation energy (or heat of activation) evaluated from experimental rate constants have any significance. Equation (7) shows that the relationship between the rate constant and the "frequency factor," A, is one of direct proportionality; and so those incidental factors such as quantity of catalyst and the concentrations of promoters and inhibitors which affect the rate of reaction will also affect the empirical value of the "frequency factor." Therefore, this term and the related entropy of activation usually can have only an *ad hoc* significance in catalytic processes. However, in evaluating an activation energy (or heat of activation) from experimental rate constants, the effects of incidental factors can be expected to cancel out, provided these effects are identical at different temperatures and provided the experimenter has taken all necessary steps to keep these factors unchanged when measuring rates at different temperatures. Therefore, an activation energy (or a heat of activation) may have as much significance when evaluated for a catalyzed reaction as when evaluated for one not catalyzed, and may be determined by the nature of the catalyst, but should be independent of the quantity of the catalyst used.

The Activation Energy of Catalytic Isomerization. Figure 8 represents an Arrhenius-type plot of rate constants in Part d of Table 24 pertaining to aluminum chloride-catalyzed isomerization of *cis*-decahydronaphthalene. The data do not fall on a single straight line. The two straight lines indicated in the figure give an activation energy of 9500 calories in the temperature range 0 to 35° and 19,000 calories in the temperature range 25 to 45°. It cannot be said at the present time whether this variation in activation energy is real or due to experimental error.

Activation energies for several isomerizations are recorded in Table 28.

The preponderance of values below 10 kcals is noteworthy, both isomerization of saturated hydrocarbons and double bond shifting in olefins falling in this range. A consideration of the data pertaining to saturated hydrocarbons alone indicates an approximate correlation between the temperature range required with a catalyst and the activation energy. A comparison of activation energies for catalyzed and noncatalyzed conversion of *cis*-2-butene to *trans*-2-butene indicates a 12–14 kcal lowering of the activation energy by the catalyst.

It is significant that the activation energy for double-bond migration in the presence of a nickel catalyst depends on whether hydrogen or deuterium is used as the carrier gas; in the presence of hydrogen it is about 2.8 kcals lower than in the presence of deuterium. This result indicates that the breaking of a hydrogen or deuterium bond is involved in the rate-controlling step of the double-bond migration[270]. The mechanism has been discussed on pages 103–106.

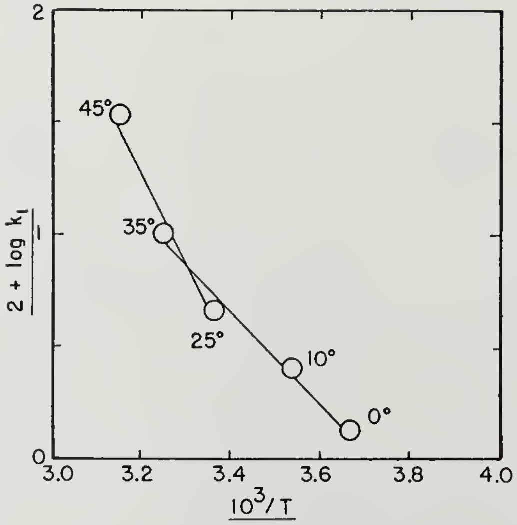


Figure 8. Arrhenius-type plot of rate constants for aluminum chloride-catalyzed isomerization of *cis*-decahydronaphthalene.

The variation of activation energy of double-bond migration with P_2O_5 content of phosphoric acid is probably related to the variation of rate of isomerization of 3-methylpentane with sulfuric acid concentration shown in Table 27 and discussed on pages 130–133. As suggested by Eq. (6) on page 133, the activation energy is probably a linear function of the "acidity function," H_0, but values for this function for phosphoric acid are not available.

Dependence of Rate on Pressure

The effect of pressure on the rate of isomerization of methylcyclopentane with aluminum chloride at 80° is shown by the data in Table 29. Pressure was applied either hydrostatically or by means of a gas, nitrogen or hydrogen. The effect of nitrogen pressure was about the same as that of hydrostatic pressure; but hydrogen produced a greater lowering of the rate.

In the transition state theory, reaction rate is related to pressure as follows. The heat of activation, ΔH^*, in Eq. (8) may be replaced by $(\Delta E^* + P\Delta V^*)$, where ΔE^* is the difference in internal energies of ground state and transition state [not to be confused with ΔE^* in the Arrhenius equation, (7)], and ΔV^* is the difference in volumes of ground state and transition state. On making this substitution and simplifying with the aid of Eq. (9), Eq. (8) becomes

TABLE 29. EFFECT OF PRESSURE ON RATE OF ALUMINUM CHLORIDE-CATALYZED ISOMERIZATION OF METHYLCYCLOPENTANE AT 80°[a]

Pressure		Cyclohexane produced in 3 hr, %	k_1[b] hr^{-1}
Kind	Atm.		
N_2	1	60.5	0.43
N_2	140	60	0.42
N_2	460	48.5	0.27
N_2	660	38.5	0.18
Hydrostatic	640	36.5	0.17
H_2	25	61	0.44
H_2	130	48.5	0.27
H_2	460	17	0.065
H_2	615	8	0.028

[a] Based on Gonikberg, Plate, and Gavrilova[81].

[b] Calculated by means of Eq. (2), with 73.4 per cent cyclohexane at equilibrium.

$$k_1 = Ae^{-(\Delta E^* + P\Delta V^*)/RT}$$

On taking logarithms and regarding the temperature as constant,

$$\log k_1 = -P\Delta V^*/2.303RT + \text{a constant} \tag{10}$$

According to Eq. (10), a plot of the logarithm of the rate constant against the pressure gives a straight line whose slope is a measure of the volume change associated with formation of the transition state. Hence, studies of the effect of pressure on rate have often contributed to an understanding of reaction mechanism[61]. If formation of the transition state is accompanied by an increase in volume, application of pressure will, in accordance with the principle of le Chatelier, decrease the concentration of molecules in the transition state and hence decrease the rate of reaction.

Figure 9 is a plot of the data in Table 29 in accordance with Eq. (10). The straight lines drawn in the figure correspond to a volume increase of 40 cc indicated by the results with nitrogen and hydrostatic pressure and to a volume increase of 132 cc indicated by the results with hydrogen. As already indicated on pages 97–98, part of the depression in rate caused by hydrogen may be due to its entering into the reaction as a carbonium ion chain stopper. Therefore the 40 cc obtained with nitrogen or hydrostatic pressure is more likely to represent the volume increase associated with formation of the transition state. Further interpretation does not seem possible at the present time.

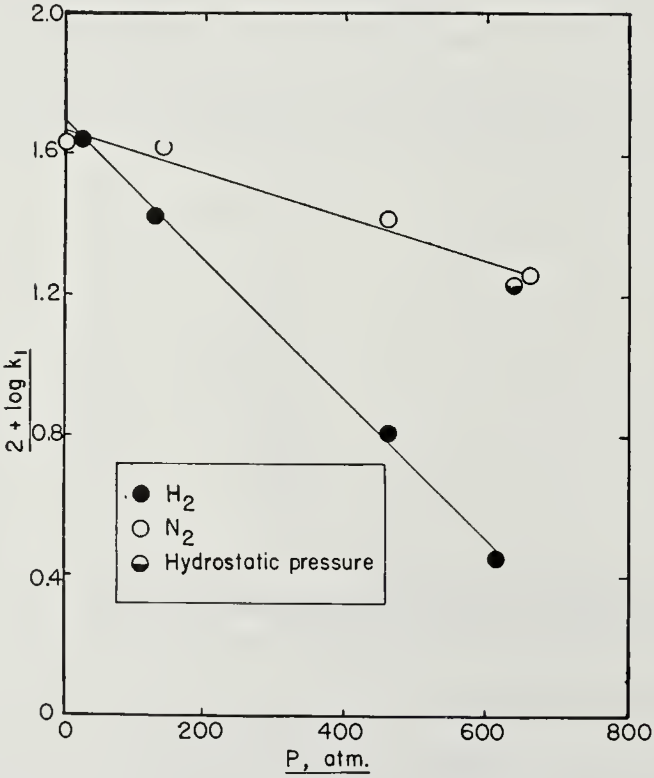


Figure 9. Effect of pressure on rate of aluminum chloride-catalyzed isomerization of methylcyclopentane at 80°.

Dependence of Rate on Hydrocarbon Structure

On pages 48–50 it was stated that interconversions of saturated hydrocarbons having at least one tertiary carbon (Type a isomerizations) are easier than those involving an isomer with no tertiary carbon (Type b); and on pages 98–101, various types of olefin isomerization were classified according to their relative ease of accomplishment. These differences are in one sense rate phenomena and illustrate the effect of hydrocarbon structure on rate of isomerization, although kinetic data are not always available to give a quantitative measure of the effect. A proper comparison of *absolute rates* requires that the isomerizations be carried out with the same catalyst and under identical conditions. One way of assuring "identical conditions" is to isomerize hydrocarbons in admixture. *Relative rates* so obtained are likely to be free of inaccuracy due to difficulty of duplicating catalyst activity in separate experiments.

Table 30. Some Absolute Rates of Isomerization with 99.8 Per Cent Sulfuric Acid at 25°

Isomerization Reaction	k_1[a] hr^{-1}	k_1/k_{-1}	K_{eq}	
			Exptl.	Thermod.
Part a. Methylalkanes				
2-Methylpentane → 3-methylpentane	0.14 ± 0.02	0.29	0.46[a]	0.41[a, b]
3-Methylpentane → 2-methylpentane	0.49 ± 0.03			
2-Methylhexane → 3-methylhexane	0.18 ± 0.03	1.06	0.74[a]	0.92[a, b]
3-Methylhexane → 2-methylhexane	0.17 ± 0.03			
2,3-Dimethylpentane → 2,4-dimethylpentane	0.15 ± 0.01	3.0	1.9[a]	0.27[a, b]
2,4-Dimethylpentane → 2,3-dimethylpentane	0.05 ± 0.01			
3-Methylheptane → 2-methylheptane	0.18			
2,4-Dimethylhexane → 2,5-dimethylhexane	0.54			
Part b. Dimethylcyclohexanes				
cis-1,2- → *trans*-1,2-	0.22	1100	19[a]	12[b]
cis-1,2- → *cis*-1,3-	0.09			
cis-1,3- → *trans*-1,3-	0.06			
cis-1,3- → *trans*-1,2-	0.009	0.45	0.18[c]	0.17[b]
cis-1,3- → *trans*-1,4-	0.04	0.45	0.66[c]	0.53[b]
cis-1,4- → *trans*-1,4-	1.5	19	13[a]	12[b]
cis-1,4- → *cis*-1,3-	0.12			
trans-1,2- → *cis*-1,2-	0.0002			
trans-1,2- → *cis*-1,3-	0.02			
trans-1,4- → *cis*-1,4-	0.08			
trans-1,4- → *cis*-1,3-	0.09			

[a] From Roebuck and Evering[234].

[b] Calculated from data in Ref. 238.

[c] From Chiurdoglu, Fierens and Henkart[35].

Absolute Rates. Rate constants for several isomerization reactions, determined with 99.8 per cent sulfuric acid at 25°, are recorded in Table 30. Two types of isomerization are represented: (1) the 1,2-shift of a methyl group along the chain in alkanes or around the ring in dimethylcyclohexanes; and (2) inversion of configuration at a saturated carbon in dimethylcyclohexanes. It is noteworthy that the rates of the two processes are of the same order of magnitude; for this means, despite the relative "simplicity" of inversion, as much "activation" of the molecule is required as for methyl migration. With each of the three *cis*-dimethylcyclohexanes, inversion of configuration is somewhat faster than methyl migration; but with *trans*-1,2- and *trans*-1,4-dimethylcyclohexane, methyl migration is faster than inversion. This means that, with the latter two compounds, a carbonium ion is converted to a methyl shift isomer more often than to a geometric isomer. That this should be so is in accordance with the thermodynamic stabilities of the several isomers. As shown in Table 44 (page 164), *cis*-1,2- and *cis*-1,4-dimethylcyclohexane comprise only small percentages of the equilibrium mixture. This fact helps to explain why these compounds do not appear as products in any of the reactions in Table 30.

Table 31. Rate Constants for Isomerization of Hexanes with $AlCl_3$-HCl at 100°[a]

Isomerization Reaction	k_1 hr^{-1}
n-Hexane $\rightarrow \begin{cases}\text{2-methylpentane}\\ \text{3-methylpentane}\end{cases}$	1.8
2-Methylpentane → *n*-hexane	0.7
2-Methylpentane → 3-methylpentane	150
3-Methylpentane → 2-methylpentane	65
2-Methylpentane → 2,3-dimethylbutane	6.0
2,3-Dimethylbutane → 2-methylpentane	3.9
2,3-Dimethylbutane → 2,2-dimethylbutane	0.8
2,2-Dimethylbutane → 2,3-dimethylbutane	0.04

[a] From Evering and Waugh[59].

Wherever in Table 30 the rate constants for both the forward reaction (k_1) and the reverse reaction (k_{-1}) are given, the ratio, k_1/k_{-1}, has been calculated for comparison with the equilibrium constant, K_{eq}; and both an experimental and a thermodynamically calculated value for K_{eq} are also given in the table. With one or two exceptions, the k_1/k_{-1} and K_{eq} values are in good agreement. In the case of the dimethylpentanes, the divergence between the experimental and thermodynamic equilibrium constants is believed to be due to error in the thermodynamic data for 2,3-dimethylpentane[291] (see page 160).

Rate constants for isomerization of the five hexanes, determined with aluminum chloride-hydrogen chloride at 100°, are recorded in Table 31. Although the isomerization of a hexane under these conditions is complicated by the number of products possible, some insight was gained as to the course of isomerization of each isomer by supplementing the rate measurements with analyses of the products at various conversions.

In principle, the primary products of a complex reaction can be determined by plotting the yields of the several products against the conversion and extrapolating to zero conversion[244]. When the yield curve for a given product intersects the ordinate at a positive value, the product may be considered a primary one; when the curve passes through the origin, a secondary product is indicated. In practice the method is complicated by difficulties of analysis at low conversions and fails when the rates of secondary reactions are very large compared to the rates of reactions giving the primary products.

When data for the isomerization of the hexanes were treated in this manner, the primary products from *n*-hexane appeared to be 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, in very nearly the same proportions as were found experimentally to be present at equilibrium: 55 per cent 2-methylpentane, 25.4 per cent 3-methylpentane, and 19.6 per cent 2,3-dimethylbutane. The primary product of isomerization of the methylpentanes appeared to be solely 2,3-dimethylbutane. (It was necessary to treat the methylpentanes as a class because they were isomerized to one another so readily that it was impossible to determine any other primary product from each one individually.) The primary product from 2,3-dimethylbutane comprised 64 per cent 2-methylpentane, 31 per cent 3-methylpentane, and 5 per cent 2,2-dimethylbutane. It was impossible to determine the primary products of isomerization of 2,2-dimethylbutane because its rate of conversion was so low that the primary products were isomerized to an equilibrium mixture of all four possible products as quickly as formed. However, since 2,3-dimethylbutane appeared to be the only isomer which gave 2,2-dimethylbutane as a primary product, it was assumed that 2,3-dimethylbutane was the primary product of 2,2-dimethylbutane isomerization. Furthermore, although *n*-hexane was not found to be a primary product of any isomerization, it was assumed to be a minor primary product of methylpentane isomerization, present at low conversions in an amount too small to be detected.

On this basis, the course of isomerization of the hexanes was proposed to be

$$\begin{array}{c} n\text{-Hexane} \\ \downharpoonleft\upharpoonright \\ \text{2-Methylpentane} \rightleftharpoons \text{3-Methylpentane} \\ \downharpoonleft\upharpoonright \\ \text{2,3-Dimethylbutane} \\ \downharpoonleft\upharpoonright \\ \text{2,2-Dimethylbutane} \end{array}$$

and first-order rate constants were calculated for each reaction, as shown in Table 31[59].

The proposed course of isomerization ignores the finding that 2,3-dimethylbutane was a primary product of isomerization of *n*-hexane. This finding is difficult to understand in terms of the classical carbonium ion theory; but newer concepts of the carbonium ion as a *pi*-complex provide an explanation, as given on page 118.

It is of interest to examine the rate constants in Table 31 and the above-given course of hexane isomerization in the light of the experimentally determined equilibrium composition; since for each isomer at equilibrium

$$\frac{\text{rate of isomerization}}{\text{rate of formation}} = \frac{R_i}{R_f} = 1$$

The equilibrium mole fractions in the liquid phase at 102° have been found to be: *n*-hexane 0.094, 2-methylpentane 0.280, 3-methylpentane 0.133, 2,3-dimethylbutane 0.102, and 2,2-dimethylbutane 0.391[57]. By using these equilibrium mole fractions, the rate constants in Table 31, and the proposed course of isomerization, there may be written:

for *n*-hexane

$$\frac{R_i}{R_f} = \frac{(1.8)(0.094)}{(0.7)(0.280)} = 0.86$$

for 2-methylpentane

$$\frac{(0.7 + 150 + 6.0)(0.280)}{(3.9)(0.102) + (1.8)(0.094)(0.280)/(0.413) + (65)(0.133)} = \frac{R_i}{R_f} = 4.8$$

for 3-methylpentane

$$\frac{R_i}{R_f} = \frac{(65)(0.133)}{(1.8)(0.094)(0.133)/(0.413) + (150)(0.280)} = 0.21$$

for 2,3-dimethylbutane

$$\frac{R_i}{R_f} = \frac{(3.9)(0.102) + (0.8)(0.102)}{(6.0)(0.280) + (0.04)(0.391)} = 0.28$$

and for 2,2-dimethylbutane

$$\frac{R_i}{R_f} = \frac{(0.04)(0.391)}{(0.8)(0.102)} = 0.20$$

In no case is the theoretical ratio of unity obtained. Since the equilibrium composition is likely to be most accurate, the rate constants and the proposed course of isomerization are very likely in error. Indeed, in order to yield an equilibrium mixture containing about twice as much 2-methylpentane as 3-methylpentane, the rate constant for isomerization of 3-methylpentane to 2-methylpentane would have to be about twice that of the reverse reaction, not $4/9$ as shown in Table 31.

Nevertheless, the rate constants are probably of the right order of magnitude. They demonstrate that reactions involving only isomers with at least one tertiary carbon are faster than reactions involving an isomer with no tertiary carbon.

Relative Rates. When two saturated hydrocarbons are isomerized in admixture, there is a question whether the amounts of isomerization give a true measure of the relative rates. In view of the demonstrated intermolecular exchange of hydrogen between saturated hydrocarbons during isomerization, the two reactions undoubtedly become coupled; and the isomerization of one hydrocarbon may induce isomerization of the other. However, the following data may be cited to show that one isomerizing hydrocarbon does not affect the *relative* rate of isomerization of another in admixture. When 2,2,4-trimethylpentane and *cis*-decahydronaphthalene were isomerized in admixture with aluminum bromide at 26°, the rate of isomerization of *cis*-decahydronaphthalene was found to be about seven times the rate of conversion of 2,2,4-trimethylpentane to all products (see page 97). When 2,2,4-trimethylpentane and methylcyclopentane were isomerized in admixture under the same conditions, the rate of isomerization of methylcyclopentane was about $1/7$ the rate of conversion of 2,2,4-trimethylpentane. Finally, when *cis*-decahydronaphthalene and methylcyclopentane were isomerized in admixture, the rate of isomerization of *cis*-decahydronaphthalene was found to be about 49 times that of methylcyclopentane, in good agreement with the rates relative to 2,2,4-trimethylpentane[41]. Despite the differences in environment in the three experiments, the *relative* rates of reaction of the three hydrocarbons remained the same.

Accordingly, data pertaining to Experiments 4, 5 and 6 in Table 19 show that isomerization of *n*-pentane is many times faster than isomerization of isobutane. Because of the very small conversion of iso-butane, the data cannot give a very accurate estimate of the relative rates; but from Experiment 5, where isomerization of isobutane was greatest, the order of magnitude can be approximated. If the reverse reactions be neglected,

$$\frac{k_1(n\text{-pentane})}{k_1(\text{isobutane})} = \frac{\ln\,(28/16)}{\ln\,(71.8/70.4)} \sim 30$$

The fact that *n*-pentane isomerization is many times faster than isobutane isomerization despite the much greater ease of formation of carbonium ions from isobutane indicates that the rate-controlling step in *competitive* isomerization, at least, is the rearrangement of the carbonium ion.

HYDROCARBON ISOMERIZATION EQUILIBRIA

Because the difference in energy content of isomers is usually small, most hydrocarbon isomerization reactions do not go to completion but produce an equilibrium mixture containing appreciable quantities of two or more isomers. This fact limits the utility of isomerization as a synthetic tool and necessitates costly separation and recycling steps in commercial applications[56]. Where separation of the isomer having the most desirable properties is impractical, as in the octane rating improvement of olefinic gasolines by isomerization, the establishment of an equilibrium imposes limits on the increase in octane number that may be realized by isomerization[71] and dictates that the charge stock for such a process have a low octane number and a high potential for isomerization[18]. These requirements are well met by gasolines produced by thermal cracking or by Fischer-Tropsch-type processes[28]. Such products contain large amounts of straight-chain 1-alkenes which have low octane numbers and can be isomerized by a shift of the double bond toward the center of the molecule or by chain branching, both being changes which increase the octane number[18].

In spite of the limitations occasioned by the reversibility of isomerization reactions, studies of hydrocarbon isomerization equilibria have provided information of considerable interest and importance to the study of chemical thermodynamics.

General Principles

Thermodynamics. Without a doubt, more thermodynamic data are available for hydrocarbons than for any other class of organic compounds. Not only has the technological importance of hydrocarbons, especially to the petroleum industry, spurred work in this field but the chemical nature and comparatively simple structure of the hydrocarbons have made possible developments which are not likely to be paralleled with more complex organic compounds for many years to come. Because hydrocarbons are comparatively stable thermally and inert chemically, they can be purified by methods not generally applicable to compounds containing a functional group; and once obtained in a pure state, they can, with reasonable precautions, be kept so for long periods of time for the purpose of heat capacity measurements, or determination of heats of combustion or hydrogenation. The combustion of a hydrocarbon, unlike a compound containing halogen or nitrogen, for example, is comparatively clean and easy to define; and therefore heats of combustion are a reliable source of data for computing heats of reactions involving hydrocarbons. Finally, the relative simplicity of hydrocarbon molecules has in many cases permitted accurate computation of thermodynamic functions from spectroscopic and molecular structure data by the methods of statistical thermodynamics.

These thermodynamic data may be used to calculate the equilibrium constant, K, for the isomerization reaction

$$a \rightleftharpoons b$$

by means of the relationship

$$\log K = \log f_b/f_a = -\Delta F^\circ/(2.303RT) \tag{11}$$

In Eq. (11), f_a and f_b are the activities (fugacities) of the isomers at equilibrium, ΔF° is the difference in standard free energies, $F^\circ_b - F^\circ_a$, of the two isomers, R is the gas constant, and T is the absolute temperature. The standard free energy is defined as the free energy per mole of substance in the ideal gas state at one atmosphere, and is related to the standard heat content, H°, and the standard entropy, S°, similarly defined, by the fundamental equation

$$F^\circ = H^\circ - TS^\circ \tag{12}$$

so that

$$\log K = -\Delta H^\circ/(2.303RT) + \Delta S^\circ/(2.303R) \tag{13}$$

In Eq. (13), $\Delta H^\circ = H^\circ_b - H^\circ_a$, the heat of isomerization, and $\Delta S^\circ = S^\circ_b - S^\circ_a$, the entropy of isomerization. A value for ΔH° may be obtained most directly from heats of combustion of the isomers. A value for ΔS° may be obtained from calorimetric heat capacity measurements on the separate isomers with assumption of the Third Law or from statistical calculations based on spectroscopic and molecular structure data.

Alternatively, ΔH° and ΔS° may be calculated by use of Eq. (13) from values of the equilibrium constant obtained at two or more temperatures. Equation (13) indicates that a plot of log K against the reciprocal of the absolute temperature will give a straight line provided the heat and entropy of isomerization are constant over the temperature range in question; or inasmuch as

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = -2.303RT \log K \tag{14}$$

a plot of $2.303RT \log K$ against the absolute temperature will give a straight line, again provided the heat and entropy of isomerization are constant.

Strictly speaking, ΔH° and ΔS° vary with temperature because of a difference in the heat capacities of two hydrocarbon isomers. However, the difference in heat capacities is usually small (on the order of 1 calorie/degree/mole); and its effect on ΔH° is partially cancelled by its effect on ΔS° in such a way as to help preserve the linearity in the relationship between ΔF° and T indicated by Eq. (14). That is, on the approximation that the difference in heat capacities, $\Delta C_p = C_{pb} - C_{pa}$, is a constant between the temperatures, T_1 and T_2,

$$\Delta H^\circ_{T_2} = \Delta H^\circ_{T_1} + \Delta C_p(T_2 - T_1)$$

$$\Delta S^\circ_{T_2} = \Delta S^\circ_{T_1} + \Delta C_p \ln T_2/T_1$$

$$\Delta F^\circ_{T_1} = \Delta H^\circ_{T_1} - T_1 \Delta S^\circ_{T_1}$$

and

$$\Delta F^\circ_{T_2} = \Delta H^\circ_{T_1} - T_2 \Delta S^\circ_{T_1} + \Delta C_p[(T_2 - T_1) - T_2 \ln (T_2/T_1)] \quad (15)$$

and it is apparent from Eq. (15) that $\Delta F^\circ_{T_2}$ differs from that calculated from $\Delta H^\circ_{T_1}$ and $\Delta S^\circ_{T_1}$ by the correction term, $\Delta C_p[(T_2 - T_1) - T_2 \ln (T_2/T_1)]$. The magnitude of this correction term is considered below.

Equation (15) was found to correlate fairly well experimental values of the free energy of the isomerization

$$cis\text{-2-butene} \rightleftharpoons trans\text{-2-butene}$$

obtained from constants for equilibration of the straight chain butenes over chalcide-type catalysts in the temperature range 200–630°[292]. With the aid of the following values based on calorimetric measurements:

$$\Delta H^\circ_{T_1} = \Delta H^\circ_{298} = -950 \text{ cal/mole}$$

$$\Delta S^\circ_{T_1} = \Delta S^\circ_{298} = -1.15 \text{ cal/deg/mole}$$

$$\Delta C_p = 1.49 \text{ cal/deg/mole}$$

Equation (15) becomes

$$\Delta F^\circ_{T_2} = -1395 + 2.64 T_2 - 1.49 T_2 \ln (T_2/298) \quad (16)$$

This equation is plotted as the solid line in Figure 10 in comparison with the experimental points drawn as arrowheads to indicate the direction of approach to equilibrium, the tips of the arrowheads representing the actual values. Equation (16) represents the experimental results fairly well.

A rough estimate of the extreme magnitude of the correction term, $\Delta C_p[(T_2 - T_1) - T_2 \ln (T_2/T_1)]$ in the general Equation (15) may be made by using $\Delta C_p = 1$ cal/deg/mole. Then over almost the entire temperature range useful for isomerization, 300 to 700°K, the correction term amounts to only 193 calories. Inasmuch as the uncertainty in the evaluation of ΔF° by experimental determination of the equilibrium constant is seldom less than 100 calories/mole, the temperature range is usually less than 400°, and ΔC_p may be less than 1 cal/deg/mole, it is manifestly impossible to establish with certainty any variation of ΔH° and ΔS° with temperature by means of equilibrium constant determinations, even though such a variation may be indicated by calorimetric measurements and by statistical mechanical calculations. There is seldom justification for doing more than fitting the experimentally determined equilibrium constants to a linear function of temperature by means of Eq. (13) or (14), and evaluating ΔH° and ΔS° from the constants for the resulting straight line. Use of the principle of least squares in determining the "best" straight line lends confidence in, if not accuracy to, the constants. Nevertheless, it is to be realized that the values of ΔH° and ΔS° so obtained are no more than averages and in reality ΔH° may vary by a few hundred calories and ΔS° may vary by a large fraction of an entropy unit over the temperature range in question, if this be wide.

Agreement is to be expected between the values of ΔH° and ΔS° obtained from measurements of the equilibrium constant over a temperature range and average values for the same constants calculated independently by the methods of thermodynamics from calorimetric data, by statistical mechanics, or by approximate analogical methods. At least it is to be hoped that the discrepancies between the two sets of values will not exceed the combined uncertainties in both, which are ordinarily a few hundred calories in ΔH° and 1 to 2 entropy units (cal/deg/mole) in ΔS°.

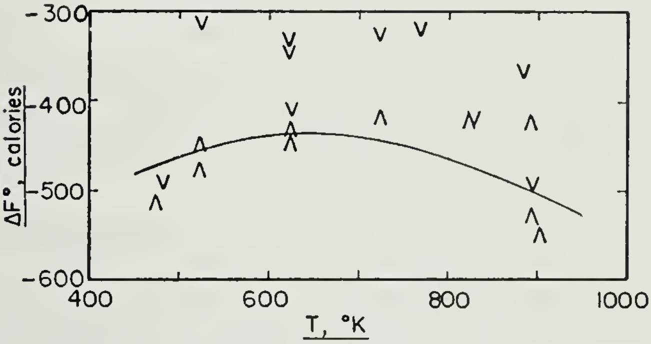


Figure 10. Free energy change for the reaction, *cis*-2-butene ⇌ *trans*-2-butene (Experimental points are drawn as arrowheads to indicate the direction of approach to equilibrium. The solid line is from the thermodynamic equation, $\Delta F^\circ = -1395 + 2.64T - 1.49T \ln (T/298)$. (Voge and May[292]).

Comparison of the two sets of values thus provides critical tests of (1) the accuracy of experimental data, whether they be calorimetric measurements of entropy and heats of reaction on the one hand or analytical data obtained in evaluating the equilibrium constant on the other; (2) the validity and accuracy of approximate relationships for estimating values of thermodynamic functions from structural parameters by the methods of statistical mechanics or by analogical methods; and (3) the validity of thermodynamic concepts such as fugacity and the Third Law. It will be seen in the ensuing review of hydrocarbon isomerization equilibria that the agreement is in some cases as good as could be expected; but in others, discrepancies exist which are greater than the combined estimated uncertainties. If further work fails to resolve these discrepancies in terms of present-day concepts, some new concepts, of chemical activity, for example, may have to be devised.

Although the equilibrium constant is given in Eq. (11) as a ratio of fugacities, the experimental determination of an equilibrium constant does not directly give a value for this ratio; nor is it experimentally practicable to measure the pressure of each component in an equilibrium mixture. Analytical methods in general can only provide numbers expressing the quantity (weight or volume) of each component in a specific sample. From these numbers, a ratio of the concentrations, most practically a ratio of the mole fractions, N_b/N_a, of the isomers at equilibrium under the conditions of the experiment may be obtained. From this ratio, the fugacity ratio, f_b/f_a, must be inferred or calculated with the aid of additional data. The procedure for doing this depends on whether the isomerization is carried out in the gas phase or in the liquid phase.

For equilibrations conducted wholly in the gas phase, it is common practice to set $N_b/N_a = f_b/f_a$, regardless of the total pressure. That is, the observed equilibrium ratio of mole fractions is used directly to evaluate the standard free energy of reaction:

$$\log K = \log N_b/N_a \text{ (gas phase)} = -\Delta F^\circ/(2.303RT)$$

Such a procedure may give a value of ΔF° which is not truly comparable with that from thermodynamic data because of non-ideality of mixtures of real gases under high pressure. However, it appears that in no instance are data available for a more rigorous treatment.

Where standard thermodynamic data pertain to substances in the ideal gaseous state, an equilibrium constant obtained under *liquid* phase conditions will differ from that calculated from the standard thermodynamic functions both because of concurrent vapor-liquid equilibria and because of deviations from ideality. As an approximation for converting an observed liquid-phase equilibrium constant to a gas-phase constant, K_g, for evaluation of the standard free energy of reaction, and for the reverse calculation, pressures may be used in place of fugacities and Raoult's Law may be assumed to hold. Then

$$K = K_g = P_b/P_a = N_bP^\circ_b/N_aP^\circ_a = K_lP^\circ_b/P^\circ_a \tag{17}$$

where P°_a and P°_b are the vapor pressures of the pure isomers at the temperature of equilibration, N_b and N_a are the observed mole fractions, and K_l may be defined as the equilibrium constant in the liquid phase. Thus, when isomerization is carried out in the liquid phase, the ratio of concentrations at equilibrium, K_l, will be observed to differ from the ratio which is related to standard thermodynamic data, K_g, by the factor,

P_a°/P_b°, within the accuracy of Raoult's Law and to the extent the vapors behave as ideal gases.

The approximation contained in Eq. (17) may be expected to be most nearly accurate when P_a° and P_b° are both very low, as with high molecular weight hydrocarbons at low temperatures. However, a more nearly rigorous treatment can be made if sufficient *P-V-T* and liquid density data are available for evaluating the fugacities of the isomers. Then, if f_a° and f_b° are the fugacities of the pure isomers at the temperature, T, and at their respective vapor pressures, the fugacities, f_a^P and f_b^P, of the pure isomers at the total experimental pressure, P, will be given by[151]:

$$f_a^P = f_a^\circ e^{(P-P_a)V_a/RT}$$

$$f_b^P = f_b^\circ e^{(P-P_b^\circ)V_b/RT}$$

where V_a and V_b are the molar volumes of the liquids. If it is assumed that the fugacity of each component at equilibrium is equal to the fugacity of the pure substance at the same temperature and pressure times its mole fraction in the liquid mixture and that the fugacities of both isomers are equally affected by minor amounts of other dissolved substances, such as catalyst[215], then

$$Kg = N_b f_b^P/N_a f_a^P = K_l \frac{f_b^\circ e^{(P-P_b^\circ)V_b/RT}}{f_a^\circ e^{(P-P_a^\circ)V_a/RT}} \tag{18}$$

Values of the fugacity ratio, f_b^P/f_a^P, have been computed for the isobutane/*n*-butane pair at several temperatures in the 20 to 110° range, and for the isopentane/*n*-pentane pair at several temperatures in the 60 to 150° range, using an estimated total hydrocarbon pressure at each temperature[215] for P. (The ratio of exponential terms in Eq. (18) is quite insensitive to changes in total pressure, P.) The values are compared with the Raoult's Law vapor pressure ratios in Table 32. They are 2 to 9 per cent lower in the case of the butanes and 3 to 5 per cent lower in the case of the pentanes. Since the percentage error from other sources is not likely to be larger, use of fugacities would seem to be a worthwhile improvement over the use of vapor pressures in work with these volatile hydrocarbons.

Effect of Side Reactions. In the experimental determination of an equilibrium constant, it is essential to show that equilibrium has been established—that the observed ratio of concentrations is the true equilibrium ratio and not merely some meaningless ratio resulting from incomplete reaction. To do this, it would seem to be sufficient to show that the same ratio of concentrations results from either isomer, or more conveniently to subject near-equilibrium mixtures to the action of a catalyst and determine the extent and direction of change in concentration ratio over a long period of time. A synthetic mixture showing no change in concentration ratio with time would presumably be an equilibrium mixture.

However, it has been shown that when irreversible side reactions which are first-order accompany the reversible reaction, a ratio of concentrations may be obtained which remains constant yet is not the equilibrium ratio. That is, for the reaction

TABLE 32. COMPARISON OF VAPOR PRESSURE AND FUGACITY RATIOS FOR BUTANES AND PENTANES[a]

Temp. (°C)	Butanes		Pentanes	
	$\overset{\circ}{P}_i/\overset{\circ}{P}_n$	f_i^P/f_n^P	$\overset{\circ}{P}_i/\overset{\circ}{P}_n$	f_i^P/f_n^P
20	1.439	1.410		
25	1.426	1.395		
30	1.412	1.378		
40	1.389	1.348		
50	1.368	1.319		
60	1.350	1.290	1.266	1.225
70	1.334	1.264	1.250	1.209
80	1.319	1.238	1.234	1.193
90	1.306	1.215	1.218	1.178
100	1.294	1.193	1.203	1.162
110	1.282	1.175	1.191	1.149
120			1.178	1.135
130			1.167	1.122
140			1.159	1.109
150			1.151	1.096

[a] From Pines, Kvetinskas, Kassel, and Ipatieff[215].

$$a \underset{k_b}{\overset{k_a}{\rightleftarrows}} b$$

accompanied by the side reactions

$$a \xrightarrow{k_a'} \text{By-products}$$

$$b \xrightarrow{k_b'} \text{By-products}$$

where k_a, k_b, k_a', and k_b' are first-order rate constants, a detailed mathematical analysis has shown that a steady ratio of concentrations, $(N_b/N_a)_\infty$, results at $t = \infty$ which is given by the equation[15]

$$(N_b/N_a)_\infty = \frac{2k_a}{k_b + k_b' - k_a - k_a' + [(k_a + k_a' - k_b - k_b')^2 + 4k_ak_b]^{1/2}} \quad (19)$$

This constant ratio is obviously different from the true equilibrium ratio

$$K = k_a/k_b$$

The magnitude of the difference is indicated by the examples in Table 33, where values of K and $(N_b/N_a)_\infty$ are compared for several sets of rate constants. It was also shown mathematically that if the side reactions were of zero order instead of first order, the ratio of concentrations, N_b/N_a, would never become constant[15].

Equation (19) has been expressed[266] as

$$(N_b/N_a)_\infty = \frac{K}{2}\left[\theta + \left(\theta^2 + \frac{4}{K}\right)^{1/2}\right] \tag{20}$$

where $\theta = 1 - 1/K - (k'_a - k'_b)/k_a$. It is apparent from this form of the equation that $(N_b/N_a)_\infty$ will approximate K if the ratio of the difference between the rate constants of the irreversible side reactions to the rate constant of the forward step of the reversible reaction, $(k'_a - k'_b)/k_a$, is small compared to $(1 - 1/K)$; while Eq. (19) itself shows that $(N_b/N_a)_\infty$ equals K in the special case that $k'_a = k'_b$ and, of course, when the rates of the side reactions are both zero. These relationships are illustrated by the examples in Table 33.

TABLE 33. EFFECT OF SIDE REACTIONS ON EXPERIMENTAL EQUILIBRIUM CONSTANTS[a]

Example	k_a	k'_a	k_b	k'_b	$(N_b/N_a)_\infty$	K (k_a/k_b)	$(N_b/N_a)_\infty/K$
1	1	0.01	0.1	0.01	10.0	10.0	1.00
2	1	0.01	1	0.01	1.0	1.0	1.00
3	1	0.01	0.1	0.001	10.5	10.0	1.05
4	0.01	0.01	0.001	0.001	18.5	10.0	1.85
5	0.01	0.005	0.001	0.001	13.6	10.0	1.36
6	0.01	0.002	0.001	0.000	11.8	10.0	1.18
7	0.01	0.01	0.005	0.005	2.74	2.00	1.37
8	0.01	0.1	0.001	0.001	110	10.0	11.0
9	0.01	0.0	0.01	0.001	0.95	1.00	0.95

[a] From Bates[15].

Although Eqs. (19) and (20) are of considerable theoretical interest and importance, it is seldom possible to apply them accurately in connection with studies of hydrocarbon isomerization equilibria because of lack of knowledge of the rate constants, because the rate "constants" depend on the activity of the catalyst, which often changes with time, and because the side reactions may be neither first order nor wholly irreversible. However, since the figures in Table 33 indicate that observed equilibrium constants may differ considerably from the true values when the isomerization is accompanied by extensive side reactions, values obtained under such conditions cannot be given the confidence that may be accorded to values obtained under conditions chosen to minimize side reactions.

Calculation of Equilibrium Composition. After evaluation of equilibrium constants by means of Eqs. (13), (17), or (18), it is frequently desirable to calculate the equilibrium composition of an isomerizate composed of several isomers. For i isomers, it is sufficient to consider the $i - 1$ equilibria:

$$a \rightleftharpoons b$$
$$a \rightleftharpoons c$$
$$\cdots$$
$$a \rightleftharpoons i$$

and the corresponding equilibrium constants:

$$K_b = N_b/N_a$$
$$K_c = N_c/N_a$$
$$\cdots$$
$$K_i = N_i/N_a$$

In terms of mole fractions,

$$N_a + N_b + N_c + \cdots + N_i = 1 \tag{21}$$

Dividing Eq. (21) by N_a and rearranging it gives

$$N_a = 1/(1 + N_b/N_a + N_c/N_a + \cdots + N_i/N_a) \tag{22}$$

Equation (22) gives the mole fraction of isomer a in terms of the several equilibrium constants. The mole fractions of other isomers are then readily obtained from N_a and the individual equilibrium constants.

Paraffin Isomerization Equilibria

Butanes. Work on the butane-isobutane equilibrium makes interesting history, resembling in itself an approach toward an equilibrium. Because this history may repeat itself with other hydrocarbon isomerization equilibria, it seems worthwhile to record its highlights here.

Early determinations of the heat of combustion of n-butane[235] and isobutane[236] gave in 1935 a value of -1630 calories for the (exothermic) heat of isomerization of n-butane[237]. The uncertainty was considered to be 150 calories. Statistical mechanical calculations provided a value of -4.1[118] to -4.3[222] cal/deg/mole for the entropy of isomerization while calorimetric measurements and the Third Law gave -5.8 entropy units[195], the statistical and Third Law entropies for isobutane being the more discordant. In 1936, therefore, the equilibrium constant for isomerization of n-butane could be calculated from theory[118].

The first experimental determination[170] of the equilibrium constant appeared in 1937 and was for a single temperature, 27°. Combination of this information with the supposedly accurate value for the heat of isomerization gave a value of −2.1 cal/deg/mole for the entropy change[119]. Although there remained a discrepancy of 2.0 entropy units, the experimental value was closer to the value calculated by statistical mechanics (−4.1 e. u.) than to the Third Law value (−5.8 e. u.); and this finding aroused suspicion that isobutane did not obey the Third Law because of failure to attain equilibrium in crystallization. This suspicion was dispelled, however, by more extensive calorimetric measurements, which gave a value of −3.7 cal/deg/mole for the entropy change[164]. This new value was closer to the experimentally based value (−2.1 e. u.) than was the value based on statistical mechanics (−4.1 e. u.).

In 1939, there appeared experimental values for the equilibrium constant at several different temperatures[168] so that the heat and entropy of isomerization could then be calculated without recourse to calorimetry. The value for the entropy change thus obtained[164], −4.0 cal/deg/mole, was in excellent agreement with those from statistical mechanics and the calorimetric measurements; but the indicated value for the heat of reaction[72], −2270 cal/mole, was several hundred calories higher than the value from calorimetric heats of combustion. Subsequent work[103, 215, 245, 291] only served to strengthen and confirm the conclusion that one or both of the heats of combustion were in error and redetermination of these values became imperative. New values were provided in 1951 and gave −2050 cal/mole for the heat of isomerization, with an estimated uncertainty of 120 calories[231]. This new value cut in half the discrepancy between the earlier value and that indicated by experimental values for the equilibrium constant over a wide range of temperature.

Figure 11 shows how well the experimental equilibrium constants agree with those which may be calculated from thermodynamic data. The experimental equilibrium compositions, with one or two exceptions, have been found to agree within a maximum deviation of 3 per cent with values based on the equation[215]

$$\ln K_g = 2318/RT - 4.250/R$$

The uncertainty in the indicated heat of isomerization (−2318 cal/mole) is believed to be less than 100 cal/mole; while the uncertainty in the indicated entropy change (−4.25 cal/deg/mole) is estimated as 0.25 cal/deg/mole[215]. The apparent constancy of these values over so wide a temperature range as 170° is noteworthy. Whether the still existing differences between the experimental equilibrium and calorimetric data (Table 34) are real or attributable to experimental errors can only be decided by further work. It is conceivable they are the consequence of deviations from ideality in the behavior of the butanes not corrected for by current concepts of chemical activity.

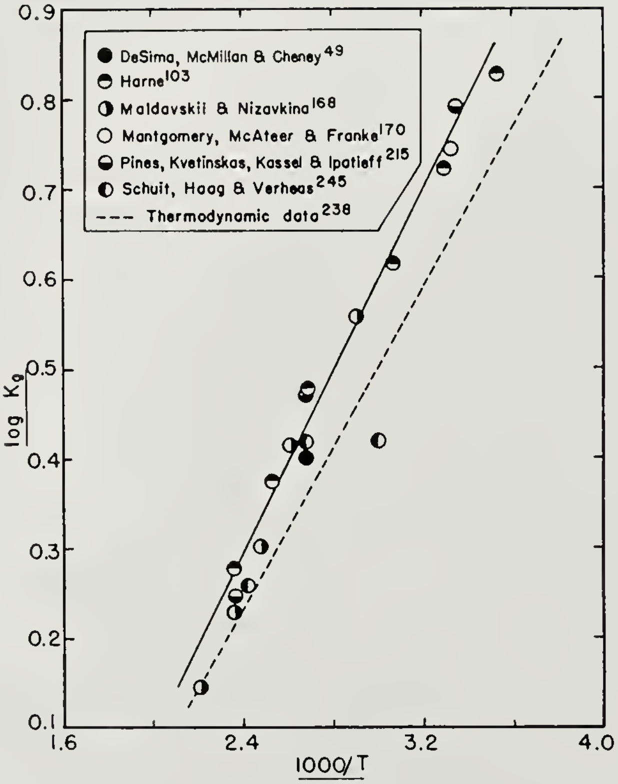


Figure 11. Comparison of experimental and theoretical equilibrium constants for isomerization of *n*-butane in vapor phase.

Table 34. Heat and Entropy of Isomerization of *n*-Butane in the Gas Phase

	Experimental[a]	Thermochemical
Heat of isomerization, $\Delta H^\circ_{298.16^\circ}$, cal/mole	−2318 ± 100	−2050 ± 120[b]
Entropy of isomerization, $\Delta S^\circ_{298.16^\circ}$, cal/deg/mole	−4.25 ± 0.25	−3.57 ± 0.35[c]

[a] Pines, Kvetinskas, Kassel, and Ipatieff[215].
[b] Prosen, Maron, and Rossini[231].
[c] Aston and Messerly[6]; Aston, Kennedy, and Schumann[6].

Pentanes. It is a curious fact that neopentane (2,2-dimethylpropane) has never been observed during pentane isomerization even though available thermodynamic data indicate it should constitute a large fraction of the equilibrium mixture at moderate temperatures (Table 35). Consistent with this fact, however, is the observation that neopentane itself is extremely resistant to isomerization, being unchanged by 2300 hours contact with aluminum bromide at room temperature[171].

In view of the absence of neopentane, only the equilibrium between

Table 35. Calculated Vapor Phase Equilibrium Compositions in Pentane Isomerization[a]

Temperature, °K	300	400	500	600
Equilibrium composition, mole %				
n-Pentane	3.4	11.3	19.3	25.6
2-Methylbutane	43.6	64.3	67.6	66.0
2,2-Dimethylpropane	52.0	24.4	13.1	8.4

[a] Calculated[42] with data from Ref. 238.

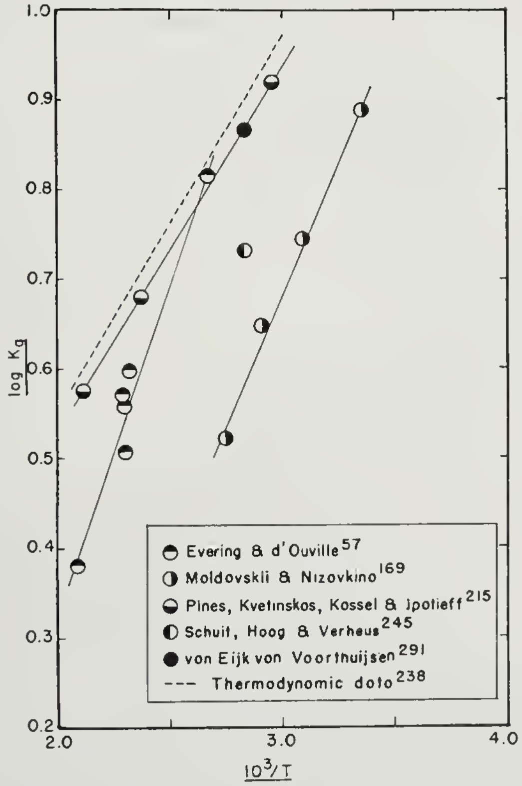


Figure 12. Comparison of experimental and theoretical equilibrium constants for isomerization of *n*-pentane to isopentane in vapor phase.

n-pentane and isopentane need be considered. Experimental values[57,169,215,245,291] for the equilibrium constant are presented in Figure 12. Where necessary, liquid phase equilibrium constants have been converted to gas phase constants by use of the fugacity ratios, f_i^P/f_n^P, from Table 32. Unlike the results with butane, those with pentane show considerable scatter;

and several values for the heat and entropy of isomerization may be calculated (Table 36). The values from the equilibrium data of Pines, Kvetinskas, Kassel and Ipatieff are in excellent agreement with the thermochemical values.

Unlike butane isomerization, pentane isomerization may be accompanied by side reactions. In the equilibrium experiments of Moldavskii and Nizovkina[169], 65 to 80 per cent of the pentane was consumed in side reactions. The experiments of Pines, Kvetinskas, Kassel and Ipatieff and most of those of Evering and d'Ouville were carried out under a high pressure of hydrogen in order to eliminate side reactions. On the one hand, the occurrence of side reactions would be expected to produce a steady state composition of the pentane fraction different from that of true isomerization equilibrium, while on the other hand, the presence of a high concentration of hydrogen may also lead to a spurious equilibrium composition[215].

TABLE 36. HEAT AND ENTROPY OF ISOMERIZATION OF *n*-PENTANE TO 2-METHYLBUTANE IN THE GAS PHASE

Source	$-\Delta H°$ cal/mole[a]	$-\Delta S°$ e. u.[a]
Thermochemical data	1930	1.33
Equilibrium data		
Evering and d'Ouville[57]	3420	5.35
Moldavskii and Nizovkina[169]	2700	4.97
Pines, Kvetinskas, Kassel and Ipatieff[215]	1861	1.30

[a] Average in the temperature range 27–227°.

In order to determine the effect of hydrogen and of side reactions, the experiments in Table 37 were performed. A comparatively small effect is indicated, not large enough to reconcile the results of the several investigations. Nevertheless, the data of Pines, Kvetinskas, Kassel, and Ipatieff show the least scatter and seem most reliable. Their agreement with the thermochemical data is probably not accidental.

Hexanes. Apparent equilibrium among all five hexanes has been observed over the extremely wide temperature range of 17 to 412°. In the lower temperature range (17 to 204°), aluminum chloride was used as a catalyst[57, 126, 291], while in the high temperature range (385 to 412°), a nickel-containing silica-alumina catalyst was used[39] (see pages 79–82 and Table 16). In all experiments, hydrogen was used to suppress side reactions. Liquid-phase equilibrium constants have been converted to those for the gas phase by application of Raoult's Law[126, 291], which is sufficiently accurate at low temperatures where the vapor pressures are much less than one atmosphere, or by use of fugacity ratios[57] (pages 149–151).

Ten equilibria are concerned; but because of their interdependency, it is sufficient to consider only four involving one isomer as a starting material. Those involving *n*-hexane have been chosen here. Experimental equilibrium constants for isomerization of *n*-hexane to each of its four isomers are plotted in Figure 13 in comparison with relationships that may be calculated from calorimetric and statistical thermodynamic[239] data (broken lines in the figure). The solid straight lines in the figure result from a treatment of the data in accordance with the principle of least squares. They correspond to the heats and entropies of isomerization listed in Table 38 in comparison with average thermodynamic values which would reproduce the broken straight lines in the figure. Finally, the average thermodynamic values were used to calculate equilibrium compositions at two widely different temperatures; and these are compared with observed compositions in Table 39. The deviations of the calculated from the observed equilibrium compositions appear to be largely the result of discrepancies in the heat content and entropy of 2,2-dimethylbutane and the entropy of 2,3-dimethylbutane.

TABLE 37. EFFECTS OF HYDROGEN AND SIDE REACTIONS ON PENTANE ISOMERIZATION EQUILIBRIUM[a]

Experiment	1	2	3
Temperature, °C	161	163	157
Total pressure, atm.	99	101	34
Charge composition, mole %[b]			
Isopentane	77.3	82.5	80.6
n-Pentane	22.7	17.5	19.4
H_2, atm. at room temp.	51	51	0
Pentane decomposed, %	1.1	2.3	44.6
Equilibrium mole %, C_5 fraction			
Liquid phase			
Isopentane	76.9	77.4	78.4
n-Pentane	23.1	22.6	21.6
Vapor phase			
Isopentane	78.3	78.8	79.9
n-Pentane	21.7	21.2	20.1

[a] From Evering and d'Ouville[57].

[b] The charge also contained 1–3 per cent benzene.

Methylpentanes. Although 2- and 3-methylpentane can be isomerized to an equilibrium mixture of all five hexanes, these two isomers are converted to one another so much more rapidly than they are converted to other isomers that it has been possible to study the equilibrium between them alone. The equilibrium composition, determined for the liquid phase with

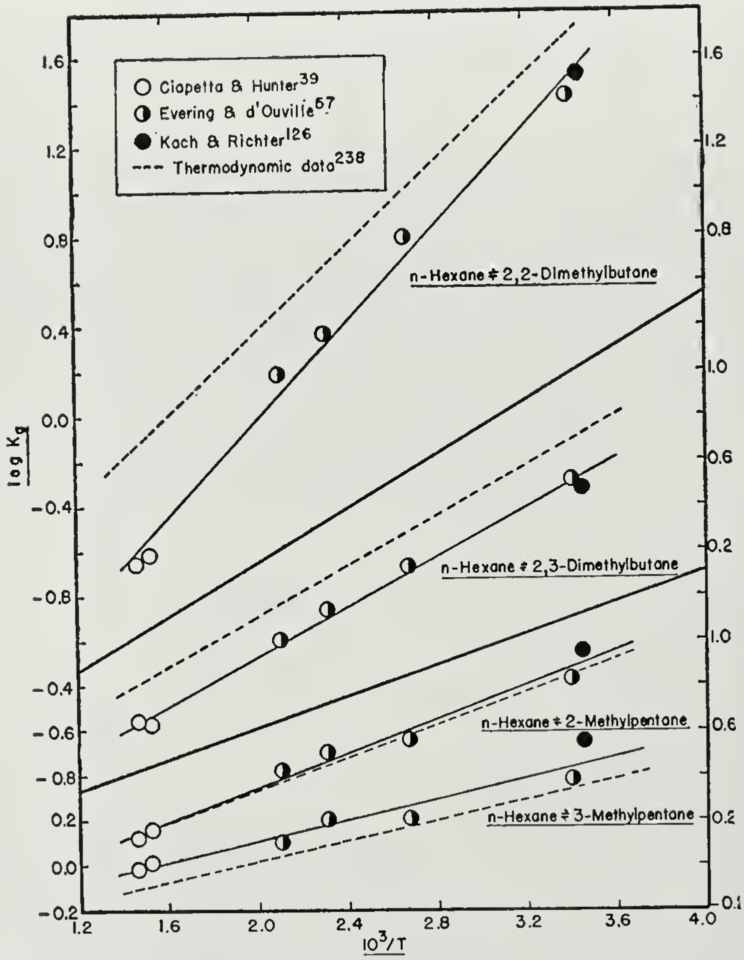


Figure 13. Comparison of experimental and theoretical equilibrium constants for isomerizations of *n*-hexane in vapor phase.

TABLE 38. HEATS AND ENTROPIES OF ISOMERIZATION OF *n*-HEXANE

Product Isomer	Equilibrium data[a]		Thermodynamic data[b]	
	$-\Delta H°$ cal/mole	$-\Delta S°$ e. u	$-\Delta H°$ cal/mole	$-\Delta S°$ e. u.
2-Methylpentane	1740	1.88	1680	1.82
3-Methylpentane	1090	1.69	1050	2.00
2,2-Dimethylbutane	4950	10.0	4300	6.89
2,3-Dimethylbutane	2500	6.20	2550	5.48

[a] These average values, obtained by the method of least squares, reproduce the solid straight lines in Figure 13.

[b] These average values, based on data in Ref. 238, reproduce the broken straight lines in Figure 13.

aluminum chloride as catalyst at 20°[291] and with 99.8 per cent sulfuric acid as catalyst at 25°[234], is in good agreement with that calculated from thermodynamic data (Table 40).

Heptanes. In a study of heptane isomerization with aluminum chloride at 20°, it was found that only six of the nine isomers were present at equilibrium. Those absent were 2,2-dimethylpentane, 3,3-dimethylpentane, and 3-ethylpentane. Of these, 2,2-dimethylpentane was unchanged after 20 hours treatment with the catalyst and conditions used[291].

Table 39. Equilibrium Compositions in Hexane Isomerization

Temperature, °C	21			412	
Source	Observed[a]		Calcd.[b]	Observed[c]	Calcd.[b]
Phase	Liquid	Vapor	Vapor	Vapor	Vapor
Equilibrium composition, mole %					
n-Hexane	4.1	2.5	1.6	26.4	21.1
2-Methylpentane	21.6	16.9	11.3	35.1	28.9
3-Methylpentane	8.4	6.0	3.6	25.4	16.6
2,2-Dimethylbutane	56.4	66.4	75.5	5.8	15.4
2,3-Dimethylbutane	9.5	8.2	8.0	7.3	18.0

[a] Evering and d'Ouville[57].

[b] Calculated[42] with average thermodynamic data in Table 38.

[c] Ciapetta and Hunter[39].

Table 40. Equilibrium Between the Methylpentanes in the Liquid Phase

Temperature, °C	20°	25°	25°
Catalyst	$AlCl_3$[a]	H_2SO_4[b]	Calcd.[b, c]
Equilibrium composition, mole %			
2-Methylpentane	72	69	71
3-Methylpentane	28	31	29

[a] van Eijk van Voorthuijsen[291].

[b] Roebuck and Evering[234].

[c] Values for vapor phase from thermodynamic data[238] converted to liquid phase by use of vapor pressures[291] and Raoult's Law.

The observed equilibrium composition is shown in Table 41 in comparison with that which may be calculated from thermodynamic data. 2-Methylhexane was chosen as a base from which to calculate standard free energy differences. The resulting values for 3-methylhexane, 2,4-dimethylpentane, and 2,2,3-trimethylbutane are in excellent agreement with thermodynamic data; but those for *n*-heptane and 2,3-dimethylpentane are quite different. The difference in the case of *n*-heptane may be due to side reactions encountered whenever isomerizing to or from this isomer[291]; but the difference in the case of 2,3-dimethylpentane is believed to be due to error in the thermodynamic functions for this compound[291].

Methylhexanes and Dimethylpentanes. Because of the rapidity of 1,2-shift of a methyl, which made it possible to study equilibrium between the methylpentanes, it has similarly been possible to study equilibrium between the two methylhexanes and between 2,3- and 2,4-dimethylpentane. These equilibria have been studied by three groups of workers at a total of five different temperatures between −33.4° and 60°. Results are presented in the top part of Table 42. The data have been used[42] to evaluate heats and entropies of isomerization for comparison with thermochemical values. Three of the data appear to be erratic from log K vs $1/T$ plots and were rejected (see Table). Four remaining results for the methylhexanes give heats and entropies of isomerization in good agreement with the thermochemical values. Three results with the dimethylpentanes give an entropy difference which is in excellent agreement with the thermochemical value; but the heat of isomerization differs from the thermochemical value by about a kilocalorie. This result, combined with the conclusion derived above from data in Table 41, firmly indicates an error of about a kilocalorie in the experimental heat of combustion of 2,3-dimethylpentane[269a]. A statement that, for the 2,3-dimethylpentane-2,4-dimethylpentane equilibrium, "$\Delta S°$ changes sign in the vicinity of 0° at which temperature $\Delta H°$ has a value of about −475 cal"[155] does not seem at all justified in view of the frequently demonstrated linearity of log K vs $1/T$ plots for hydrocarbon isomerizations. More likely the rejected equilibrium data (Table 42) are incorrect.

TABLE 41. EQUILIBRIUM AMONG SIX OF THE NINE HEPTANES AT 20°

Isomer	Equilibrium Mole %			$\Delta F°$, Calories	
	Liquid Exptl.[a]	Vapor Exptl.[b]	Vapor Calcd.[c]	Exptl.	Thermod.[c]
n-Heptane	15	10	2.2	460	1160
2-Methylhexane	23.6	21.8	15.7	0	0
3-Methylhexane	14.5	11.7	8.6	360	350
2,3-Dimethylpentane	14.4	13.3	44.6	300	−610
2,4-Dimethylpentane	21.5	28.6	17.7	−160	−70
2,2,3-Trimethylbutane	11	15	11.2	210	200

[a] From van Eijk van Voorthuijsen[291].

[b] Liquid phase equilibrium composition converted to vapor phase by use of vapor pressures and Raoult's Law[291].

[c] Calculated[42] by use of data in Ref. 238.

Naphthene Isomerization Equilibria

The Methylcyclopentane-Cyclohexane Equilibrium. Experimental equilibrium constants for the isomerization of methylcyclopentane to cyclohexane in the temperature range 20 to 140° are plotted in Figure 14 in comparison with a relationship which may be calculated from calorimetric data on the two hydrocarbons. The solid line in the figure, drawn by the method of least squares, fits the equation

Table 42. Equilibrium Between 2- and 3-Methylhexane and Between 2,3- and 2,4-Dimethylpentane in the Liquid Phase

Temp. °C	Catalyst	3-MH $\rightleftharpoons$ 2-MH		2,3-DMP $\rightleftharpoons$ 2,4-DMP	
		Mole % 2-MH	K_l	Mole % 2,4-DMP	K_l
−33.4[a]	$ClSO_3H$	65.5	1.90	72.8	2.68[d]
0[a]	H_2SO_4: $ClSO_3H$	62.8	1.69	70.6	2.40
20[b]	$AlCl_3$	62	1.63	60	1.50[d]
25[c]	H_2SO_4	56–59	1.35[d]	65–66	1.90
60[a]	H_2SO_4	59.5	1.47	59.6	1.48
$-\Delta H°_l$, cal/mole					
Equilibrium data		440		1460	
Thermochemical, 25°[e]		580		360	
$-\Delta S°_l$, cal/deg/mole					
Equilibrium data		0.55		3.60	
Thermochemical, 25°[e]		0.94		3.80	

[a] Maury, Burwell, and Tuxworth[155].

[b] van Eijk van Voorthuijsen[291]. From Table 41.

[c] Roebuck and Evering[234].

[d] Rejected in evaluating $\Delta H°_l$ and $\Delta S°_l$.

[e] Calculated[42] for liquid phase from data in Ref. 238.

$$\log K = 866/T - 2.018 \qquad (23)$$

which yields −3960 cal/mole for the heat and −9.22 cal/deg/mole for the entropy of the reaction

$$\text{Methylcyclopentane (liquid)} \rightleftharpoons \text{Cyclohexane (liquid)}.$$

The observed equilibrium compositions differ by less than 4 per cent from values calculated with Eq. (23).

The heat of reaction evaluated in this way is in excellent agreement with the value based on heats of combustion, −3930 cal/mole[172]; but the entropy of reaction differs significantly from the value, −10.44 ± 0.3 cal/deg/mole[266], obtained from calorimetric heat capacity measurements on methylcyclopentane[52] and cyclohexane[7,240]. Chiefly because of the higher calorimetric entropy difference, equilibrium compositions calculated from the calorimetric data are about 9 per cent richer in methylcyclopentane near 25° and about 16 per cent richer in methylcyclopentane near 100° than observed.

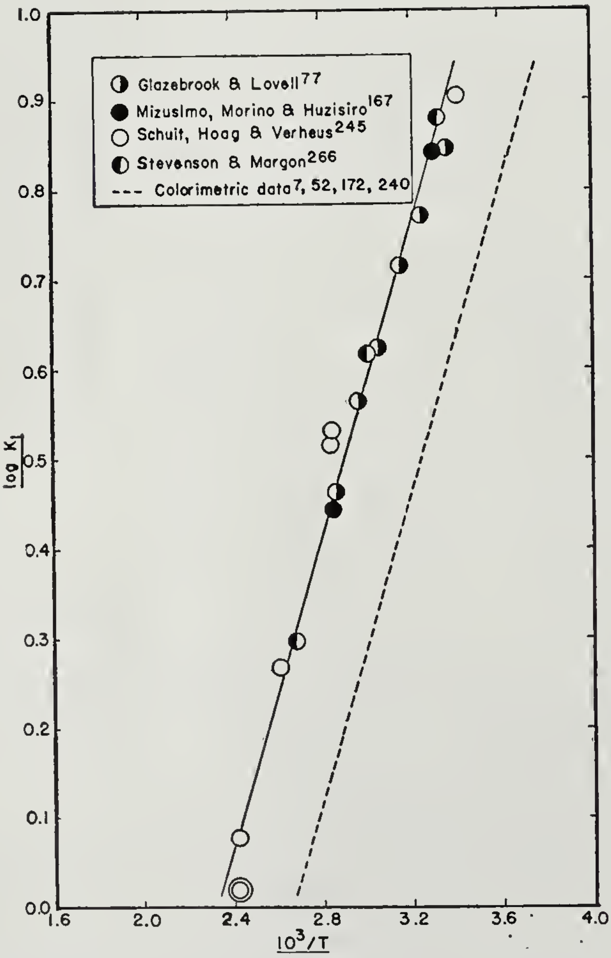


Figure 14. Comparison of experimental and theoretical equilibrium constants for isomerization of methylcyclopentane to cyclohexane in liquid phase.

In seeking an explanation for the discrepancies between the observed equilibrium compositions and those calculated from calorimetric data, the following two factors have been considered: (1) side reactions during isomerization may have led to steady state compositions different from those of true equilibrium; and (2) the presence of isomeric cyclopropane and cyclobutane hydrocarbons may have led to incorrect analyses of the isomerization product[266]. Neither of these possibilities seems a likely cause of the discrepancies. In the first place, the isomerization of a naphthene containing a five- or six-membered ring is, unlike that of a paraffin with the same number of carbons, practically free of side reactions, mere traces (less than 1 per cent) of by-products having been detected mass spectrometrically in the products of isomerization of methylcyclopentane or cyclohexane with moist aluminum chloride or bromide at 27 to 100°[266]. A comparison of the apparent rates of the side reactions with the rate of isomerization in accordance with Eq. (20) indicated the error in the equilibrium ratio from this source to be less than 0.5 per cent[266]. Secondly, although dimethylcyclobutanes have been reported to result from the action of moist aluminum bromide on cyclohexane[318], there is reason to doubt the identification. A consideration of strain energies of cyclic hydrocarbons, together with a liberal estimate of the entropy difference, has led to the conclusion that the amount of a cyclopropane or cyclobutane isomer of cyclohexane could not exceed 0.01 per cent at equilibrium[266]. Consequently, it does not seem likely that the presence of such isomers is a source of error in the methylcyclopentane-cyclohexane equilibrium. It seems very likely that the calorimetric entropy difference is incorrect.

TABLE 43. EQUILIBRIUM AMONG C_7H_{14} NAPHTHENES[a]
Catalyst: nickel-silica-alumina
Pressure: 24.8 atm.
Liquid Space Velocity: 1 hr.$^{-1}$
H_2/Hydrocarbon: 4 mole/mole

Temperature, °C	342		370	
Equilibrium composition, mole %	Exptl.	Calcd.	Exptl.	Calcd.
1,1-Dimethylcyclopentane	8.0	9.2	8.9	9.1
cis-1,2-Dimethylcyclopentane *trans*-1,2-Dimethylcyclopentane	24.3	20.3	24.0	21.2
cis-1,3-Dimethylcyclopentane *trans*-1,3-Dimethylcyclopentane	23.7	23.5	25.8	25.2
Ethylcyclopentane	9.8	10.5	10.2	11.8
Methylcyclohexane	34.2	36.5	31.2	32.7

[a] From Ciapetta[38].

C_7H_{14} Naphthenes. Excluding cyclopropane and cyclobutane derivatives and cycloheptane, there are seven isomeric C_7H_{14} naphthenes. Apparent equilibrium among these seven hydrocarbons was obtained by isomerization of methylcyclohexane over a nickel-silica-alumina catalyst at 342 to 370°[38] (Table 43). The observed compositions are in good agreement with those calculated for equilibrium from thermodynamic data; and the similarity in composition of products obtained at 342° and 370° supports the belief that equilibrium was established under these conditions.

At 25°, the calculated equilibrium constants for liquid-phase isomerization of methylcyclohexane to alkylcyclopentanes are all less than 10^{-2} and so isomerization is difficult to observe at low temperatures[215a]. However, it has been demonstrated that rearrangement occurs by treatment of methylcyclohexane labeled with C^{14} in the methyl group with aluminum bromide, hydrogen bromide and *sec*-butyl bromide (promoter) for 21 hours at room temperature. About 31 per cent of the radioactive carbon appeared in the cyclohexane ring[215a]. Isomerization beyond the limitations imposed by thermodynamics has been accomplished by refluxing methylcyclohexane with aluminum chloride and removing the lower-boiling alkylcyclopentanes by constantly distilling them away from the reaction zone[291a].

TABLE 44. EQUILIBRIUM AMONG C_8H_{16} ALKYLCYCLOHEXANES IN THE LIQUID PHASE

Temperature, °C	25–100°	25°
Equilibrium composition, mole %	Exptl.[a]	Calcd.[b]
Ethylcyclohexane	—	1.9
1,1-Dimethylcyclohexane	12	5.4
cis-1,2-Dimethylcyclohexane	—	0.7
trans-1,2-Dimethylcyclohexane	8	8.5
cis-1,3-Dimethylcyclohexane	45	50.1
trans-1,3-Dimethylcyclohexane	5	4.5
cis-1,4-Dimethylcyclohexane	—	2.3
trans-1,4-Dimethylcyclohexane	30	26.6

[a] Chiurdoglu, Fierens, and Henkart[35].

[b] Calculated[42] with data in Reference 238. Vapor phase equilibrium constants were converted to the liquid phase by use of vapor pressures and Raoult's Law.

C_8H_{16} Naphthenes. There are 23 isomeric C_8H_{16} alkylcyclopentanes and alkylcyclohexanes. Fifteen of these, namely, *n*-propylcyclopentane, isopropylcyclopentane, *cis*- and *trans*-1-methyl-2-ethylcyclopentane, the three 1,2,4-trimethylcyclopentanes, ethylcyclohexane, 1,1-dimethylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexane, *cis*- and *trans*-1,3-dimethylcyclohexane, and *cis*- and *trans*-1,4-dimethylcyclohexane, were separately isomerized with aluminum chloride at 100° and appeared to give the same equilibrium mixture, according to Raman spectroscopic examination[34, 35]. Unfortunately, Raman spectroscopy is not a very sensitive method of analysis. No difference could be detected by this method in isomerizates produced at three different temperatures, 25°, 56°, and 100°; and only dimethylcyclohexanes were identified in the isomerizate produced from the several hydrocarbons. The observed equilibrium composition is compared with that calculated from thermodynamic data on the C_8H_{16} alkylcyclohexanes in Table 44. Although thermodynamic data for C_8H_{16} alkylcyclopentanes are not generally available, it seems probable that significant amounts of some of these would be present at equilibrium, inasmuch as the isomerization of ethylcyclohexane over a nickel-silica-alumina catalyst at 343 to 372° produced isomerizates containing 14 to 17 per cent of trimethylcyclopentanes in the C_8H_{16} naphthene fraction[38, 217a].

Cis-trans Equilibria among the Dimethylcyclohexanes. Equilibrium compositions have been determined for *cis-trans* isomerization of each of the three pairs of dimethylcyclohexanes in the liquid phase at 25° with 99.8 per cent sulfuric acid as catalyst[234]. The *cis-trans* isomerization was accompanied by much methyl group migration producing chiefly *cis*-1,3-dimethylcyclohexane from the 1,2- and 1,4-isomers and chiefly *trans*-1,4-dimethylcyclohexane from the *cis*-1,3-isomer (see pages 48–49). Nevertheless, the indicated equilibrium compositions were in approximate agreement with those predicted from thermodynamic data, as shown in Table 45.

TABLE 45. *CIS-TRANS* EQUILIBRIA AMONG THE DIMETHYLCYCLOHEXANES IN THE LIQUID PHASE AT 25°[a]

Isomer	Equilibrium, mole %	
	Observed[a]	Calcd.[b]
cis-1,2-Dimethylcyclohexane	5	8.0
trans-1,2-Dimethylcyclohexane	95	92.0
cis-1,3-Dimethylcyclohexane	95	91.8
trans-1,3-Dimethylcyclohexane	5	8.2
cis-1,4-Dimethylcyclohexane	7	7.9
trans-1,4-Dimethylcyclohexane	93	92.1

[a] Roebuck and Evering[234].
[b] See note b, Table 44.

C_9H_{18} Naphthenes. A number of the isomeric C_9H_{18} alkylcyclopentanes and alkylcyclohexanes were isomerized with aluminum chloride in the liquid phase at 100°; and the isomerizates were analyzed by Raman spectroscopy, as was done with the C_8H_{16} naphthenes. The equilibrium composition, the same from all isomers, was as follows[36, 37]:

	(%)
1,1,2-trimethylcyclohexane	5
1,1,3-trimethylcyclohexane	14
1,1,4-trimethylcyclohexane	10
1,2,3-trimethylcyclohexanes	5
1,2,4-trimethylcyclohexanes	27
"*cis*-1,3,5-trimethylcyclohexane"	34
"*trans*-1,3,5-trimethylcyclohexane"	5

Thermodynamic data are not available for a comparison.

Olefin Isomerization Equilibria

Butenes. Many groups of workers have studied equilibrium among the straight-chain butenes[159, 270, 290, 292, 320] but not all have assayed the isomerizate completely because of the difficulty of analyzing mixtures of *cis*- and *trans*-2-butene. When only the total 2-butene content is known, it is not possible to compute values for the equilibrium constants of the individual reactions:

$$\text{1-butene} \rightleftharpoons \textit{trans}\text{-2-butene} \tag{XXXVI}$$

$$\text{1-butene} \rightleftharpoons \textit{cis}\text{-2-butene} \tag{XXXVII}$$

$$\textit{cis}\text{-2-butene} \rightleftharpoons \textit{trans}\text{-2-butene} \tag{XXXVIII}$$

without assuming a value for the equilibrium constant of one of them.

Kistiakowsky and Smith[124] obtained a value for the equilibrium constant of Eq. (XXXVIII) at 390° by heating mixtures of *cis*- and *trans*-2-butene having near-equilibrium compositions and noting the percentage change in *trans*-2-butene content in 500 minutes. No change occurred in mixtures containing 52.8 per cent of the *trans* isomer; and therefore an equilibrium constant of 1.12 was indicated. A cryoscopic method of analysis was used, and although evidence for the absence of 1-butene was presented, the equilibrium constant is not in agreement with values obtained by others in the presence of catalysts nor with a value (1.59) that may be calculated from thermodynamic data[238].

Frey and Huppke[68] have reported values for the equilibrium constants for dehydrogenation of *n*-butane to each of the three straight-chain butenes over a chromium oxide catalyst at 350°, 400°, and 450°; and from them there may be calculated equilibrium constants for the isomerization reactions (XXXVI), (XXXVII), and (XXXVIII).

Voge and May[292] studied the isomerization of the straight-chain butenes over a wide temperature range with three catalysts having a silica-alumina base. They used an infrared spectroscopic method of analysis and reported equilibrium contents of all three isomers. Their equilibrium compositions for any one temperature (±2°) have been averaged[42] and equilibrium constants for the three isomerization reactions have been calculated from the average compositions for ten different temperatures in the range 200 to 630°. The results are presented as log K_g *vs.* $1/T$ plots in Figure 15. The results of Kistiakowsky and Smith and of Frey and Huppke are included for comparison. The solid straight lines in the figure are the result of least squares treatments[42] of the data of Voge and May. The broken line curves were calculated[42] with selected thermodynamic data[238].

In Table 46, average values of the heats and entropies of isomerization given by the data of Voge and May are compared with values based on calorimetric measurements and statistical mechanics. Because the difference in heat capacities of isomeric olefins is often large, compared to that between isomeric paraffins, the thermodynamic heats and entropies of isomerization show considerable variation with temperature. An alternative treatment of the *cis*-2-butene ⇄ *trans*-2-butene equilibrium data[292], which takes into account this variation, has been presented on pages 146–147 and in Figure 10.

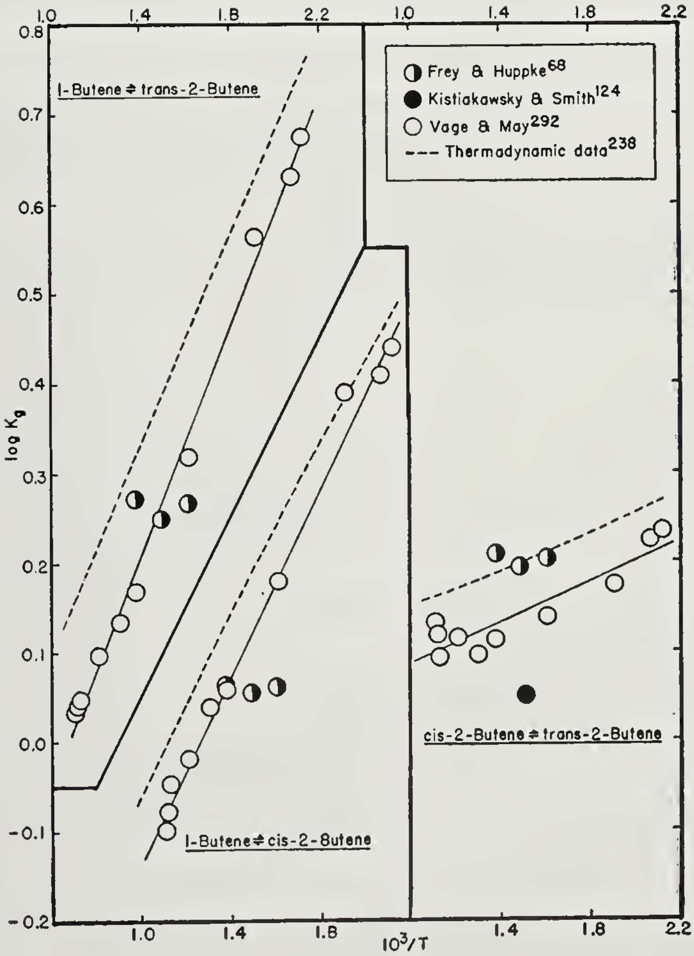


Figure 15. Comparison of experimental and theoretical equilibrium constants for isomerizations of straight-chain butenes in vapor phase.

As stated above, several workers have determined the content of 1-butene in equilibrium with the 2-butenes without determining the proportions of *cis*- and *trans*-2-butene. These results have generally been in good agreement with predictions based on thermodynamic data, as shown by the lower part of Figure 16. By comparison, the findings of Voge and May included in the figure appear to be high.

In the upper part of Figure 16 are curves representing the percentage of isobutene in equilibrium with all the butenes as a function of temperature. This equilibrium was studied by Frost, Rudkovskaya, and Serebryakova[73] in the temperature range 265 to 426° with several catalysts, including aluminum sulfate, phosphoric acid on carriers, and acidic clays. According to these authors, the results may be represented by the equation

$$\log K_g = \log (\text{isobutene})/(n\text{-butenes}) = 304/T - 0.528 \qquad (24)$$

Equation (24) may be used to calculate the percentage of isobutene at equilibrium and it yields the solid line curve in the upper part of Figure 16. The curve parallels the broken line curve calculated from thermodynamic data[238]; but the corresponding equilibrium percentages of isobutene are appreciably lower than those predicted.

TABLE 46. HEATS AND ENTROPIES OF ISOMERIZATION OF 1-BUTENE

Product isomer	*cis*-2-Butene	*trans*-2-Butene
Reaction	(XXXVII)	(XXXVI)
Equilibrium data[a]		
$-\Delta H^\circ$, cal/mole	2390	2920
$-\Delta S^\circ$, cal/deg/mole	3.00	3.14
Thermodynamic data		
$-\Delta H^\circ_{355^\circ\mathrm{K}}$, cal/mole[b]	1771	2720
$-\Delta H^\circ$, cal/mole[c]	1980–2430	2640–2770
$-\Delta S^\circ$, cal/deg/mole[c]	2.01–2.70	2.16–2.35

[a] Average for the temperature range 200–630°. These values reproduce the solid straight lines in Figure 15.

[b] From heats of hydrogenation[123].

[c] Values in the temperature range 223–623° from Ref. 238, which were used to calculate the broken line curves in Figure 15.

Pentenes. Equilibration of all six pentenes was studied with various catalysts, including aluminum sulfate and supported phosphoric acid, at 200° and 380°[321]. The observed equilibrium compositions are compared with those calculated[42] from thermodynamic data[238] in Table 47. Agreement is only fair.

According to Schuit, Hoog, and Verheus[245], the equilibrium mixture obtained with "Permutit" as catalyst at 400° contains about 80 per cent branched-chain pentenes. This result is in good agreement with that calculated for 380° from data in the last column of Table 47.

Equilibrium among the three branched-chain pentenes was studied with activated alumina at 251 to 400°. Apparently no unbranching to form 1- and 2-pentenes occurred under the conditions used[60]. Equilibrium constants for the three reactions:

2-methyl-1-butene ⇌ 2-methyl-2-butene (XXXIX)

3-methyl-1-butene ⇌ 2-methyl-2-butene (XL)

3-methyl-1-butene ⇌ 2-methyl-1-butene (XLI)

were obtained at 251°, 300°, 358° and 400°. Heats of isomerization were

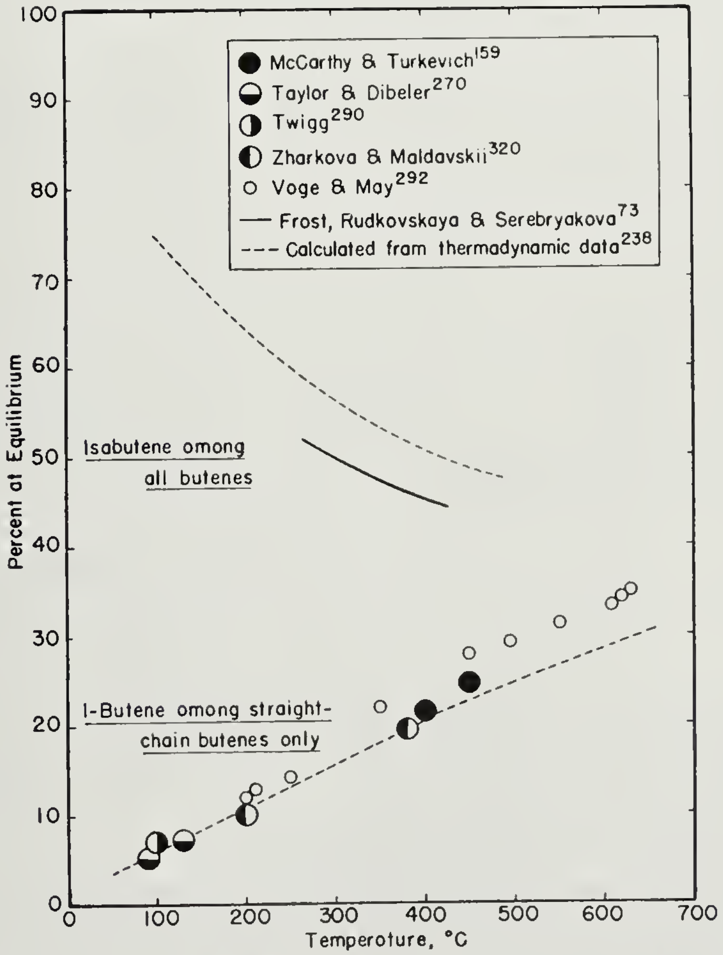


Figure 16. Equilibrium percentages in vapor-phase butene isomerization.

obtained from published heats of hydrogenation of the isomers at 82°. The equilibrium constants and heats of isomerization were then combined to get entropies of isomerization on the approximation that the heat capacities of the three isomers differed so little that the heats and entropies of isomerization could be considered constant over the temperature range in question. The average entropies of isomerization so obtained are presented in Table 48. Subsequent calculations of the entropies of the three isomers by statistical mechanics[120, 246] have given the quite different values included in the Table for comparison. The composition of an equilibrium mixture calculated[42] from thermodynamic data[238] is in fair agreement with that found by experiment (Table 49, Part a.)

Hexenes. There are 17 isomeric hexenes; and mixtures are difficult to analyze because the chemical and physical properties of individual isomers are similar. In order to simplify the analysis of isomerizates produced from 1-hexene with a variety of catalysts at about 260°, 315°, 400°, and 480°, they were hydrogenated to mixtures of the five hexanes and these mixtures were analyzed by mass spectroscopy[175]. In some cases (with activated alumina at about 400°, with 10 per cent boria on alumina at about 315°, and with phosphoric acid at 315°), a mixture of hexanes was obtained with a composition close to that which thermodynamic data indicated would result from a mixture of all 17 hexenes at equilibrium (Table 50). However, since no tests for the establishment of equilibrium were made, and since hexene contents of the isomerizates were not found in this work, the data cannot be used to calculate equilibrium constants for hexene isomerization reactions.

Table 47. Equilibrium among the Pentenes in the Gaseous State

Temperature, °C	200		380	
Equilibrium composition, mole %	Exptl.[a]	Calcd.[b]	Exptl.[a]	Calcd.[b]
1-Pentene	18.7–19.5	0.7	27.8–28.6	2.6
cis-2-Pentene		4.1		8.2
trans-2-Pentene		5.5		9.4
2-Methyl-1-butene	77.3–77.8	22.3	64.3–64.8	28.6
2-Methyl-2-butene		66.1		48.0
3-Methyl-1-butene	3.2–3.5	1.3	7.0–7.5	3.2

[a] Zharkova and Moldavskii[321].

[b] Calculated with thermodynamic data in Ref. 238.

Table 48. Heats and Entropies of Isomerization of the Methylbutenes

Reaction	$-\Delta H^{\circ a}$ cal/mole	$-\Delta S^{\circ}$, e. u.	
		Exptl.[b]	Theor.[c]
2-methyl-1-butene ⇄ 2-methyl-2-butene	1571	0.64	2.07
3-methyl-1-butene ⇄ 2-methyl-2-butene	3416	−0.8	1.06
3-methyl-1-butene ⇄ 2-methyl-1-butene	1845	−1.4	−1.01

[a] From heats of hydrogenation[51, 123] at 82°.

[b] Ewell and Hardy[60]. Average in the temperature range 251–400° from experimental equilibrium constants and tabulated heats of isomerization.

[c] From entropies at 323° calculated by statistical mechanics[120, 246].

By suitable choice of catalyst and conditions, Koch and van Raay[127] were able to study equilibria among several groups of branched-chain hexenes without complication due to formation of isomers more or less highly branched. Comparison of the experimental compositions with those calculated from thermodynamic data is shown in Table 51.

TABLE 49. EQUILIBRIUM COMPOSITIONS FOR THE METHYLBUTENES

Part a. Monomethylbutenes at 358°

Equilibrium composition, mole %	Exptl.[a]	Calcd.[b]
3-Methyl-1-butene	3.5	4.3
2-Methyl-1-butene	27.3	37.6
2-Methyl-2-butene	69.2	58.1

Part b. Dimethylbutenes

Temperature, °C	275		300	
Equilibrium composition, mole %	Exptl.[c]	Calcd.[b]	Exptl.[d]	Calcd.[b]
3,3-Dimethyl-1-butene	3.7	2	3.2	2
2,3-Dimethyl-1-butene	32.8	41	32.9	43
2,3-Dimethyl-2-butene	63.5	57	63.8	55

[a] Ewell and Hardy[60].
[b] Calculated[42] with data from Ref. 238.
[c] Cramer and Glasebrook[47].
[d] Laughlin, Nash and Whitmore[133]; Whitmore and Meunier[301].

TABLE 50. COMPOSITIONS OF HYDROGENATED HEXENES FROM ISOMERIZATION OF 1-HEXENE[a]

Catalyst	Approx. Temp. (°C)	Composition of Hydrogenated Product, mole %				
		2,2-Dimethylbutane	2,3-Dimethylbutane	2-Methylpentane	3-Methylpentane	*n*-Hexane
Thermodynamic data[b]	315	0.7	12.2	40.5	33.7	12.9
“ “	400	0.6	10.7	39.9	33.0	15.8
Activated alumina	400	0.0	11.0	38.0	33.9	17.1
10% boria-90% alumina	315	0.0	12.1	40.7	34.5	12.7
Phosphoric acid	315	0.2	12.4	41.2	34.6	11.6

[a] From Naragon[175].
[b] Calculated[175] for equilibrium among all 17 hexenes.

Mixtures of the three dimethylbutenes having practically the same composition have been obtained by isomerization of 3,3-dimethyl-1-butene with aluminum sulfate at 275°[47], by treatment of each isomer separately with phosphorus pentoxide on silica gel[133] at 300°, and by dehydration of 3,3-dimethyl-2-butanol with aluminum sulfate at 275°[47] or with phosphorus pentoxide on silica gel at 300°[301]. As shown in Part b of Table 49, the observed equilibrium compositions are in fair agreement with predictions based on thermodynamic data, the discrepancies being similar to those observed with the monomethylbutenes (Part a of Table 49). The source of these discrepancies probably lies in approximation methods used to evaluate the thermodynamic functions.

TABLE 51. EQUILIBRIA AMONG BRANCHED HEXENES[a]

Equilibrium composition, %	Exptl.	Calcd.[b]
2-Methyl-1-pentene	21.8[c]	30.6
2-Methyl-2-pentene	78.2[c]	69.4
2-Methyl-1-pentene	15–18[d]	25.2
2-Methyl-2-pentene	70–74[d]	57.2
cis-2-Methyl-3-pentene	15–8[d]	6.1
trans-2-Methyl-3-pentene		10.0
2-Methyl-4-pentene	—	1.5
2-Methyl-1-pentene	trace[e]	13.9
2-Methyl-2-pentene	43 ± 10[e]	31.3
cis-2-Methyl-3-pentene	25 ± 10[e]	3.5
trans-2-Methyl-3-pentene		5.7
2-Methyl-4-pentene	—	0.9
3-Methyl-1-pentene	—	0.7
cis-3-Methyl-2-pentene	32 ± 10[e]	16.2
trans-3-Methyl-2-pentene		24.4
2-Ethyl-1-butene	—	3.5
2,3-Dimethyl-1-butene	26.0[f]	36.8
2,3-Dimethyl-2-butene	74.0[f]	63.2

[a] From Koch and van Raay[127].

[b] Calculated[127] from thermodynamic data for the ideal gaseous state at 227°.

[c] Mole per cent in ideal gaseous state at 200°.

[d] Liquid volume per cent (20°) in equilibrium mixture obtained in gaseous state at 190°.

[e] Liquid volume per cent (20°) in mixture obtained in liquid state at 200°.

[f] Liquid volume per cent (20°) in mixture obtained in liquid state at 190°.

The experimental results on the dimethylbutenes provide an interesting comparison with those on the monomethylbutenes; for the three dimethylbutenes differ from the three monomethylbutenes only in having an extra methyl group on the number three carbon. The experimental equilibrium compositions reported in Table 49 illustrate two generalizations relating the structure and stability of olefins[60]. For olefins having the same carbon skeleton:

(1) one having a non-terminal double bond is more stable than one with a terminal double bond; and

(2) one having a chain branch at a double bonded carbon is more stable than one with the chain branch at a saturated carbon.

These generalizations are also supported by the extensive data on heats of hydrogenation[123].

Octenes. An apparent exception to the first of the above mentioned rules is provided by the two isomeric 2,4,4-trimethylpentenes. Either isomer, treated with silica gel at 25°, gave the same equilibrium mixture containing 80 per cent 2,4,4-trimethyl-1-pentene and 20 per cent 2,4,4-trimethyl-2-pentene[74]. Thermodynamic data are not available for comparison.

Cyclic Olefins. No studies of isomerization equilibria among cyclic olefins have been reported and thermodynamic data on these substances are sparse. However, a number of qualitative observations indicate that isomers having the double bond in the ring (*endo*) are much more stable than those having the double bond outside the ring (*exo*). Thus both methylenecyclopentane[142b, 273a] and methylenecyclohexane[142b, 273a, 296a] and certain of their homologs[296a] are converted by acids essentially quantitatively into 1-alkylcyclopentenes and 1-alkylcyclohexenes. Available thermochemical data indicate the conversion would be exothermic to the extent of 2–10 kcals[239a, 273a]. Isomers having an *exo* double bond not directly attached to a carbon ring also appear to be unstable with respect to those having an *endo* double bond. Thus both vinyl- and allyl-cyclopentane and -cyclohexane were converted largely to the isomeric 1-ethyl- and 1-propylcycloalkenes by passage over a chromia-alumina catalyst at 250°[142b].

Aromatic Hydrocarbon Isomerization Equilibria

Xylenes. Results of experiments in which equilibrium among the three xylenes appears to have been reached are summarized in Table 52. The experiments make use of a variety of catalysts and cover the temperature range 50 to 121°. The fact that the equilibrium composition does not change much over this temperature range indicates that the differences in heat contents of the three isomers are small. Values for these differences were computed for the ideal gaseous state with the aid of entropies determined calorimetrically and after conversion of selected values for the liquid-phase equilibrium composition at 50° to the vapor phase by use of vapor pressures and Raoult's Law[223]. Subsequently, the heats of combustion of the three xylenes were carefully determined[230] and these values were used to compute heats of isomerization[116]. A comparison of the calorimetric values with those based in part on experimental equilibrium constants is presented in

Table 53. The two sets of values agree within their combined estimated uncertainties; and xylene equilibrium compositions calculated wholly from calorimetric data (for example, *ortho* 20 ± 6, *meta* 58 ± 10, *para* 22 ± 8 in the liquid state at 50°)[271] approximate those observed experimentally, rather large uncertainties being admitted.

The xylene equilibrium composition obtained in the presence of a large excess of hydrogen fluoride depends markedly on the amount of boron fluoride simultaneously present[160]. When the boron fluoride content approaches or exceeds one mole per mole of xylenes, a large portion of the xylene is present as HF-BF_3-xylene complexes, which are soluble in anhydrous hydrogen fluoride. Then there are two equilibria: the isomerization equilibrium in the hydrocarbon phase and an equilibrium among the three HF-BF_3-xylene complexes in the acid layer. The interrelationships may be depicted as shown in Figure 17[160]. Now the *m*-xylene complex is much more stable than the other xylene complexes[162]; and therefore the *m*-xylene content in equilibrium in the acid phase is much higher than that in equilibrium in the hydrocarbon phase. With so much as three moles of boron fluoride and six moles of hydrogen fluoride per mole of xylene, 100 per cent *m*-xylene was obtained from *p*-xylene at 30°[160]. The results recorded in Table 52 were realized with comparatively small amounts of boron fluoride

TABLE 52. EXPERIMENTAL EQUILIBRIA AMONG THE XYLENES IN THE LIQUID STATE

Temp. (°C)	Catalyst	Total Xylenes[a]	Equilibrium, Mole %			Ref.
			ortho	*meta*	*para*	
50	$AlCl_3$-HCl	72–90	13–16	65–69	15–19	185
50	$AlBr_3$-HBr	80–85	12–13	71–72	16–17	223
82	HF-BF_3	98	15	64	22	160
100	"	83–91	19	60–61	20–21	160
121	"	91	18	60	22	160

[a] The isomerization is accompanied by disproportionation.

TABLE 53. HEATS OF ISOMERIZATION OF XYLENES IN THE GASEOUS STATE AT 50°

Reaction	$\Delta H°$, cal/mole	
	Exptl.[a]	Calorimetric[b]
m-xylene ⇌ *p*-xylene	460 ± 150	160 ± 270
m-xylene ⇌ *o*-xylene	950 ± 200	450 ± 280

[a] From Pitzer and Scott[223]. Based on experimental equilibrium composition and calorimetric entropies.

[b] Based on heats of combustion[160, 230].

(0.06 to 0.13 mole/mole xylene), where the effect of complex formation is negligible.

Xylenes-Ethylbenzene. Ethylbenzene was not formed in the isomerizations of xylenes with aluminum halides or hydrogen fluoride-boron fluoride described above, but was produced from xylenes over a silica-alumina catalyst at 515° (data in Table 23, page 112)[24]. The data indicate equilibrium was reached in Experiments 2 and 3, since a halving of the space velocity did not have much effect on product composition. An average equilibrium composition calculated from these data is compared in Table 54 with the equilibrium composition calculated from thermodynamic data. The p-xylene and ethylbenzene contents are in good agreement, but the observed m-xylene content is higher and the observed o-xylene content is lower than calculated.

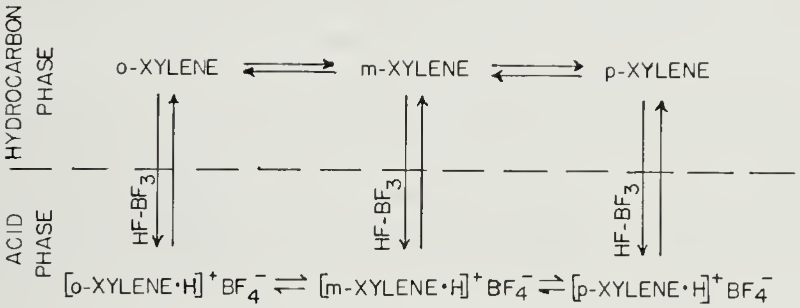


Figure 17. Equilibria among the xylenes in the presence of HF and BF_3. (McCaulay and Lien[160]).

Table 54. Equilibrium between Xylenes and Ethylbenzene at 515°

Equilibrium composition, mole %	Observed[a]	Calcd.[b]
m-Xylene	61	47
o-Xylene	8	22.5
p-Xylene	20	21.5
Ethylbenzene	11	9

[a] Boedeker and Erner[24]. Calculated from data in Table 23.

[b] Calculated[42] from data in Ref. 238.

Trimethylbenzenes. As with the xylenes, the equilibrium mixture obtained by isomerization of trimethylbenzenes in the presence of hydrogen fluoride was found to depend on the amount of boron fluoride present because of the formation of acid-soluble complexes. Here, the complex with mesitylene (1,3,5-trimethylbenzene) is most stable, being even more stable than the complex with m-xylene[162], so that with only one mole of boron fluoride per mole of trimethylbenzenes, 100 per cent conversion of pseudocumene (1,2,4-trimethylbenzene) to mesitylene (as the HF-BF_3 complex) was realized at 82°[160]. In order to determine the true percentage of mesitylene at isomerization equilibrium, several equilibrations with varying boron fluoride content were made and the mesitylene percentage at equilibrium was extrapolated to zero mole boron fluoride[160]. This gave 34 per cent mesitylene, 66 per cent pseudocumene for the equilibrium composition in the liquid state in the temperature range 82 to 121°. By means[42] of vapor pressures[238] and Raoult's Law, this becomes 37 per cent mesitylene, 63 per cent pseudocumene in the gaseous state (at 100°). Thermodynamic data[238] indicate the equilibrium mixture of trimethylbenzenes in the gaseous state at 100° would comprise 31 per cent mesitylene, 60 per cent pseudocumene, and 9 per cent hemimellitine (1,2,3-trimethylbenzene). The observed equilibrium ratio of mesitylene and pseudocumene is therefore in fair agreement with thermodynamic data; but no hemimellitine was detected among the products of isomerization of mesitylene or pseudocumene with HF-BF_3 at 82–121°[160]. Either the rate of interconversion of mesitylene and pseudocumene is very much faster than the rate of formation of hemimellitine, or hemimellitine is actually less stable than indicated by thermodynamic data.

Alkyne-Alkadiene Isomerization Equilibria

Propyne-Allene. Isomerization of either propyne or allene by means of Floridin[257] gave an equilibrium mixture comprising 61.5 per cent propyne and 38.5 per cent allene at 325°. Thermodynamic data[238] give 86.5 per cent propyne and 13.5 per cent allene for the equilibrium composition at 327°. It has been suggested that the experimental values are in error[67].

Pentynes-1,2-Pentadiene. Isomerization of 1-pentyne or 2-pentyne by means of alcoholic potassium hydroxide in sealed tubes at 175° gave equilibrium mixtures containing 1.3 per cent 1-pentyne, 95.2 per cent 2-pentyne, and 3.5 per cent 1,2-pentadiene[115]. A mixture having almost the same composition was obtained from 1,2-pentadiene under the same conditions. At 125°, an equilibrium mixture containing about 10.5 per cent 1-pentyne, 84.5 per cent 2-pentyne, and 5.0 per cent 1,2-pentadiene resulted from 2-pentyne. Equilibrium constants corresponding to these compositions at the two temperatures lead to unrealistic values for the heats and entropies of isomerization; and it may be that secondary equilibria were involved. Inasmuch as a mole ratio of potassium hydroxide to pentyne of about 0.3 was used, it may be that a large fraction of the 1-pentyne was present as the alkynide ion, $CH_3CH_2CH_2C{\equiv}C{:}^-$, at the lower temperature. The equilibrium composition observed at 175° is close to that calculated[42] (for the gaseous state) from thermodynamic data[238] (1.6 per cent 1-pentyne, 97 per cent 2-pentyne, and 1.4 per cent 1,2-pentadiene). *cis*- and *trans*-1,3-Pentadienes were not formed although thermodynamic data indicate they should constitute a large fraction of the equilibrium mixture (see pages 112–114).

1,3-Pentadienes. Both *cis-* and *trans*-1,3-pentadiene (piperylene) were converted to a mixture containing about 14 per cent *cis-* and 86 per cent *trans*-piperylene by refluxing with iodine[66] (about 45°). This result is at variance with thermodynamic data[238], which yield[42] 58.4 per cent *cis-* and 41.6 per cent *trans*-piperylene for the equilibrium composition in the ideal gaseous state at 27°.

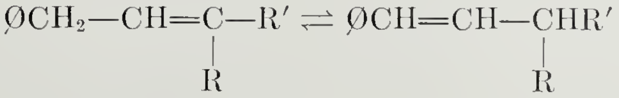
TABLE 55. TAUTOMERIC EQUILIBRIA IN PHENYLPROPENES AT 165°[a]

R	R′	$\phi CH_2—CH=\underset{\mid \atop R}{C}—R'$ Equil. (%)	$\phi CH=CH\underset{\mid \atop R}{C}HR'$ Equil. (%)	$-\Delta F$ kcal/mole
H	H	0	100	—
H	*tert*-Butyl	9	91	2.02
H	Isopropyl	11	89	1.83
H	Methyl	18	82	1.32
Methyl	Methyl	43	57	0.25

[a] From Bateman and Cunneen[12].

Miscellaneous Hydrocarbon Isomerization Equilibria

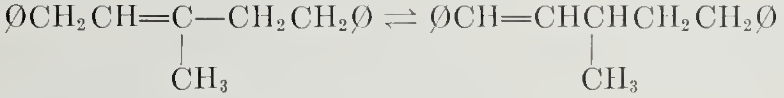
Phenylpropenes. The effect of various alkyl groups on the tautomeric equilibrium:



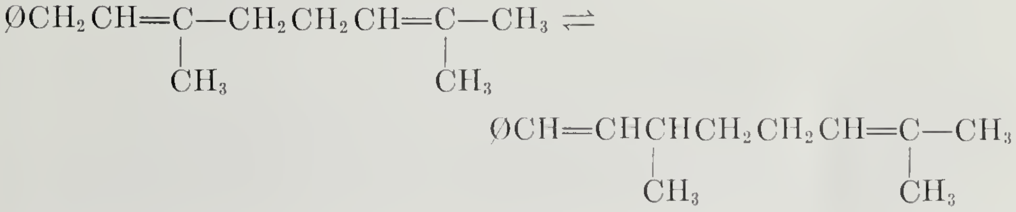
$$\phi CH_2—CH=\underset{\mid \atop R}{C}—R' \rightleftharpoons \phi CH=CH—\underset{\mid \atop R}{C}HR'$$

has been used as a measure of stabilization by hyperconjugative resonance[12]. Equilibrium was established by use of alkali in methyl alcohol at 165°. Results are shown in Table 55. It was concluded that hyperconjugation is an effective competing influence opposing the development of styryl conjugation[12].

The two tautomeric equilibria



$$\phi CH_2CH=\underset{\mid \atop CH_3}{C}—CH_2CH_2\phi \rightleftharpoons \phi CH=CH\underset{\mid \atop CH_3}{C}HCH_2CH_2\phi$$



$$\phi CH_2CH=\underset{\mid \atop CH_3}{C}—CH_2CH_2CH=\underset{\mid \atop CH_3}{C}—CH_3 \rightleftharpoons \phi CH=CH\underset{\mid \atop CH_3}{C}HCH_2CH_2CH=\underset{\mid \atop CH_3}{C}—CH_3$$

were compared in order to determine whether there is any stabilizing resonance between double bonds separated by two methylene groups, as was proposed to explain certain structural peculiarities in 1,5-dienes. The equilibrium mixture, obtained by the use of methyl alcoholic alkali at 165°, in each case contained 36 per cent of the non-conjugated isomer. Hence it was concluded that such stabilizing resonance is absent[13].

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CHAPTER 3

MECHANISMS OF POLYMER FORMATION AND DECOMPOSITION

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INTRODUCTION

There are two principal types of reactions involving large molecules. The one leads to their formation, the other to their breakdown. The first class encompasses polymerization and polycondensation processes. We shall deal only with the former. As a part of general developments in the field of high polymers during the last decades, intensive research has been carried out on the mechanism and kinetics of the chain reactions involved in polymerization. The results of these investigations will be outlined. We are concerned with the formation of long chains containing hundreds or thousands of units. Hence the propagation step will be comparatively rapid and the initial production of an active species, radical or ion, comparatively slow and sensitive to the reaction conditions. Therefore, after presenting the kinetics and results on the magnitudes of the rate constants for the subsequent steps, we turn to a consideration of the various mechanisms by which the reaction is started, that is, the initiation of the active species. Two modes of initiation occur, free radical and ion formation, respectively. Production of these species is achieved by initiators, that is, substances which become chemically combined with the final reaction product, or catalysts in the proper sense of the word. Radicals can, of course, also be produced by radiation.

Copolymerization has been amply treated previously both by the present authors and by others.* It is not included here.

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* "Copolymerization," T. Alfrey, Jr., John J. Bohrer, and H. Mark, Interscience Publishers, N. Y., 1952; American Chemical Society Monograph No. 115, Edited by R. N. Boundy and R. F. Boyer, Reinhold Publishing Corp., 1952, Chapter by R. Simha and L. A. Wall; F. R. Mayo and C. Walling, *Chemical Reviews*, **46**, 191 (1950).

In the second part we discuss breadkown processes. Consistent, in a sense, with the omission of polycondensation, hydrolytic and enzymatic cleavage reactions are not treated. In recent years, significant advances have been made in the elucidation of the mechanism and kinetic theory of those degradation reactions which proceed through free radicals. These include thermal as well as radiative initiation and both are reviewed.

In recent years several monographs dealing with the same general subject matter have appeared.† In part they are more extensive and detailed than we can be here, and in part, it will be noted, they have an emphasis somewhat different from ours.

FREE RADICAL POLYMERIZATION

Over-All Kinetics of Chain Polymerization Reactions

Addition polymerizations are chain reactions involving as intermediates long chain radicals or ions. In this chapter we are concerned mainly with the rate of production of these intermediates, or, in other words, in the initiation which is the crucial step. Our chapter has been essentially subdivided according to the method of production of the active centers. Nevertheless we must devote attention also to the other elementary acts which propagate and terminate the intermediates. The interplay between these determines the over-all rate of polymerization, the molecular weight distribution of the polymer, and the lifetime of growing radicals. A measurement of these quantities in turn yields the absolute values of the rate constants, including the rate of initiation.

The simplest mechanism which may be considered includes an initiation, propagation, and termination. The latter may occur by interaction of two long chain radicals. Whether this consists of a combination or disproportionation depends on the system. Another alternative is that the initial active center participates in the termination. For example:

$$\begin{aligned} &\text{Stable molecule} \xrightarrow{I(M,\ C,\ h\nu)} R_1 \\ &R_i + M \xrightarrow{k_2} R_{i+1} \qquad\qquad (1) \\ &R_i + R_k \xrightarrow{k_4} P_{i+k} \quad \text{or} \quad P_i + P_k \end{aligned}$$

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† American Chemical Society Monograph No. 115, Edited by R. N. Boundy and R. F. Boyer, Reinhold Publishing Corp., 1952, Chapter by L. C. Rubens and R. F. Boyer; "Polymerisationskinetik," L. Küchler, Springer-Verlag, Berlin (1951); "Mechanism of Polymer Reactions," Vol. III, G. M. Burnett, Interscience Publishers, N. Y., 1954; "Degradation of Vinyl Polymers," H. H. G. Jellinek, Academic Press, Inc., New York, 1955; "Chemistry of High Polymer Degradation Processes," Interscience Publishers, Inc., New York, 1956; "Free Radicals in Solution," C. Walling, John Wiley & Sons, Inc., New York, 1957.

R_1 is the initial active center, R_i a growing radical with i units in the chain and P_i the corresponding stable polymer. M is the monomer, C the catalyst, $h\nu$ a photon, and $I(M, C, h\nu)$ the initiation constant which in the most general case will be a function of the monomer, catalyst concentration, or light intensity. For instance, in a thermal polymerization $I(M, C) \approx k_1M^2$, whereas in the presence of peroxide, when centers are started by its decomposition, $I = k_1C$, provided fragments do not recombine. The assumption is implicit in Eq. (1) that the rate constants do not depend on chain length.

It is customary to introduce the assumption of a steady state in respect to each species of intermediates. This is justified if the mean lifetime of a growing radical λ is much shorter than the life of the reaction, a condition which is fulfilled in all but exceptional cases of interest, at least at moderate conversions. This introduces a considerable simplification by transforming the differential equations for the R_i into difference equations. For our purposes it suffices to consider only the total radical concentration $R = \sum R_i$. The individual R_i's must be calculated in order to obtain the molecular weight distribution and composition fluctuations in the case of copolymers[1, 2, 3]. From Eq. (1) the following is derived:

$$\begin{aligned} \frac{d \sum R_i}{dt} &= I - k_4(\sum R_i)^2 = 0 \\ \frac{-dM}{dt} &= I(M) + k_2(\sum R_i)M \end{aligned} \tag{1a}$$

In a catalyzed polymerization the term $I(M)$ does not appear in the second equation. In any case, it is negligible under conditions which lead to the formation of long chains. Thus the over-all rate of reaction becomes:

$$-\frac{1}{M}\frac{dM}{dt} = k_2\left(\frac{I}{k_4}\right)^{1/2} \tag{2}$$

where the factor in the parentheses represents the steady state radical concentration R. It is noted that the square root arises from the mutual termination of radicals. The number average degree of polymerization (D.P.), $\bar{P}_n$, can be found without explicit knowledge of the distribution. The loss of monomer per unit time due to chains of length i equals the rate of production of active centers, I, times the fractional number of monomer units combined in chains of length i, iP_i. Thus, for the total loss:

$$\frac{-dM}{dt} = I \sum iP_i = I\bar{P}_n \tag{3}$$

where the left-hand side is given by Eq. (2). Thus a simultaneous determination of the over-all rate and the osmotic molecular weight of the polymer formed at low conversion gives I.

We can now formulate the condition for the establishment of a steady state, viz. $\lambda(\text{radical}) \ll \lambda(\text{reaction})$, in terms of the elementary rate constants. The mean lifetime of a state or species is defined as the reciprocal of the rate of disappearance per unit concentration. Hence

$$\left(\frac{-1}{M}\cdot\frac{dM}{dt}\right)^{-1} \gg \frac{1}{k_4R} \qquad \text{or} \qquad \frac{k_2}{k_4} \ll 1$$

This does not contradict the existence of a large D.P. or kinetic chain length k_2MR/k_4R^2, since R is very small. The simple mechanism of Eq. (1) establishes the principal features of the polymerization kinetics. However, a complete description requires the consideration of at least three points, namely, the mechanism of initiation, the mechanism of termination, and the effect of chain transfer. The first is to be emphasized in this chapter and we mention only the following here. In the peroxide catalyzed reaction, the crux of the matter is the decomposition of the peroxide molecule, as described in detail on pages 208–217. Since $I = k_1C$, Eq. (2) becomes:

$$\frac{-dM}{dt} = k_2\left(\frac{k_1}{k_4}\right)^{1/2} C^{1/2}M$$

Actually one finds, particularly at low temperatures, that this expression must be multiplied by a factor

$$\left(\frac{KM}{1 + KM}\right)^{1/2}$$

where the parameter K increases with an increase in temperature[4, 5]. This has been interpreted by Schulz and Husemann as an equilibrium between a complex of catalyst and monomer yielding upon rearrangement an R_1 radical, and the dissociated species. K then represents the equilibrium constant. Matheson[6] has shown that an alternative and simpler picture leads to the same result. It is based on the cage model of a liquid[7]. Two reactants remain trapped for some time in the cage before diffusing apart. This is sufficient to produce a reaction if its activation energy is small in comparison to that for diffusion. In our problem this picture leads to a finite probability of recombination of two catalyst fragments. This process competes with the addition to a neighboring monomer which causes the formation of R_1. The quantity KM appears thus as the ratio between the latter and the former probability and should increase with temperature. The treatment of such reactions has recently been refined[8]. The observed dependence of initiation rates on the monomer concentration has been recently reviewed on the basis of these mechanisms[8a].

There is an additional elementary mechanism which plays an important role, particularly in solution polymerization, namely, transfer between an active polymer center and a solvent or monomer molecule. What happens is the shift of a labile atom or group such as a Cl-atom from a solvent or a hydrogen from a monomer to a growing radical. The catalyst can also participate in a transfer process. This terminates the life of the particular radical but does not affect the total radical concentration R. Hence the rate of reaction remains the same as for vanishing transfer probability, provided the radical created by transfer has the same activity as the original one. However, the molecular weight distribution is changed and the average degree of polymerization reduced, since the relative probability of propagation is smaller. These concepts were used by Cuthbertson, Gee, and Rideal[9] in their discussion of the system vinyl acetate-toluene and by Kamenskaya and Medvedev[10] for vinyl acetate-benzene. Several authors[11, 12, 13] developed quantitative expressions which correspond to the additional steps:

$$\begin{aligned} R_i + M &\xrightarrow{k_3} P_i + R_1 \\ R_i + S &\xrightarrow{k_{3s}} P_i + R_s \end{aligned} \tag{1'}$$

where R_s is a solvent radical, S is a solvent molecule, and no distinction has been made between an active center produced by initiation and by transfer with monomer. Previously we had for $\bar{P}_n$ from Eq. (3) and Eq. (2)

$$\bar{P}_n = \frac{k_2 M}{(k_4 I)^{1/2}} = \frac{k_2 M R}{k_4 R^2} = \frac{\text{rate of propagation}}{\text{rate of termination}}$$

Equation (3) remains valid if $\bar{P}_n$ is interpreted as the number average length of a kinetic chain. For the osmotic degree of polymerization, however, one now has:

$$\bar{P}_n(S, M) = \frac{k_2 M R}{k_3 R M + k_{3s} R S + k_4 R^2}$$

Where $S = 0$, this reduces to $\bar{P}_n(M)$, the chain length for transfer with monomer, provided the rate constants do not change with solvent composition and provided we neglect the propagation of solvent radicals by means of monomer. The solvent effect is given by the equation:

$$\frac{1}{\bar{P}_n(S, M)} - \frac{1}{\bar{P}_n(M)} = \frac{k_{3s}}{k_2} \frac{S}{M} \tag{4}$$

and shows clearly the competition of monomer and solvent for the radical. In this derivation it is assumed that all the pertinent ratios between the rate constants k_2, k_{3s} and k_4 are independent of molecular weight. In a study of the polymerization of styrene in CCl_4, Mayo[14] was able to show that this is actually the case. A marked increase in the ratio k_{3s}/k_2 from $<6 \times 10^{-4}$ to 7×10^{-3} between a chain length of one and three and subsequent constancy at 1.15×10^{-2} at 76°C were observed. It must be added that $P_n(M)$ is independent of M in Eq. (4) only if the radical concentration is proportional to M. This is fulfilled in thermal polymerization.

TABLE 1. TRANSFER CONSTANTS $k_{3s}/k_2 \times 10^4$ AND ACTIVATION ENERGIES $E_{3s} - E_2$ FOR VARIOUS TEMPERATURES, SOLVENTS AND STYRENE MONOMER

Solvent	80°C	100°C	132°C	E_{3s}-E_2, kcal mole^{-1}	Ref.
Cyclohexane	—	0.31	0.81	9.0	16
Benzene	0.15	0.40	—	12.6	15
	—	0.31	0.81	9.0	16
Chlorobenzene	—	0.54	—	—	15
Toluene	0.41	1.01	—	11.7	15
	—	0.53	1.12	7.0	16
Ethyl benzene	1.40	2.42	—	11.7	15
	—	1.38	2.31	4.8	16
1,2 Dichloroethane	—	3.84	—	—	15
	1.14	3.76		14.7	20
sym-Tetrachloroethane	—	17.9	—	—	15
Carbon tetrachloride	191	270	—	4.2	20

TABLE 2. TRANSFER CONSTANTS $k_3/k_2 \times 10^4$ AND ACTIVATION ENERGIES $E_3 - E_2$ FOR VARIOUS MONOMERS[18, 19, 20]

Monomer	−15°C	0°C	25°C	$E_3 - E_2$ kcal mole^{-1}
Styrene	—	0.11	0.36	7.7
p-Methoxystyrene	—	0.20	—	—
Methyl methacrylate	—	0.15	—	—
Vinyl acetate	0.37	0.50	—	2.9

Mayo[11, 14] evaluated data on the thermal polymerization of styrene in several solvents[15, 16]. The linear relationship predicted by Eq. (4) is confirmed. In an extensive study of the absolute rate constants in thermal and photopolymerization, Bamford and Dewar considered also the transfer with monomer[17]. A more detailed discussion of the results of these authors on styrene and methyl methacrylate and of Axford[18] and Dixon-Lewis[19] on *p*-methoxystyrene and vinyl acetate will be deferred until later. At the temperatures in question transfer is by no means negligible, even in bulk polymerization. This is shown in Table 2 which gives transfer constants k_3/k_2. Furthermore, having determined k_2, and using Eq. (4), we can find the absolute value of k_{3s}. This was carried through for several temperatures and a series of solvents, in part identical with those of References 15 and 16, by Bamford and Dewar[20] by recasting Eq. (4) in terms of intrinsic viscosities, determining these and establishing the relation between $[\eta]$ and $\bar{P}_n$. Table 1 contains the evaluation of experimental data in Reference 16 by Mayo[11]. Bamford and Dewar[20] corrected the data in Reference 15 for the fact that an invalid $[\eta]$-M relation had been used. Some of their own experimental data are also included.

It is seen that the magnitude of the transfer constant for styrene is similar to that of its solvent analogs. At 100°C, the value for styrene is 6.1×10^{-4}. In conjunction with the values for the initiation constant derived, one comes to the conclusion that in pure styrene at 25°C, for instance, approximately eleven transfer acts occur during the life of a kinetic chain. In a few cases, notably with allyl acetate monomer, transfer can result in relatively stable radicals incapable of further growth[21]. Allylic resonance in the α-acetoxyallyl radical produced by this transfer process is the cause of the stability. This step then acts as an apparent unimolecular termination and is often referred to as degradative chain transfer. Substitution with deuterium at the α-position in this monomer led to an increase in rate of polymerization and an increase in the molecular weight compatible with a degradative transfer process one-third as fast as in the undeuterated monomer[21], in agreement with the anticipated deuterium isotope effect. This is direct evidence for the mechanism of the termination process.

TABLE 3. TRANSFER CONSTANTS $k_{3s}/k_2 \times 10^5$ OF HYDROCARBON WITH STYRENE[22]

Solvent	60°C	100°C
Benzene	0.18	1.84
Toluene	1.25	6.45
Ethyl benzene	6.7	16.2
Isopropyl benzene	8.2	20.0
tert-Butyl benzene	0.6	5.5
Diphenylmethane	23	42
Triphenylmethane	35	80
Fluorene	750	1240
Pentaphenylethane	2×10^5	—

Table 3 from the work of Gregg and Mayo[22] shows the effect of structural variations on the ability of the styrene radical to abstract H-atoms from a molecule. Briefly, increasing substitution favors the process by weakening the bond between C and the benzyl hydrogen and increasing the stability of the radical left behind. Transfer constants for several vinyl polymers in a large number of solvents have been measured and compared by Sen[22a].

The way described is not the only one in which a solvent can affect vinyl polymerization. Recently Stockmayer and Peebles[23] found that the polymerization of vinyl acetate in benzene can apparently not be described in terms of the above transfer mechanism. The retardation of the rate characteristic of an aromatic solvent is not accompanied by a corresponding decrease in molecular weight. It is suggested that a polymer radical adds to benzene, producing a radical of lower activity. Determinations with radioactive benzene indicate about 20 benzene residues in a chain of degree of polymerization 700. Mayo[24] found that the polymerization of styrene in bromobenzene also shows an unexpected behavior giving, however, fewer solvent fragments in the chain than expected from ordinary transfer.

So far we have been concerned with a radical attack on a monomer or solvent molecule. Active radicals such as those derived from polyvinyl acetate[25] or polyethylene[26] are capable, at high temperatures and conversions, of attacking stable polymer molecules which thereby become reactivated. This leads to the formation of branched structures and profound effects on the molecular weight distribution[26, 27], solution properties[26], and mechanical behavior[26]. This phenomenon of branched polymer formation can be altered in several ways. It has been demonstrated that polyvinyl acetate which is normally highly branched becomes predominantly linear when polymerized at −30°C[28]. Another feasible method for reducing polymer branching is the deuteration of possible polymer transfer sites[29]. One method for estimating chain transfer by polymer utilizes model analogs of low molecular weight. If in a homologous series the parameters turn out to vary systematically with chain length, extrapolation to infinite M becomes feasible. The chain transfer constant for methyl acrylate was estimated to 5×10^{-5} in this manner[29a].

Such interactions between growing radicals and dead chains can also become important in instances in which polymer precipitates out of the mixture. This is the case in the bulk polymerization of acrylonitrile[30, 42, 43], vinyl, and vinylidene chloride[31]. In these cases the rate of reaction is accelerated beyond the values under homogeneous conditions. Similar effects can be produced by the use of nonsolvents[32]. Finally, the transfer between polymer radical and catalyst is another possible step[33].

We have left open in Eq. (1) the exact nature of the interaction between two radicals terminating each other. Several investigations have been undertaken in an attempt to answer the question whether it consists of a disproportionation or combination[33-39]. These are based on a determination of the catalyst efficiency in starting chains, of retarder effects, and the number of catalyst residues per chain produced by various means, including the use of radioactive initiators[36, 37]. There seems to be agreement that combination is at least the preferred step in styrene. The situation is more doubtful in methyl methacrylate.

If both disproportionation and combination are operative, earlier expressions converting $\bar{P}_n$ and dM/dt are modified. For example, we now have

$$\bar{P}_n(M) = \frac{k_2 MR}{k_3 RM + (k_{4d} + k_{4c}/2)R^2}$$

However, the first part of Eq. (1a) remains unchanged, with k_4 simply replaced by $k_{4d} + k_{4c}$. As a consequence, an uncertainty arises when number average D.P.'s are used in conjunction with other measured quantities to determine absolute rate constants (see pp. 192–195). Usually it has been assumed in such cases that either k_{4d} or $k_{4c} = 0$.

Another unsettled problem has to do with the nature of the radical produced in photo or thermal polymerization. Diradicals may be formed, whereas conventional catalysts, such as benzoyl peroxide or 2-azo-bis-isobutyronitrile yield monoradicals. At low radical concentrations and moderate chain lengths self-termination by ring formation of biradicals would be favored over mutual termination of styrene chains[40]. Furthermore, these radicals would be unable to propagate very far and would not reach a large size before self-termination occurs[41]. In conformity with this, diradicals are apparently not observed in thermally activated styrene polymerization[51]. Evidence has been presented that the photopolymerization of styrene proceeds through monoradicals[35].

Regardless of details, we have so far considered cases in which termination of the kinetic chain occurs by interaction of two radicals. Although this is the prevalent mechanism, there are exceptions. For instance, when the reaction occurs under heterogeneous conditions, as mentioned above, the termination of a "buried" radical may become effectively of first order[43]. However, the concentration of such radicals has been found to be only about 1 per cent of the total, at least in photopolymerized acrylonitrile at 25°C[44].

Reactions under heterogeneous conditions and bulk polymerizations at higher conversions can lead to kinetic complications, although the reasons for these need not be the same in the two cases. It has been observed, first in methyl methacrylate, and subsequently in other vinyl polymers, particularly methyl acrylate, that an acceleration in the rate occurs simultaneously with an increase in average molecular weight above conversions which vary with the nature of the polymer[45]. This effect implies a decrease of the termination relative to the propagation constant. It has been variously ascribed to a reduction in the accessibility of radical ends to each other produced by precipitation or formation of a cross-linked structure and/or to a reduction in mobility caused by the high viscosity of the medium. A decrease in the magnitudes of the two constants has been actually observed for styrene, methyl methacrylate, methyl acrylate, and decamethylene glycol dimethacrylate[46-48]. These variations naturally affect the molecular weight distribution also. It remains to be seen whether multiple peaks observed in sedimentation diagrams[49] can arise from the gel effect. The requisite kinetic equations can be worked out, assuming reasonable empirical expressions for the variation of the rate parameters with conversion and size of the reacting radical[50]. However, no numerical results have been obtained as yet. Vaughan[50a] and Robertson[50b] have treated the change from normal to diffusion activated reaction in terms of relations worked out by Rabinowitch[50c] for small molecules. Burnett and Loan[50d] considered the trapping of radicals and the increase in their concentration above the steady state level when the conversion reaches a critical value. By making certain ad hoc assumptions, they describe the course of the polymerization in methyl methacrylate, including the sharp decrease observed beyond a second critical conversion of the order of 70 per cent.

The simple scheme (1a) leads to proportionality of the rate $-dM/dt$ with the square root of the initiation rate. Deviations in radiation induced polymerization in dilute solution have been observed[52]. A general kinetic scheme containing this and other results as special cases has been considered recently[53]. Equation (1a) is extended by making a distinction between the propagation rate k_2' of the primary radicals R_1 produced in the initiation, and k_2 referring to the growth of the first and higher, radical adducts. This introduces additional possibilities k_4' and k_4'' for mutual termination of primary radicals and primary with long chain radicals, respectively. The equations replacing (1a) and (2) are readily derived. These earlier relations are recovered when

$$I \ll (k_2'M)^2/4k_4'^2$$

If, on the other hand, the opposite inequality holds and

$$k_4''\mathrm{R}_1/4k_4 \gg k_2'M$$

a condition which can be approached in dilute solution,

$$-dM/dt = (k_2k_2'/k_4'')M^2 \tag{2a}$$

and the rate is independent of I. Thus, with increasing rate of initiation, the dependence on I will become gradually weaker than according to the one-half power. The actual magnitudes corresponding to the above inequalities depend on temperature, monomer concentration, and nature of the monomer which affects primarily the valueof k_2'.

Photo and Thermal Initiation; Determination of Absolute Rate Constants

There are two purposes of studying the rate of photoinduced reactions. The obvious one of determining the accelerating effect and the other to obtain in conjunction with thermally or otherwise induced free radical polymerizations the absolute magnitudes of the elementary rate constants, I, k_2, and k_4. The kinetic analysis (pp. 192–195) provided two relations between the k's from a measurement of the number average molecular weight and the over-all rate of reaction. If transfer is negligible, the ratio between the two quantities gives the rate of initiation. Otherwise the kinetic chain length must be known. Alternatively, comparative reaction rates may be utilized to obtain relative initiation rates. Finally, retarders may be used, provided the ratio between retarder concentration and radical concentration, that is the mechanism of retardation, is known. In photo-reactions the rate may be measured for varying light intensities. Other procedures are discussed below. In the most general case of practical validity we have the following information available:

Quantity	Method
I	Inhibitors or retarders. Comparison with catalyst initiated rate. Variation of rate with light intensity.
$k_3RM + k_{3s}RS + \underbrace{k_4R^2}_{\equiv I}$	Measurement of $-dM/dt$ and $\bar{P}_n$.
$k_2(I/k_4)^{1/2}$	$-dM/dt$
k_{3s}/k_2	Variation of $\bar{P}_n$ with S.

Again, if radicals can terminate both by disproportionation and combination, the second line is replaced by

$$k_3RM + k_{3s}RS + [k_{4d} + (k_{4c}/2)]I/(k_{4d} + k_{4c})$$

The determination of I as indicated above is not always satisfactory and another procedure is discussed below. It makes use of a fifth relation which is needed in any case to complete the picture. This might consist in a determination of R. However, the concentration is too low, of the order of $10^{-10} - 10^{-8}$ mole l^{-1}, to detect the radicals directly, even by magnetic means. A feasible way is to measure the mean life time $\lambda = 1/k_4R$ of the radicals. If λ is looked upon as a "relaxation" time, three possible methods of determination can be visualized: (a) The effect of a periodic "field" of varying frequency on the rate of reaction; (b) a study of the rate of decay after removal of the field; and (c) a measurement of the rate of assumption of a steady state after application of the field. The field is supplied by an activator of free radicals, that is, in practice, radiation for procedures (a) and (b). Its intensity is varied either in space, by partial illumination of the reaction vessel or in time by the device of a rotating disk with alternatingly cut out sectors in front of the light source[54]. The theory of the latter procedure is simpler. (b) involves the photochemical after effect and (c) an analysis of the induction period.

The theory of the rotating sector was worked out by Briers, Chapman, and Walters[55] and applied first to the polymerization of gaseous methyl methacrylate by Melville[56]. The frequency of the field is determined by the sector width and the speed of rotation. As the latter decreases, the length of a dark period increases, the rate of reaction falls off and somewhere in between the effect of a relaxation time becomes apparent. The limiting values are readily obtained by considering that the rate of reaction is proportional to $I^{1/2}$, where I is the intensity of the radiation, provided the radicals terminate each other. This must be established by experiment. If the duration of a dark period is small in comparison with λ, then, on the average, no active centers are destroyed. The only effect of the sector is a reduction of the total intensity obtained in steady illumination by a factor $1/(q + 1)$, where q represents the ratio between a dark and light period and is determined by the sector width. Hence the rate is decreased by a factor $(q + 1)^{-1/2}$. If, on the other hand, the disk rotates very slowly, all centers die off and this is equivalent to a steady illumination of equal intensity, but only for a fraction $1/(q + 1)$ of the time. The number of radicals produced and hence the rate are reduced by a factor $1/(q + 1)$. Since the theory of the function of rate *vs.* sector speed is often not discussed in monographs on polymerization[57], it will be summarized here. Introducing the dimensionless quantities $y = R/R_s$ and $\tau = t/\lambda$, where R_s is the value in steady illumination, one has:

$$\begin{array}{lll} \text{Light:} & \tau_1 \leqq \tau \leqq \tau_2\,, & dy/d\tau = 1 - y^2 \\ & y_1 \leqq y \leqq y_2 & \\ \text{Dark:} & \tau_2 \leqq \tau \leqq \tau_3\,, & dy/d\tau = -y^2 \\ & y_2 \leqq y \leqq y_3 & \end{array} \tag{5}$$

A steady state will be reached between dark and light periods, such that $y_1 = y_3$. Considering that $\tau_3 - \tau_2 = q(\tau_2 - \tau_1)$, y_2 and y_1 are related by virtue of Eq. (5):

$$\ln \frac{1 + y_2}{1 - y_1} + \frac{2}{q}\frac{1}{y_2} = \ln \frac{1 + y_1}{1 - y_1} + \frac{2}{q}\frac{1}{y_1} \tag{6}$$

τ_2 and τ_1 in turn, are connected by the equation following from (5)

$$\begin{array}{llll} \text{Light period:} & y = tgh\tau, \text{ for } \tau = 0, & y = 0 & \\ \text{Dark period:} & y = y_2/(1 + \tau y_2), & \tau = 0, & y = y_2\,. \end{array} \tag{6a}$$

What is actually measured, is the radical concentration averaged over a dark and light period, thus:

$$\bar{y}(q + 1)(\tau_2 - \tau_1) = \tau_2 - \tau_1 - \ln \frac{1 + y_2}{1 + y_1} + \ln [1 + qy_2(\tau_2 - \tau_1)] \quad (7)$$

For $\tau_2 - \tau_1 \to \infty$, $\bar{y} \to 1/(q + 1)$, as is expected. For

$$\tau_2 - \tau_1 \to 0, \qquad y_2 = y_1 = y_3 .$$

Hence $\bar{y}$ is constant $= y_2$. This condition is fulfilled at the minimum of the function represented by Eq. (6), that is for $y_2 = (q + 1)^{-1/2}$, in conformity with the intuitive deduction.

A plot of $\bar{y}(q + 1)^{1/2}$ as a function of $\tau_2 - \tau_1$ with the aid of the auxiliary conditions (6) and (6a) for the y_1 and τ_1 shows the sigmoid shape characteristic of relaxation phenomena which is the more pronounced, the larger q. As is usual in fundamental investigations of this kind, one operates at low conversions, M is approximately constant and the rate is proportional to R. Thus $\bar{y}$ becomes identical with the ratio:

$$\frac{\text{Rate of reaction at arbitrary sector speed}}{\text{Rate of reaction at infinitely rapid sector speed}}$$

The abscissas, and hence the experimental and theoretical plots, can be made to coincide by the choice of the proper time scale, which determines λ. Or, characteristic points, such as the mid-points of the two curves, may be used. In this manner Melville obtained for the gaseous polymerization of methyl methacrylate[56] $\lambda = 4 \times 10^{-3}$ sec.

It has been assumed so far that the light intensity and consequently the radical concentration are constant throughout the reaction vessel. The effect of a finite absorption coefficient has been considered[58, 59]. By using simultaneous illumination from two opposing sides and studying the deviations from additivity in the rates, the amount of overlap of the two irradiated regions and the extent of absorption can be estimated. In the experiments with methyl methacrylate and styrene discussed later, it turns out that the whole volume was available for the reaction under the experimental conditions used. In vinyl acetate, on the other hand, only about one-fourth of the reaction volume was effectively utilized and the rate of termination has therefore only one-fourth of the value obtained without the correction[68]. The error introduced by the assumption of a rectangular light pulse has been shown to be unimportant[59]. So far the influence of radical diffusion and convection due to temperature differences has been recognized but not treated.

Bamford and Dewar[17] devised a procedure based on viscosity which allows the use of small conversions. Furthermore, their kinetic scheme includes transfer with the monomer which they showed to be not negligible at low temperatures. A necessary requirement is a knowledge of the relation between molecular weight and intrinsic viscosity in the polymerizing system. This depends somewhat on whether monoradicals formed by catalyst fragments and transfer or diradicals produced by thermal or photoinitiation are involved. Both kinds are considered in the kinetic analysis and thus the rate of increase of viscosity with time as a function of light intensity is the first quantity to be evaluated. The number average molecular weight of the thermally prepared polymer provides a further relation. A fourth results from an analysis of the photo-after effect, which may be expressed as $\Delta\eta_I^t$, where η is the specific viscosity of a dilute solution. It represents the difference between η actually observed at a time t and that calculated on the assumption that the rate adapts itself to the thermal value instantaneously after cutting off the light source. Thus, if the sample is irradiated for a period t_1, then the total increase $\delta\eta$ in viscosity at a time $t_1 + t_2$ is:

$$\delta\eta = (d\eta/dt)t_{1_{\text{photo}}} + (d\eta/dt)t_{2_{\text{thermal}}} + \Delta\eta_I^{t_2} - \Delta'\eta_I^{t_1}$$

where $\Delta\eta_I^t$ represents the "pre-effect," due to the time lag in reaching the stationary photo rate. By plotting $\delta\eta - (d\eta/dt)_{\text{thermal}}t_2$ as a function of t_1, the necessary relations are obtained. For the analytical expressions the reader is referred to the original literature[17].

The requisite additional relation can also be derived from a study of the induction period. Integration of Eq. (1a) (p. 193) gives without the steady state assumption, provided that I can be regarded as constant:

$$R = (I/k_4)^{1/2}[1 - (M/M_0)^{2k_4/k_2}]^{1/2}$$

where M_0 is the initial monomer concentration. From the geometry of the $M - t$ curve at very low conversion, the ratio k_4/k_2 can be found in principle. In the case of vinyl acetate[60], the natural induction period was found to be too low, that is k_4/k_2 was too large, to obtain more than lower limits for k_2 and k_4. More recently, the problem was reconsidered by Burnett[61], using an adaptation of a dilatometer developed by Schulz and Harborth[62]. For $M/M_0 \approx 1$ and $t \gg \lambda$ it can be shown by integration of the second part of Eq. (1a) with the aid of the above expression for R, that the plot of $1 - M/M_0$ *vs.* t yields a straight line with a slope $k_2/(k_4\lambda)$ and an intercept $\lambda \ln 2$ on the t-axis. In the photopolymerization of styrene at 25°C, for instance, the necessary extrapolation involves accurate determinations down to conversions of 10^{-2} per cent. It is estimated[61] that the temperature rise due to the heat of polymerization causes an error of 20 per cent in the life time and probably an error of 100 per cent in the absolute rates.

Another very sensitive method for the required low degrees of conversion involves the change in dielectric constant with polymerization, which arises mainly from the heat of reaction[63]. Application to several polymers investigated also by other means showed reasonable agreement for the ratios k_2/k_4. A refractomatic procedure in which the reaction is carried out in an interferometer has been developed[64].

Table 4 summarizes the results of absolute rate studies and includes values for I in thermal polymerization. There is a relatively wide spread among several of these values obtained by the same or different methods. This is due to a number of experimental reasons, as indicated before.

Initiation by Peroxide Type Molecules

The decomposition of chemical compounds is the most frequently used and most convenient source of free-radicals for the initiation of polymerization. The most common of these are organic peroxides[76]; more recently azonitriles have also come into prominence. The crucial quantity is the rate of decomposition of the accelerator molecule. In the following we discuss the effects of temperature, environment and molecular structure on this quantity.

Early work[77] on benzoyl peroxide showed the products of decomposition to be carbon dioxide, diphenyl, phenyl benzoate and some benzene. In solution, reaction with the solvent occurs producing benzoic acid. Although certain peroxides may, under special conditions, decompose via an ionic mechanism, it is generally accepted that the thermal or photo decomposition in a wide variety of solvents occurs through free radical mechanism. Studies involving the Gomberg type free radicals and the gas phase detection of radicals have lead to the general acceptance of free radical intermediates in these and similar decompositions. The action of known inhibitors, and known free radicals, and the fact that peroxides do induce polymerization of ethylenic derivatives all support such a mechanism. The various products are also readily explained on this basis.

The initial step in this mechanism is the splitting of the peroxide link which has been estimated by various methods to have a bond strength of from 36 to 65 kcals[78]. Most of the kinetic data point to a value of 30 to 40 kcal. The subsequent reactions of the benzoyloxy radical, in the case of benzoyl peroxide, consist of either a unimolecular split to carbon dioxide and a phenyl radical and a coupling of radicals to give diphenyl and phenyl benzoate or an attack on the original peroxide by the phenyl radical to produce phenyl benzoate and benzoyloxy radical (induced decomposition). The question of the nature of the radicals from benzoyl peroxide, and other catalysts which become the ends of the polymer chains has been investigated with the use of radioactive catalysts labeled in specific positions[78a]. Essentially all initiating radicals are benzoyloxy radicals when pure styrene is polymerized with benzoyl peroxide at 60°C. As the concentration of monomer in benzene decreases relatively fewer benzoyloxy radicals

TABLE 4. ABSOLUTE RATE CONSTANTS†

Monomer	A_1 $\text{sec}^{-1}\ \text{mole}^{-1}\ \text{l}$	E_1 kcal mole^{-1}	A_2 $\text{sec}^{-1}\ \text{mole}^{-1}\ \text{l}$	E_2 kcal mole^{-1}	A_3 $\text{sec}^{-1}\ \text{mole}^{-1}\ \text{l}$	E_3 kcal mole^{-1}	A_4 $\text{sec}^{-1}\ \text{mole}^{-1}\ \text{l}$	E_4 kcal mole^{-1}	Method	Ref.
Styrene	1.23×10^{12}	37.0 ± 2	1.02×10^{6}	6.5 ± 1	1.50×10^{7}	14.2 ± 1	3.07×10^{8}	2.8 ± 1	After effect	17
do[a]	4.15×10^{11}	36.4	1.44×10^{6}	6.3	4.08×10^{7}	14.4	1.43×10^{8}	1.9	Induction period	61
do[b]	—	—	2.16×10^{7}	7.8	—	—	2.59×10^{9}	2.4	Rotating sector	46
do[a]	—	—	$k_2(30°C) = 52$		$k_3(30°C) = 1.66 \times 10^{-3}$		$k_4(30°C) = 1.05 \times 10^{7}$		Rotating sector	65
p-Methoxystyrene	$I(0°C) = 5.94 \times 10^{-16}$		$k_2(0°C) = 2.92$		$k_3(0°C) = 5.78 \times 10^{-5}$		$k_4(0°C) = 1.06 \times 10^{6}$		After effect	18
4-Vinylpyridine	$I(25°C) = 5 \times 10^{-13}$		$k_2(25°C) = 12$		$k_3(25°C) = 8 \times 10^{-3}$		$k_4(25°C) = 3 \times 10^{6}$		After effect	18a
Methyl methacrylate	—	—	5×10^{5}	4.4	—	—	1×10^{8}	0(16–30°C)	Rotating sector	66
do[a]	$I(0°C) = 6.82 \times 10^{-15}$		$k_2(0°C) = 41.6$		$k_3(0°C) = 6.13 \times 10^{-4}$		$k_4(0°C) = 2.69 \times 10^{6}$		After effect	67
do[b]	—	—	5.1×10^{6}	6.3	2.75×10^{6}	12.3	1.36×10^{9}	2.8	Rotating sector	47
do[a]	—	—	$k_2(25°C) = 122$		—	—	$k_4(25°C) = 8.1 \times 10^{6}$		Rotating sector	46
do[a]	—	—	$k_2(25°C) = 273$		—	—	$k_4(22°C) = 22.8 \times 10^{6}$		Rotating sector	73
do[a]	—	—	$k_2(25°C) = 513$		—	—	$k_4(25°C) = 4.7 \times 10^{7}$		Rotating sector	73
Vinyl acetate	—	—	1.65×10^{6}	4.4	—	—	3.92×10^{8}	0(16–31°C)	Rotating sector	68
do	—	—	$k_2(25°C) = 5.5 \times 10^{2}$		—	—	$k_4(25°C) = 4 \times 10^{7}$		Rotating sector	69
do	—	—	2.43×10^{8}	7.3	$k_3(50°C) = 5$		4.2×10^{11}	5.2	Rotating sector	70
do	—	—	$k_2(25°C) = 1 \times 10^{3}$		$k_3(25°C) = 0.23$		$k_4(25°C) = 5.9 \times 10^{7}$		Rotating sector	71

Vinyl acetate	I = 0(−15–0°C)		9.8×10^5	3.2	9.9×10^3	6.1	2.2×10^8	(0−15–0°C)	After effect	19
do[c]	—	—	$k_2(16°C) = 7 \times 10^2$		—	—	$k_4(16°C) = 2.6 \times 10^9$		Rotating sector	68
Butyl acrylate	—	—	4.4×10^2	2.1	—	—	1.8×10^4	0(25–30°C)	Rotating sector	72
Methyl acrylate	—	— —	$k_2(25°C) = 1.6 \times 10^3$		—	—	$k_4(25°C) = 5.5 \times 10^7$		Rotating sector	73
do	—	—	9×10^7	7.1	—	—	2.8×10^{10}	5.3	Rotating sector	46a
Propyl methacrylate	—	—	$k_2(25°C) = 4.7 \times 10^2$		—	—	$k_4(25°C) = 4.5 \times 10^7$		Rotating sector	74
Butyl methacrylate	—	—	6.4×10^6	4.5	—	—	$k_4(25°C) = 1 \times 10^7$		Rotating sector	74
Vinyl chloride[d]	—	—	3.3×10^6	3.7	—	—	1.3×10^{12}	4.2	Rotating sector	75

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† I, A_1, E_1—Values refer to thermal initiation. Bulk polymerization, unless stated otherwise.

[a] Authors assumed disproportionation.

[b] Authors assumed combination. Values reported are those originally given by the authors. These involve the alternatives of radical disproportionation and combination. Moreover, later work has led in some instances to a revision of the mechanism. This should be kept in mind when comparing our tabulation with those in other monographs. Present evidence tends to favor disproportionation in methyl methacrylate and combination in styrene. By analogy one may assume the first mechanism to apply in the other methacrylates. The pertinent relations are discussed in Section 1 and earlier in this section.

[c] Hexane solution.

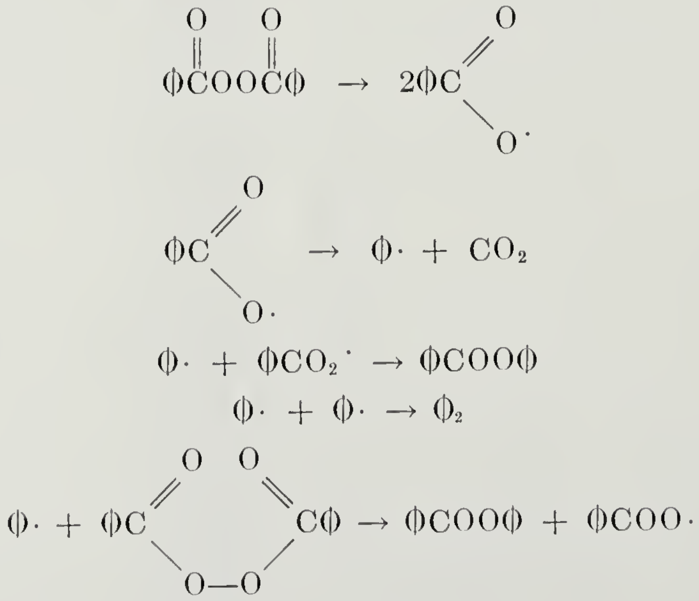
[d] Tetrahydrofuran solution.

initiate. With 1.5 molar styrene in benzene, 80 per cent of the initiating radicals are benzoyloxy[78a].

The presence of a solvent permits additional types of radicals to be formed and, hence, leads to further possibilities for termination and attack on peroxide. This results in a number of variations in the kinetics.

Quite generally the over-all rate of reaction will consist of two terms representing the spontaneous and induced decomposition, respectively. The order of the latter will vary; the first will always be of first order.

Assuming the absence of solvent reactions, the following steps are likely to occur:



$$\phi\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}\phi \rightarrow 2\phi C(=O)O\cdot$$

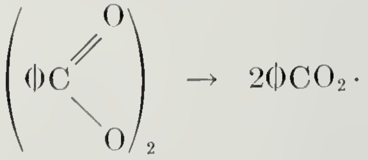
$$\phi C(=O)O\cdot \rightarrow \phi\cdot + CO_2$$

$$\phi\cdot + \phi CO_2^{\cdot} \rightarrow \phi COO\phi$$

$$\phi\cdot + \phi\cdot \rightarrow \phi_2$$

$$\phi\cdot + \phi C(=O)O{-}OC(=O)\phi \rightarrow \phi COO\phi + \phi COO\cdot$$

For a kinetic formulation this can be reduced to[79]:



$$\left(\phi C(=O)O\right)_2 \rightarrow 2\phi CO_2\cdot \qquad P \xrightarrow{k_1} 2R$$

$$2\phi CO_2\cdot \rightarrow \phi COO\phi + CO_2 \qquad 2R \xrightarrow{k_4} RR$$

$$\phi CO_2\cdot + \phi CO_2O_2C\phi \rightarrow \phi COO\phi + \phi COO\cdot$$

$$R + P \xrightarrow{k_5} X + R$$

The steady state condition then leads to the following expression for the over-all rate of peroxide decomposition:

$$-dP/dt = k_1P + k_5PR = k_1P + k_5\left(\frac{k_1}{k_4}\right)^{1/2}P^{3/2} \qquad (8)$$
$$= k_1P + k_iP^{3/2}$$

The k_i term represents the induced decomposition. In this special case it is of the $\frac{3}{2}$ order. In the presence of solvent (SH) the reaction may proceed as follows:

$$R\cdot + SH \xrightarrow{k_3} RH + S\cdot$$

$$R\cdot + S\cdot \xrightarrow{k_4} RS$$

$$S\cdot + P \xrightarrow{k_5} X + R\cdot$$

TABLE 5. DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENTS AT 79.8°C[79]

Solvent	k_1 hr^{-1}	$k_i(M/l)^{-1/2}$ hr^{-1}
Carbon tetrachloride	0.075	0.133
Benzene	0.118	0.154
Toluene	0.118	0.154
Nitrobenzene	0.118	0.154
tert.-Butyl benzene	0.118	0.552
Cyclohexene	0.0695	0.167
Ethyl acetate	0.323	1.32
Ethyl iodide	0.145	0.244
Cyclohexane	0.229	1.17
Acetic acid	0.293	1.84
Acetic anhydride	0.270	1.10
Acetic anhydride + reaction products	0.242	0.321

In this case the rate equals:

$$-dP/dt = k_1P + k_5S\cdot P = k_1P + (k_5k_3/k_4)SH\ P \tag{8a}$$

and the whole reaction is of first order in peroxide. If, instead, solvent radicals mutually terminate, we arrive again at the $\frac{3}{2}$ order for the induced term, i.e., Eq. (8). It has the integral

$$\ln\left(\frac{\sqrt{P} + k_1/k_i}{\sqrt{P_0} + k_1/k_i}\right)\left(\frac{\sqrt{P_0}}{\sqrt{P}}\right) = \frac{k_1t}{2} \tag{9}$$

where P_0 represents the initial peroxide concentration. From Eq. (9) k_1 and k_i can be found. In this manner Nozaki and Bartlett[79] obtained Table 5. There is a wide variation both in k_1 and k_i. It is seen in Table 6 that the activation energy for the k_i is lower by eight kcal for benzoyl peroxide in benzene than the activation energy for k_1. Thus, at sufficiently large concentrations of peroxide and low temperatures the induced step is more important. This is particularly significant in polymerization since only the spontaneous decomposition is effective in initiating the reaction. The in-

Table 6. Activation Energies for Catalysts Decomposition

Catalyst	Solvent	Temp. Range (C°)	A		E		Ref.
			A_1 sec^{-1}	A_i $l^{1/2}m^{-1/2}$ sec^{-1}	E_1 kcal	E_i kcal	
Benzoyl peroxide	Benzene	60–80	$10^{16.02}$	$10^{11.14}$	33.3	25.2	79
do	do	70–90	10^{14}		29.9		85e
do	do	50–75	$10^{13.48}$		29.6		99
do	Acetophenone	70–90	$10^{14.22}$		30.2		85d
do	Vinyl acetate	25–45	$10^{13.43}$		28.3		69
do	Acetic anhydride	60–80	$10^{14.73}$	$10^{11.87}$	30.7	25.0	79
do	Carbon tetrachloride	50–75	$10^{13.5}$		29.6		99
do	Toluene	50–75	$10^{13.7}$		29.6		99
do	Nitrobenzene	50–75	$10^{13.5}$		29.6		99
do	Methyl acetate	50–75	$10^{13.5}$		29.6		99
do	Ethyl acetate	50–75	$10^{13.78}$		29.6		99
Benzoyl peroxide	Styrene	35–100	$10^{16.24}$		33.1		82
p-Chlorobenzoyl peroxide	Styrene	35–100	$10^{14.29}$		29.9		82
2,5-Dichlorobenzoyl peroxide	Styrene	35–100	$10^{11.58}$		23.9		82
Lauroyl peroxide	Styrene	35–100	$10^{16.8}$		33.1		82
p-Methoxybenzoyl peroxide	Acetophenone	60–90	$10^{13.89}$		28.7		85d
m-Methoxybenzoyl peroxide	do	60–90	$10^{13.61}$		28.9		85d
o-Methoxybenzoyl peroxide	do	60–90	$10^{14.07}$		27.2		85d
p-Methylbenzoyl peroxide	do	60–90	$10^{14.22}$		29.9		85d
m-Methylbenzoyl peroxide	do	60–90	$10^{14.3}$		30.2		85d
o-Methylbenzoyl peroxide	do	60–90	$10^{15.09}$		30.2		85d
p-Chlorobenzoyl peroxide	do	60–90	$10^{14.32}$		30.4		85d
m-Chlorobenzoyl peroxide	do	60–90	$10^{14.36}$		30.7		85d
o-Chlorobenzoyl peroxide	do	60–90	$10^{14.71}$		29.4		85d
p-Cyanobenzoyl peroxide	do	60–90	$10^{14.6}$		31.2		85d
m-Nitrobenzoyl peroxide	do	60–90	$10^{14.16}$		30.2		85d

p-Nitrobenzoyl peroxide	do	60–90	$10^{14.29}$		30.3		85d
o-Nitrobenzoyl peroxide	do	60–90	$10^{14.73}$		28.6		85d
3,5-Dinitrobenzoyl peroxide	do	60–90	$10^{14.69}$		31.2		85d
o-Phenoxybenzoyl peroxide	do	60–90	$10^{14.55}$		29.0		85d
2,4,4-Trimethylpentane-2-hydroperoxide	2,2,4-Trimethylpentane	134–184	$10^{13.07}$		33.4		85b
2,3,3-Trimethylbutane-2-hydroperoxide	2,2,3-Trimethylbutane	119–164	$10^{12.48}$		32.0		85b
t-Butyl hydroperoxide	*n*-Octane	150–180	$10^{14.99}$		39.0		85a
1,4-Dimethyl cyclohexane hydroperoxide	1,4-Dimethyl cyclohexane	110–130	$10^{13.2}$	$10^{11.4}$	32.8	28.6	85e
Di-*tert*-amyl peroxide	Gas phase	130–150	$10^{16.68}$		39.0		84
Di-*tert*-butyl peroxide	Cumene	125–145	$10^{15.8}$		37.5		84
do	*t*-Butyl benzene	125–145	$10^{16.04}$		38.0		84
do	Tri-*n*-butylamine	125–145	$10^{15.54}$		37.0		84
Di-ethyl peroxide	Gas phase	200–250	$10^{13.32}$		31.7		99a
Di-*tert*-butyl peroxide	do	125–145	$10^{16.5}$		39.1		84
do	do	120–280	$10^{14.7}$		36.1		98
2,2′-Azo-bis-isobutyronitrile	Benzene	50–75	10^{15}		30.7		99
do	Ethyl acetate	50–75	$10^{14.9}$		30.7		99
do	Carbon tetrachloride	50–75	$10^{14.54}$		30.7		99
do	Toluene	60–80	$10^{17.14}$		34.0		86

duced one does not augment the total radical concentration and such decomposition is wasted.

Besides varying with the concentration of peroxide, the induced reaction is dependent on the structure of the solvent and peroxide, and the temperature. In the light of the above kinetic considerations the solvent can affect the radical concentration in several ways. In addition to the dilution effect, the lifetime of peroxide derived radicals can be changed by transfer with the solvent and what seems to be the main effect, the creation of a new type of radical, which influences mainly the induced decomposition. Differences in the k_i-values for the various solvents are due to differences in the ability of solvent radicals to attack peroxide and to terminate each other. Since the activity of a radical is reflected in both acts, it is impossible to separate them without additional information.

In certain solvents, such as ethers, amines and phenols, very rapid decomposition takes place[80]. In these instances the over-all rate is of first order indicating termination between solvent and peroxide radicals and attack of peroxide by the former. It is impossible then to separate by a kinetic analysis as done previously (see Eq. 9) the two mechanisms. However, the absence of an increase in polymerization rate when monomer is added, may indicate a relatively high induced contribution.

The degree to which the solvent takes part in the decomposition appears to be determined by the ease with which peroxidic radicals may remove hydrogen atoms from the medium. For instance, the rate in the system diethyl ether benzoyl peroxide is eight times that in benzene[81]. This alone is not sufficient to account for differences in various solvents. The rate of attack by solvent radicals on the peroxide is perhaps the most important step.

In considering the effect of peroxide structure, one must again distinguish between the modes of decomposition. The fraction W of peroxide lost by induced decomposition is given by:

$$W = \frac{\text{Rate of induced decomposition}}{\text{Over-all rate}}$$

The "waste" from the point of view of polymerization is shown in Table 7, due to Redington[82], for four different peroxides. The successive substitution of chlorine in the phenyl ring increases W considerably. This is due to the induced mechanism. Its magnitude is evaluated in the following manner: k (total) in Table 7 represents the over-all rate of peroxide loss, that is:

$$k\ (\text{total}) = k_1 + k_i P^{n-1}$$

where we have written n to account for the possibilities mentioned before. From k (total) and W the last two columns are obtained.

It is illustrative to consider Table 8 which gives the comparative inhibiting action of a series of compounds on benzoyl peroxide studied in dioxane by Swain, Stockmayer, and Clarke[83]. It will be noted that among the best inhibitors are substances such as acrylonitrile, 3,4-dichlorostyrene, iodine and trinitrobenzene, all of which contain electron attracting groups. Finally we recall the increased decomposition in ethers and amines, both good electron donors. Swain, *et al.* also noted the enhanced reaction of peroxide derivatives having electron attracting groups. This suggests that the transition state of the k_5 step contains contributions from polar resonance structures involving electron transfer from the attacking radical[83].

Table 7. Peroxide Decompositions in Styrene[82]

Peroxide	Temp.	k (Total) hr^{-1}	W	k_1 hr^{-1}	$k_i P^{n-1}$ hr^{-1}
Benzoyl	34.8	0.00028	0.39	1.71×10^{-4}	1.09×10^{-4}
	49.4	0.0038	0.29	2.7×10^{-3}	1.1×10^{-3}
	61.0	0.0186	0.24	14.14×10^{-3}	4.46×10^{-3}
	74.8	0.132	0.15	11.22×10^{-2}	1.98×10^{-2}
	100	3.30	−0.08	3.30	0.0
Lauroyl	34.8	0.00148	0.74	0.38×10^{-3}	1.1×10^{-3}
	49.4	0.0162	0.71	0.47×10^{-2}	1.15×10^{-2}
	61.0	0.102	0.64	3.7×10^{-2}	6.5×10^{-2}
	74.8	0.72	0.69	.22	.50
	100.0	17.2	0.30	12.0	5.2
Bis-*p*-chlorobenzoyl	34.8	0.0006	0.81	1.14×10^{-4}	4.86×10^{-4}
	49.4	0.006	0.72	1.68×10^{-3}	4.32×10^{-4}
	61.0	0.024	0.54	1.1×10^{-2}	1.3×10^{-2}
	74.8	0.16	0.52	7.7×10^{-2}	8.3×10^{-2}
	100.0	3.0	0.12	2.64	3.6×10^{-1}
Bis-2,4-dichlorobenzoyl	34.8	0.028	0.97	1×10^{-3}	2.7×10^{-2}
	49.4	0.172	0.95	9×10^{-3}	1.63×10^{-1}
	61.0	0.36	0.87	0.44×10^{-1}	3.16×10^{-1}
	74.8	2.0	0.76	0.48	1.52
	100.0	30.	0.45	16.50	13.50

The use of inhibitors allows one to separate the induced and spontaneous steps. This is accomplished by extrapolating the rates to zero concentration of peroxide in the presence of 3,4-dichlorostyrene as an inhibitor as shown in Figure 1. The extrapolated values are exhibited in Table 9. To interpret the effect of a substituent on k_1, the authors apply the Hammett equation. It relates the rate constants k for *m*- or *p*-substituted phenyl derivatives to the value in the unsubstituted one through a constant σ, characteristic of the substituent only. Thus, Log $k/k_0 = \rho\sigma$. ρ is characteristic only of the type of reaction. Considering the uncertainties in the σ values the equation

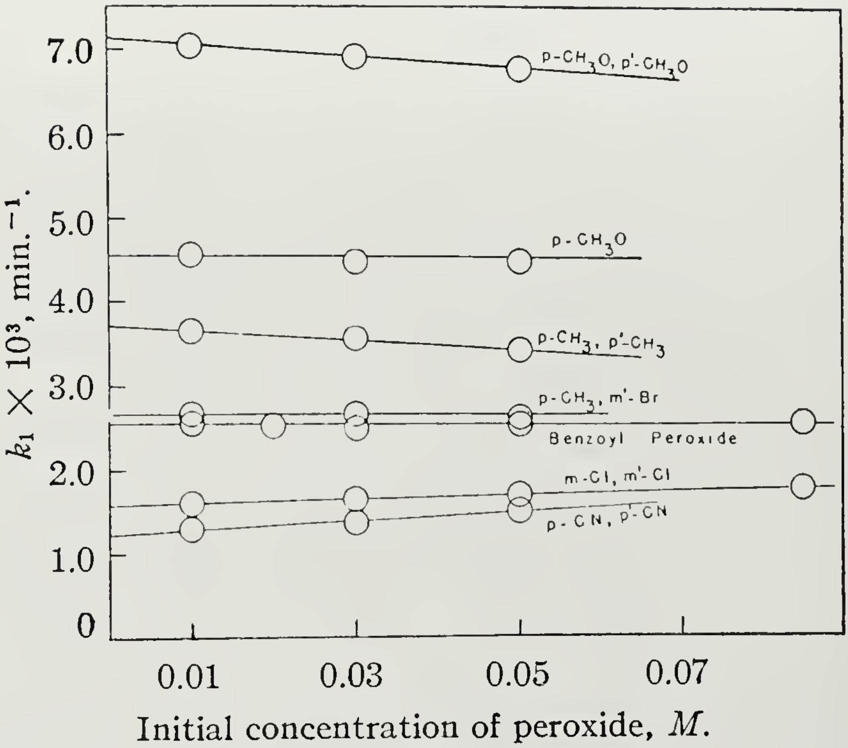


Figure 1. Extrapolation of rates of peroxide decomposition to zero concentration of peroxide in the presence of 3,4-dichlorostyrene.

TABLE 8. HALF-LIFE OF 0.05*M* BENZOYL PEROXIDE IN 0.2*M* SOLUTIONS OF INHIBITORS IN DIOXANE AT 80°C[83]

Compound	Min.	Compound	Min.
Pure dioxane	23	Triphenylmethane	75
N-Phenylsuccinimide	23	Maleic anhydride	90
Acetamide	23	1,1-Diphenylethylene	105
Ethyl acetoacetate	23	Diacetyl	110
Urethan	23	Nitromethane	115
Trioxane	23	*m*-Cresol	130
Benzene	26	*p*-Nitrotoluene	130
Anisole	27	Benzyl cyanide	175
Allyl acetate	28	Nitrobenzene	200
Toluene	28	Benzil	225
Benzamide	30	Diphenyl disulfide	225
Vinyl acetate	34	Diethyl fumarate	230
Polystyrene	35	Stilbene	270
Cumene	37	Acrylonitrile	275
Benzoic acid	40	3,4-Dichlorostyrene	275
Cyanacetamide	42	Styrene	275
Cyclohexanone	50	1,4-Diphenylbutadiene	275
Benzyl benzoate	50	Iodine	280
N-phenylurethan	60	Methyl methacrylate	ca. 300
Acetanilide	70	Trinitrobenzene	ca. 275

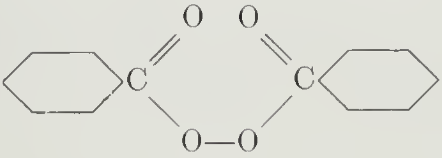
represents the data very satisfactorily (see Figure 2). The uncertainties in both k_1 and $\sigma_1 + \sigma_2$ are indicated in the Figure; the σ_1 refers to the first substitutent, the σ_2 to a second.

TABLE 9. EXTRAPOLATED RATE CONSTANTS IN DIOXANE WITH 0.2*M* 3,4-DICHLOROSTYRENE AT 80°C[83]

Substituents	$k_1 \times 10^3$, min.$^{-1}$	log (k/k_0)	$\sigma_1 + \sigma_2$
p,p'-Dimethoxy	7.06	0.447	−0.536
p-Methoxy	4.54	.255	−.268
p,p'-Dimethyl	3.68	.164	−.340
p,p'-Di-*tert.*-butyl	3.65[a]	.161	−.394
m,m'-Dimethoxy	3.45	.137	+.230
m-Methoxy	2.89	.059	.115
p-Methoxy-*m'*-bromo	2.66	.023	.221
m,m'-Dimethyl	2.64	.019	−.138
Benzoyl peroxide	2.52	.000	.000
p,p'-Dichloro	2.17	−.065	+.454
p,p'-Dibromo	1.94	−.113	.464
m-Cyano	1.64	−.187	.517[b]
m,m'-Dichloro	1.58	−.203	.746
m,m'-Dibromo	1.54	−.215	.782
p,p'-Cicyano	1.22	−.314	1.30[b]
m,m'-Dicyano	1.02	−.393	1.03[b]

[a] Estimated from rate of decomposition in doxane with 0.2*M* styrene.
[b] From k/k_0 for *p*- and *m*-cyanobenzoic acids.

Contrary to the findings in the induced case, electron donating groups increase the rate of decomposition. The suggestion is made that the two halves of the peroxide molecule behave as two opposing dipoles:



$$\delta^{\oplus} \longrightarrow \delta^{\ominus}\delta^{\ominus} \longleftarrow \delta^{\oplus}$$

Electron donor groups increase the effective dipole moment. The increased rate observed[83] in polar solvents is ascribed to the interaction of the solvent dipoles with opposing dipoles of peroxide.

In contrast to the benzoyl type peroxides, studies on di*tert.*-butyl peroxide in cumene, in *tert.*-butyl benzene, tri-*n*-butyl-amine and in the vapor phase[84] indicate the absence of induced or chain mechanisms. This conclusion is based on the lack of inhibition with nitric oxide, and absence of solvent effects. The principal products in the vapor phase reaction, ethane and acetone, are consistent with a mechanism involving the split of the peroxidic link, the resulting radicals decomposing into acetone and methyl radicals which combine to form ethane. The over-all rate is first order and equivalent to the rate for the initial scission. The activation energy obtained is 39.1 kcal, somewhat higher than for the previously discussed compounds. It may be mentioned that in the vapor phase there is evidence[85] that the presence of hydrogen chloride leads to an induced chain decomposition.

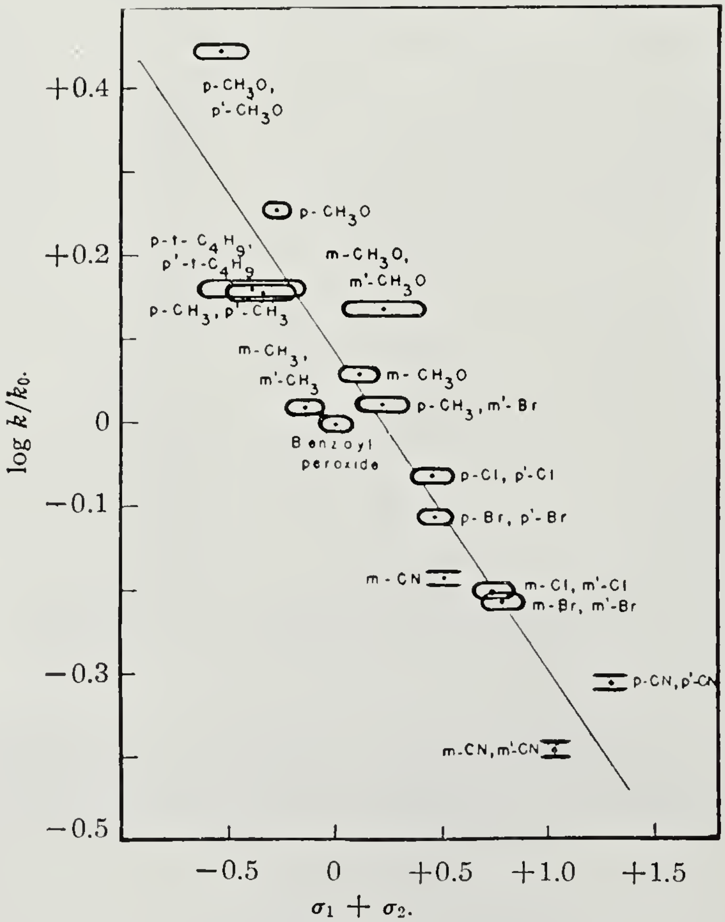
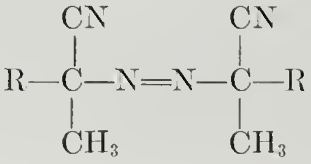


Figure 2. Correlation of extrapolated first-order rate constants with Hammett's sigma values.

In a class with di-*tert.*-butyl peroxide as to order of reaction and lack of an induced process are the aliphatic azonitriles of the type[86]



$$\begin{array}{ccccc} & CN & & CN & \\ & | & & | & \\ R— & C & —N{=}N— & C & —R \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

These compounds possess the labile azo link and decompose into radicals and nitrogen. Overberger, O'Shaughnessy, and Shalit have reported rates for a series of such compounds where R was systematically varied (see Table 10). A study of four different solvents, Table 11, indicated no dependence on the medium. The dependence on the nature of the R-substituent can be made plausible by considering steric effects (compare *iso*-C_4H_9 and *iso*-C_3H_7) which increase the probability of decomposition.

TABLE 10. RATES OF DECOMPOSITION OF AZO NITRILES IN TOLUENE AT 80.2°C[86]

R-group	Concn. Range, (moles/liter)	k (sec^{-1} × 10^4) range	No. of Runs	Average Deviation
CH_3-[a]	0.137 –0.0463	1.72–1.60	3	0.06
C_2H_5-	0.0274–0.0154	0.94–0.80	4	0.06
n-C_3H_7	0.0181–0.0143	1.74–1.65	2	0.05
iso-C_3H_7	0.0183–0.0135	1.03–1.02	2	0.01
n-C_4H_9	0.0142	1.58	1	—
iso-C_4H_9	0.0193–0.0163	7.1	2	0.00
C_6H_{11}[b]	0.0165	0.083	1	—

[a] Not flushed with nitrogen.
[b] Cyclohexanone.

ENERGIES OF ACTIVATION FOR THE DECOMPOSITION OF AZO NITRILES[86]

Run	R-group	k (sec^{-1} × 10^4) at 69.8°	Energy of Activation (kcal/mole)
37	CH_3-	0.38	34(±3)[a]
38	C_2H_5	0.23	31(±3)
33	*n*-C_3H_7	0.42	33(±4)
36	*iso*-C_3H_7	0.26	32(±4)
32	*iso*-C_4H_9	1.98	29(±4)

[a] Limits of error of activation energies calculated on assumption maximum error in individual rate constants is 10 per cent.

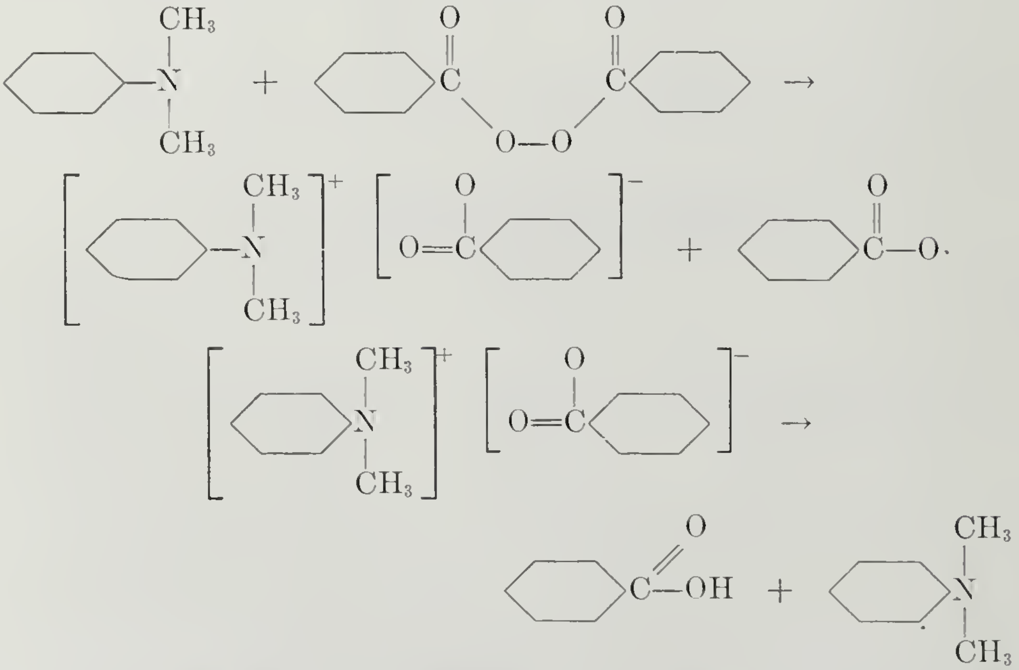
TABLE 11. EFFECT OF SOLVENTS ON THE RATE OF DECOMPOSITION OF 2,2′-AZO-BIS-ISOBUTYRONITRILE AT 80.2°C[86]

Solvent	Concn. (moles/liter)	Dielectric Constant at 20°	k (sec^{-1} × 10^4)
Isobutyl alcohol	0.0278	18.7	1.76
Isobutyl alcohol	0.0234	18.7	1.67
Toluene	0.0463	2.4	1.60
tert.-Amyl alcohol	0.0501	11.7	1.40
Aniline	0.0262	7.2	1.68

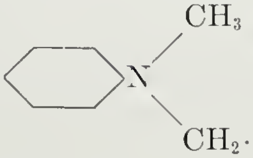
Promoted Peroxide Decomposition

For many practical purposes, for example, in the use of plastics for dental fillings[87] it is desirable to have rapid polymerization at lower temperatures than are attainable with common peroxides alone. This requires systems capable of producing numerous active free radicals at such temperatures. In the production of synthetic rubber the discovery of aqueous redox systems allowed one to carry out emulsion polymerization at temperatures around 0°C. With bulk systems similar results are being achieved along analogous lines, that is, the acceleration of peroxide decomposition by reducing agents. A brief survey of developments in this field is the subject of this section.

With benzoyl peroxide it has been found that dimethyl aniline promotes the spontaneous decomposition steps producing large numbers of radicals, and achieving polymer formation at low temperatures[88]. With primary and secondary amines, which also accelerate benzoyl peroxide decomposition, the process operating is presumably the induced mechanism which does not yield large numbers of free radicals. Hence these amines together with peroxide fail to activate polymerization processes. The observation that oxygen absorption is high with the tertiary amine system, in contrast to the other types of amines, is indicative of the presence of great numbers of radicals[88]. This supports the premise that the *tert.* amine is not operating to increase the rate of the induced decomposition. The suggested mechanism[88] for this decomposition of benzoyl peroxide is:



It is seen that an electron transfer from the amine to the peroxide is involved. The net result is the same number of radicals per molecule of peroxide decomposed as would be expected in the unpromoted reaction. The evidence for the *ortho*-dimethyl aniline radical includes the isolation of its dimer. Other possible radical intermediates, such as



are possibilities in the above reaction[89].

Inhibiting properties of primary and secondary amines may also contribute to their inactivity as promoters although this effect does not appear to be needed to interpret the behavior described.

Several kinetic studies of the dimethyl aniline activation of benzoyl peroxide catalyzed polymerization have been reported[90, 91, 92]. With styrene[90] the rate of initiation was apparently bimolecular between amine and peroxide at 0°C as would be expected from the above chemical equations; that is, $R_i = k[Bz_2O_2]^a[DMA]^a$, with $a = 1$. At higher temperatures, 30 to 60°C, the exponent a has values from 0.79 to 0.71 which suggests a more complicated mechanism. With vinyl chloride[91] the dimethyl aniline benzoyl peroxide system is effective in the initial stages of polymerization. However, the effect dies out at low conversion, although polymerization could be reinduced by addition of peroxide. This result suggests[91] that peroxide derived radicals are responsible for the polymerization. An alternative possibility may be that the amine groups are still effective even though the original molecules are altered after the peroxide is used up.

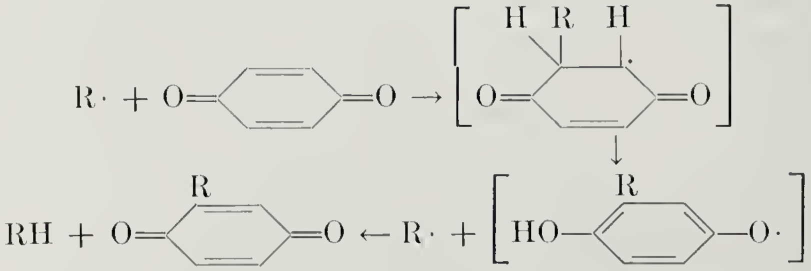
Ring substituted benzoyl peroxides with dimethyl aniline have also been studied[92] and variations in activity observed which can be correlated with the Hammett equation. These observations support the electron transfer mechanism for these reactions as shown in the above chemical equation. In this connection it is worth noting that dimethyl toluidine is more active than dimethyl aniline[93]. Presumably the electron donating property of the *para*-methyl group is responsible for this enhanced activity.

The quaternary salts of the amines under discussion are even better promoters[94], as studies with the product from dimethyl aniline and benzyl chloride, i.e., dimethylbenzylphenyl ammonium chloride, have demonstrated. Here again substituent groups on the benzyl chloride molecule had significant effects in line with the electron donating or attracting properties of the groups. Aryl sulfinic acids alone initiate polymerization but are even better with peroxide present[95]. A more complicated initiator system involves the salts of sulfinic acids and dimethyl toluidine or related amines with benzoyl peroxide[93]. Ferrous iron also enhances the initiation reaction in bulk with peroxide and tertiary amines present[96]. There is also evidence that *tert.*-butyl catechol and hydroquinone, common inhibitors, act to facilitate peroxide decomposition[97].

Mechanism of Inhibition and Retardation

Many substances[100] interfere with the polymerization process. The more effective ones produce a definite induction period during which the rate of reaction is for all purposes negligible and are termed "inhibitors." Those which only reduce the rate are referred to as "retarders." Both effects may occur concurrently in a polymerizing system, and the distinction is merely one of degree. For free radical polymerization, some common compounds of this type are the hydroquinones, quinones, catechols, and aromatic nitro[101] derivatives. Stable free radicals such as diphenyl picryl hydrazyl and triphenyl methyl, and phenyl acetylene also act as retarders as well as certain inorganic substances, for example, sulfur, oxygen, iodine and copper metal.

The most generally accepted view is that these materials function by removing free radicals from the system. They may add to a radical and produce a relatively inactive species which in turn may remove a second radical. For example, in the quinone case the following steps have been suggested[100]:



Such a scheme agrees qualitatively with the general features of inhibition.

However, the mechanisms involved are perhaps the least well-defined ones in the polymerization field and are presumably the most complex. The general principles of reaction mechanisms lead one to anticipate numerous possibilities[102] which may be outlined as follows:

A. In the attack on the chain carrier, the retarder (or inhibitor) may
   1. Combine by direct addition.
   2. React by transfer of an atom (or group) to or from the chain carrier, producing a molecule and a fragment coming from the retarder.

B. In either case the following possibilities must be considered for the disposal of the new free radical formed:
   1. Union with another free radical
      (a) With a radical of its own kind (dimerization)
      (b) With a second chain carrier
   2. Reaction by transfer of an atom (or group)

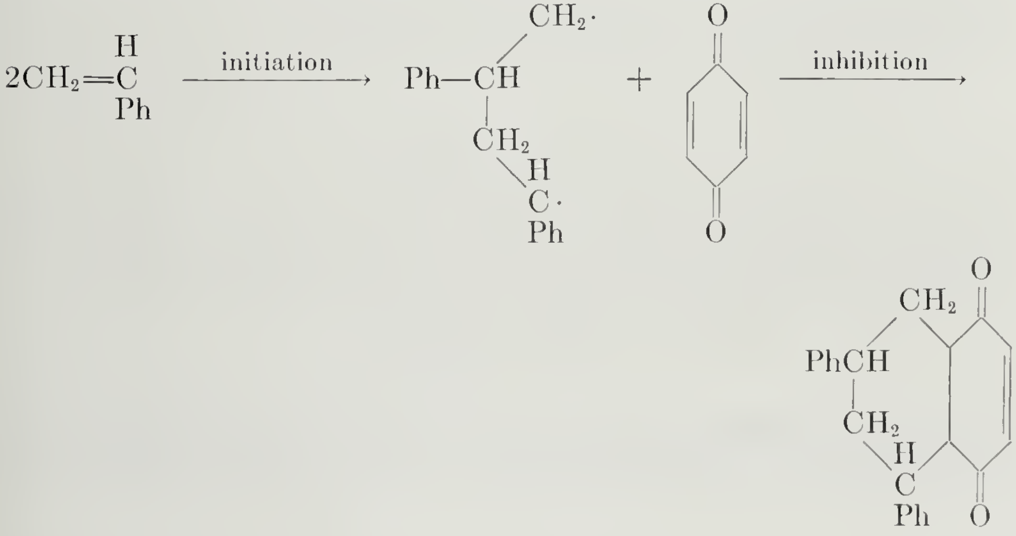
        (a) With a radical of its own kind (disproportionation)
        (b) With a second chain carrier
        (c) With another retarder molecule, producing a further radical
    3. Union with a molecule (chain propagation)
        (a) With a monomer
        (b) With a retarder

C. The molecules produced by these processes may be
    1. Inert
    2. Initiators
    3. Retarders
    4. Chain-transfer agents
    5. Substances entering into copolymerization.

The possibilities are further complicated by different degrees of specificity of retarder for different monomers and also by the fact that temperature will also affect the relative behavior of these substances and of the possible intermediates.

Investigations[102, 103] of the products formed during the inhibition period when quinone is used, indicate in general a mixture of products. The possible products of quinone inhibition of the benzoyl peroxide induced polymerization of styrene appear to be hydroquinone diethers, monosubstituted hydroquinone monoethers, disubstituted hydroquinones and disubstituted dihydroquinones[103]. Thus alkylation of the quinone probably occurs both on the ring carbons and on the oxygen atoms[102, 103].

In the thermal polymerization of styrene, quinone is a much more efficient inhibitor than in the peroxide catalyzed system[104]. Also an inhibition product of the thermal polymerization has been reported, corresponding empirically to the adduct of one quinone and two styrene molecules. This suggests the following processes [104] for thermal initiation and for inhibition by quinone.



It is also possible to visualize reaction of the diradical with an oxygen molecule to produce a stable six-membered ring peroxide which could be the reaction involved in inhibition by oxygen.

Another line of evidence for the specific type of inhibition reaction shown above is that unsensitized photo-polymerizations are strongly inhibited by quinone whereas peroxide sensitized photo reactions are not[104]. This points again to a diradical mechanism for the former reaction and a monoradical for the latter. Hydroquinone which is also formed during inhibition by quinone[104] is used extensively as a stabilizer for monomers during storage. However, its efficiency has been found to depend upon the presence of oxygen which oxidizes it to quinone. In the absence of oxygen it has no retarder action compared to quinone[105]. There is also some evidence that hydroquinones and perhaps catechols have a promotional effect on peroxide catalyzed polymerization.

Several authors[102, 104, 106-109] have studied the kinetics of certain polymerization systems in the presence of inhibitors. Goldfinger, Skeist and Mark showed that benzoquinone affects the rate and molecular weight of thermally produced polystyrene. The induction period is proportional to the initial inhibitor concentration. To account for the observed inhibition and retardation, the mechanism proposed assigns a dual role to the benzoquinone. In addition to the initiation (k_1M) propagation (k_2MR) and termination (k_4R^2) there appear an inhibition ($k_{4i}Ri$) and retardation ($k_{4r}Rr$) step. The concentration of benzoquinone is denoted by i while that for the adduct with a monomer is r. The latter species is assumed to be responsible for the retardation effect.

These assumptions and the steady state condition:

$$k_1M = k_4R^2 + k_{4i}Ri + k_{4r}Rr$$

lead to the following relations provided the normal termination is small in comparison to the other chain stopping processes.

For inhibition:

$$\frac{-di}{dt} = \frac{k_{4i}ik_1M}{k_{4i}i + k_{4r}r}$$

During the inhibition period the right-hand side reduces to k_1M. Thus inhibitor is used up linearly with time as observed experimentally[101, 106].

$$\frac{-dM}{dt} = \frac{k_2M \cdot k_1M}{k_{4i}i + k_{4r}r}$$

During the initial stages the rate is negligible due to the magnitude of the i-term. Late in the induction period the r-term becomes comparable to the former. Beyond this the over-all rate is in a first approximation inversely proportional to the concentration of r. Experimentally[106] the production of polymer is less rapid the longer the induction period.

For the initial number-average degree of polymerization; during the inhibition and retardation period:

$$\bar{P} = \frac{k_2M}{k_{4_i}i + k_{4_r}r}$$

while after the inhibition period,

$$\bar{P} = k_2M/k_{4_r}r$$

When appreciable polymer is being formed, the i-term can thus be disregarded and we find that the degree of polymerization is inversely proportional to the amount of inhibitor originally added. For this, there is also some experimental evidence[106].

Some attempts have been made to evaluate quantitatively retarders[102, 109]. A simplified version of the kinetics utilized for this evaluation is as follows. First, one assumes that the inhibitor disappears only by reaction with the growing radicals and that the majority of the radicals are terminated by this process. Thus $-di/dt = k_{4_i}Ri$. Also one assumes that monomer disappears only by propagation, $-dM/dt = k_2RM$. Hence: $di/dM = k_{4_i}/k_2 i/M$ or $\ln i_0/i = k_{4_i}/k_2 \ln M_0/M$. The result is a linear relationship between monomer concentration and the logarithm of inhibitor with a slope which is a measure of the efficiency of inhibition relative to that for propagation of the monomer utilized. Table 12 contains values of k_{4_i}/k_2 for various inhibitors in several monomer-systems, and, for comparison, the oxidation potentials of the quinones. It is seen that inhibition increases with oxidation potential. However, there is no linear relation with the logarithms or other functions of the relative rate ratios and no theoretical correlations of these quantities has appeared. The relationship between structure and oxidation potential has been the subject of a recent review[110].

In methyl acrylate polymerization in the presence of quinones a similar correspondence of oxidation potential and retardation has been noted[111]. The inhibitory power of phenolic antioxidants on the oxidation of olefins has also been observed to run parallel to oxidation-reduction potentials[112].

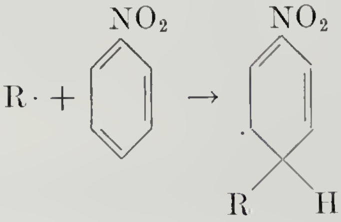
Substitution with chlorine improved the inhibition power of quinone and it should be mentioned that tetrabromo and tetraiodo quinones are also good retarders. It is reported that bromanil is 3 times and iodoanil 1.5 times as effective as benzoquinone[104].

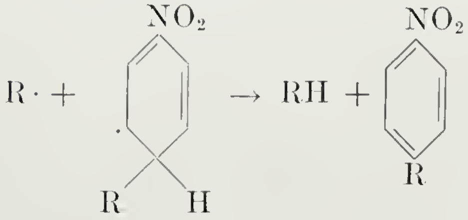
The data in Table 12 also disclose a degree of specificity between monomer and inhibitor. Comparison of the results for duroquinone shows a wide variation in behavior depending on the monomer used. It should also be mentioned that the data in the table assume that one radical is stopped by one inhibitor molecule. In the following discussion results on nitro compounds, indicating more than one chain stoppage per inhibitor molecule, will be presented.

A study which indicates the complexities in inhibitory phenomena is that by Hammond and Bartlett[107] on the effect of nitro compounds in polymerization. Polystyrene prepared in the presence of aromatic nitro derivatives has been found to contain nitrogen[113] while in nitromethane solution no detectable nitrogen is incorporated in the polymer. These considerations have led to the following mechanism for inhibition by a compound such as nitrobenzene.

Table 12. Relative Rates of Inhibition (k_{4i}/k_2)[102, 109]

Inhibitor	Allyl Acetate (80°C)	Styrene (90°C)[117]	Vinyl Acetate (45°C)	Oxidation Potential (E_0)
Chloranil	160	950		0.657
Trichloroquinone	55			0.635
Benzoquinone	52	566		0.570
Toluoquinone		210		0.528
p-Xyloquinone		43		0.486
Trimethyl quinone		26		0.444
Duroquinone	4	0.7	95	0.402
p-Dinitrobenzene			267	
m-Dinitrobenzene			105	
o-Dinitrobenzene			96	
Nitrobenzene			19	
p-Nitrotoluene			20	
Dinitrodurene			1	
2,2-Diphenyl picryl hydrazyl			$>10^3$	
Iodine			$\approx 10^3$	





The polymerization of allyl acetate in the presence of a series of di- and tri-nitro substituted aromatics has been studied and the results interpreted. It may be mentioned that allyl acetate is subject to a phenomenon called by Bartlett "degradative chain transfer." That is, the monomer plays the role of an inhibitor because it is prone to transfer and the resultant radical is incapable of propagating. Thus to the set of elementary reactions employed above we must add the degradative transfer step

$$R' + M \xrightarrow{k_{3d}} RH + m$$

There one must distinguish between three radical species in the termination step, the growing polymer radical R, the radical m, and the radical formed as the result of direct inhibition. If one neglects termination of the R^2 type, this leaves five possible termination steps. The quantity dM/dP, i.e., the instantaneous kinetic chain length, has been shown to be essentially constant[114] in the absence of inhibitors in allyl acetate.

In this case the above set of reactions leads to the following expression in the absence of inhibitors

$$\frac{dM}{dP} = \frac{2(k_2 + k_d)}{k_d}$$

With inhibitors the result is:

$$\frac{dM}{dP} = \frac{2(k_2 + k_d)M}{k_dM + k_ii}$$

The systems lack a well-defined induction period; hence, it is not possible to estimate the stoichiometry of the inhibition from the length of the induction period. This means of course, that these nitro materials should be considered as retarders. Hammond and Bartlett estimated the stopping power of the retarders by the following method. If x = total number of chains stopped by the transfer step then

$$\Delta M = x\left(\frac{k_2 + k_d}{k_d}\right)f, \qquad \text{where } f = 1 \text{ or } 2$$

This expression is valid even in the presence of inhibitors or retarders provided the termination of the allyl radical produced by degradative transfer is the same in both circumstances.

For two different runs then the relation,

$$\frac{\Delta M_1}{x_1} = \frac{\Delta M_2}{x_2}$$

holds.

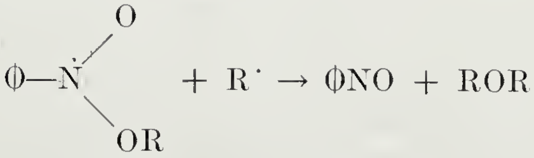
The assumption is then made that in two given runs, one with inhibitor, and one without inhibitor, the same number of chains are involved, if the initial and final concentrations of initiator are the same. In this case, y_2 is the number of chains stopped by the inhibitor molecule:

TABLE 13. APPARENT CHAIN-STOPPING CAPACITIES OF NITRO COMPOUNDS AT 80° IN ALLYL ACETATE POLYMERIZATION[107]

Inhibitor	Initial concentration moles/kg		Monomer Used (m/kg)	Chains Stopped by Inhibitor Molecule
	Peroxide	Inhibitor		
m-Dinitrobenzene	0.256	0.0427	2.98	4.1
m-Dinitrobenzene	0.257	0.127	1.18	2.3
o-Dinitrobenzene	0.250	0.0427	4.02	2.4
p-Dinitrobenzene	0.250	0.127	0.88	2.6
sym.-Trinitrobenzene	0.250	0.0427	1.90	5.9
Dinitrodurene	0.250	0.0427	4.37	1.8
Dinitrodurene	0.250	0.125	3.87	0.90
Nitromethane	0.250	0.385	4.02	0.2
None	0.257		5.45	

$$y_2 = x_1 - x_2 = x_1 - x_1 \frac{(\Delta M_2)}{(\Delta M_1)}$$

Knowing the degree of polymerization and assuming it to be approximately equal to the kinetic chain length as a consequence of the occurrence of degradative chain transfer one can calculate the value of x. This method of estimating chain length does not assume that each peroxide molecule starts two chains and that none is wasted by induced chain decomposition. Table 13 gives the results for various nitro compounds. Although based on several assumptions, these results present some quantitative aspects of retardation. The larger number of chains were stopped at the lower concentration of retarder. The retardation of trinitrobenzene which was still apparent even after 5.9 chains per molecule were stopped, is taken to indicate that radicals are attacking the ring and the nitro group. Hammond and Bartlett suggest the following mechanism for retardation via the nitro group. In the first step radical *R* adds to the nitro group. A second radical reacts as shown below:



$$\Phi\text{—}\dot{N}(O)(OR) + R^{\cdot} \rightarrow \Phi NO + ROR$$

In contrast to retarder molecules that stop more than one free radical, careful study has revealed that seventeen molecules of quinone are consumed per chain of polystyrene initiated[108]. In this system the induction period is not really proportional to initial quinone concentration. As a matter of fact the few data reported[108] appear to indicate a closer proportionality of the induction period with the square root of the initial quinone concentration.

With styrene monomer, the triphenyl methyl free radical does more than just stop growing chains. It apparently also initiates, 77 molecules of triphenyl methyl disappearing for each molecule of polystyrene that would have been formed in its absence. The net effect is some retardation. Diphenyl picryl hydrazyl on the other hand is much less active than triphenyl methyl in initiating chains below 80 to 90°C[109] but at higher temperatures it is believed to become active and to initiate reactions. Hydrogen abstraction by diphenyl picryl hydrazyl from mercaptans has been reported[115] to occur readily in the temperature range of 30 to 60°C with an activation energy of 15 kcal per mole.

Of the inorganic inhibitors oxygen is probably the most important and is most efficient as an inhibitor at lower temperatures. Since the inhibition products are peroxides, they catalyze polymerization at somewhat elevated temperatures. Oxygen is also in a sense a co-inhibitor, since, as mentioned earlier, hydroquinone inhibits only in its presence. Very likely, all phenolic stabilizers (for instance catechols) may utilize oxygen for the production of the actual inhibitor. Sulfur inhibition probably occurs by processes analogous to those for oxygen. Inhibition by copper metal and phenyl acetylene has been a problem in the commercial production of polystyrene[116].

Redox Polymerization

The initiation of polymerization by the decomposition of a single, usually relatively unstable compound has been discussed above. The production of polymers at lower temperatures presumably requires an activation energy for the production of radicals which is lower than the 30 or so kilocalories required for the decomposition of peroxides and like substances. The term "redox" has been applied to systems where a reducing agent facilitates the decomposition of an oxidizing agent. These systems are highly effective in bringing about polymerization and usually operate in an aqueous medium since the reducing agent is often a metallic ion. The most common example is the ferrous ion-hydrogen peroxide system. Many organic peroxides and hydroperoxides will also react with ferrous ion.

Haber and Weiss[118] established the following series of reactions for the decomposition of hydrogen peroxide induced by ferrous ion:

$$\begin{aligned} H_2O_2 + Fe^{2+} &\xrightarrow{k_f} HO^- + HO\cdot + Fe^{3+} \\ HO\cdot + Fe^{2+} &\longrightarrow HO^- + Fe^{3+} \\ HO\cdot + H_2O_2 &\longrightarrow H_2O + HO_2\cdot \\ HO_2\cdot + H_2O_2 &\longrightarrow HO\cdot + H_2O + O_2 \end{aligned}$$

That the hydroxyl radical intermediate reacts with added monomer is evidenced by the reduction or cessation of oxygen evolution and the formation of polymer. Since relatively large concentrations of radicals are easily produced, rapid polymerization ensues. This system is utilized in emulsion polymerization and is the basis for the production of the so called low temperature or "cold" synthetic rubber. Kinetic investigation of polymerization initiated by this peroxide system supports the idea that hydroxyl radicals start the growth in the polymer[119, 120].

Baxendale and Evans[121] in a study of the polymerization system showed that $k_f = 1.78 \times 10^9 \exp(-10{,}000/RT)$ mol^{-1} l^{-1} sec^{-1} and established its independence of the presence of monomer. Assuming the usual polymerization steps and steady state conditions one obtains the following equation for termination by the reaction of two growing polymer chains.

$$\log M/M_0 = \left(\frac{k_2}{(k_f k_4)^{1/2}}\right) \log (1 + a_0 k_f t)$$

The initial concentration of ferrous ions which is equal to the initial concentration of peroxide is represented by a_0. The experimental results agree with the above expression, and establish the concept of termination by the interaction of two growing polymer chains. An alternate expression based on the proposition that termination occurs by the reaction of a hydroxyl radical with a growing chain was not compatible with the kinetic results. The molecular weight distributions of methyl methacrylate polymers prepared with hydrogen peroxides are compatible with a mechanism such as is shown below[122].

Although the ferrous ion system is the most studied and used, other metals or metal ions such as chromous, mercury, cuprous, titanous, and manganous are effective with hydrogen peroxide in inducing polymerization. In practice, organic peroxides[123] are employed to a great extent instead of hydrogen peroxide in redox systems for emulsion polymerization. The generally accepted reaction scheme is as follows:

$$\mathrm{ROOR} + \mathrm{Fe}^{2+} \xrightarrow{k_f} \mathrm{RO}\cdot + \mathrm{RO}^- + \mathrm{Fe}^{3+}$$

$$\mathrm{Fe}^{2+} + \mathrm{RO}\cdot \xrightarrow{k'_f} \mathrm{Fe}^{3+} + \mathrm{RO}^-$$

$$\mathrm{RO}\cdot + \mathrm{M} \xrightarrow{k_1} \mathrm{R{—}O{—}M}\cdot$$

$$\mathrm{R{—}C{—}M}_n\cdot + \mathrm{M} \xrightarrow{k_2} \mathrm{R{—}O{—}M}\cdot_{n+1}$$

$$\mathrm{R{—}O{—}M}_n\cdot + \mathrm{ROOR} \xrightarrow{k_i} \mathrm{R{—}O{—}M}_n\mathrm{{—}O{—}R} + \mathrm{RO}\cdot$$

$$2\ \text{Radicals} \xrightarrow{k_4} \text{Polymer}$$

In order to obtain the maximum efficiency in the utilization of the initiating ingredients it is necessary to choose concentrations and conditions unfavorable to reactions k'_f and k_i . The first of these reactions removes a radical and the second decomposes peroxide without contributing additional radicals to the system. The k_i step is the same as that postulated by Nozaki and Bartlett[79] in the decomposition of peroxides. In the above scheme this step would also operate to reduce the chain length, i.e. function as a modifier. Such a process is sometimes referred to as peroxide or catalyst transfer. In order to sustain a smooth polymerization there must be available sufficient quantities of both peroxide and ferrous ion.

For controlling the redox system several additional ingredients are used in emulsion polymerization. A common recipe involves the following substances:

Monomer	100
Water	200
Benzoyl peroxide	0.5
Ferric ammonium sulfate	0.5
Sorbose	0.5
Sodium pyrophosphate	0.5
Sodium stearate	5.0

The sorbose reduces ferric ion to ferrous and the pyrophosphate will complex both states of iron and hence reduce the rate of the reactions involving iron ions. Since the organic peroxide is soluble mainly in loci containing monomer while the ferrous is to a large extent soluble in the aqueous phase their interaction is again retarded. The ferric or ferrous ions presumably react not as shown in the above reaction scheme but in the form of complexed or bound ions with either the pyrophosphate or the stearate. Wall and Swoboda[124] have demonstrated the function of the various ingredients in such redox activated emulsion polymerizations. Their results were best explained by the following scheme:

WATER LAYER

$$\begin{tikzcd} \begin{array}{c}\text{Fe}^{2+}\\ \text{(pyrophosphate complex)}\end{array} \arrow[r, "\text{Sorbose}"] \arrow[d, shift right] & \begin{array}{c}\text{Fe}^{3+}\\ \text{(pyrophosphate complex)}\end{array} \arrow[d, shift right] \\ \text{Fe}^{2+}\text{ (stearate)} \arrow[u, shift right] \arrow[r, "\text{Benzoyl peroxide}"] & \text{Fe}^{3+}\text{ (stearate) Free radicals} \arrow[u, shift right] \end{tikzcd}$$

MONOMER LAYER

The monomer layer undoubtedly refers to the soap micelles as well as the monomer-polymer particles derived from the micelles[125]. The greater portion of the ferric or ferrous iron is retained in the aqueous medium where the sorbose can reduce the ferric form to ferrous. The aqueous solubilization of the iron facilitates this process since the sorbose is water soluble. The stearate, although originally only an emulsifier, plays a primary role in the scheme by solubilizing the ferrous iron in the oil phase where the benzoyl peroxide requires it for the free radical generating step. If a cationic emulsifier is used, such as quaternary ammonium salts, the reaction fails through lack of ferrous iron in the oil saturated loci. In view of the theoretical treatments of Smith and Ewart[126, 142] and of Haward[127] it is interesting to note that the radical producing step generates a single radical.

A photochemical method of initiating polymerization in aqueous solutions which is related to the redox systems has been described by Evans, Santappa, and Uri[128]. The absorption of light by ferric ion complexes is assumed to result in an electron transfer within the complex.

$$\text{Fe}^{3+}\,\text{X}^- \xrightarrow[h\nu]{k_\epsilon \text{I}} \text{Fe}^{2+}\text{X}\cdot$$

where X^- represents OH^-, Cl^-, and N_3^-. The wave length of the light used by the above workers ranged from 313 to 435 mμ. The species produced by the absorption process may react in several ways.

$$\text{Fe}^{2+}\text{X} \xrightarrow{k_s} \text{Fe}^{2+} + \text{X}\cdot$$

The X· is a free radical which can presumably add to monomer to start polymer chains. It may also be possible that:

$$\text{Fe}^{2+}\text{X} + \text{M} \xrightarrow{k'_1} \text{Fe}^{2+} + \text{XM}\cdot$$

Other reactions which could occur are:

$$\text{Fe}^{2+}\text{X} \xrightarrow{k_b} \text{Fe}^{3+}\text{X}^-$$

$$\text{Fe}^{2+} + \text{X} \xrightarrow{k_0} \text{Fe}^{3+}\text{X}^-$$

With the usual initiation, propagation steps and termination by combination the over-all rate of polymerization is:

$$\frac{-dM}{dt} = k_2\left(\frac{k_1}{k_4}[X\cdot][M]\right)^{1/2}[M] = \frac{k_2}{k_4^{1/2}}\left(\frac{k_s k_\epsilon I}{k_b + k_s}\right)^{1/2}[M]$$

The step k_1' was found to be negligible. The experimental rate of monomer disappearance plotted against monomer concentration gave straight lines in accordance with the above expressions when acrylonitrile, methyl methacrylate, and methyl acrylic acid were used with $Fe^{3+}Cl^-$. The expression:

$$\frac{1}{d[Fe^{2+}]/dt} = \frac{k_b + k_s}{k_s k_\epsilon I}\left(1 + \frac{k_0}{k_1}\frac{[Fe^{2+}]}{[M]}\right)$$

enables one to evaluate k_0/k_1 from a plot of $1/(d[Fe^{2+}]/dt)$ *vs.* $[Fe^{2+}]$ and $k_s k_\epsilon/(k_b + k_s)$ from a plot of $(d[Fe^{2+}]/dt)[1 + (k_o[Fe^{2+}]/k_1[M])]$ *vs.* light intensity I. An estimate of $k_2/k_4^{1/2}$ can then be made from the data on the rate of monomer consumption as a function of monomer concentration. Table 14 contains these results.

TABLE 14. CONSTANTS FOR POLYMERIZATION WITH FERRIC ION PAIR COMPLEXES AS PHOTO-INITIATORS[128]

Ion pair	Monomer	k_0/k_1	$k_2/k_4^{1/2}$ (mole/l)$^{1/2}$ sec$^{-1/2}$
$Fe^{3+}O\bar{H}$	Acrylonitrile	4×10^3	
$Fe^{3+}\bar{C}l$	Acrylonitrile	6×10^3	0.156
	Methyl methacrylate		0.98
	Methyacrylic acid		1.56
$Fe^{3+}\bar{N}_3$	Acrylonitrile	5×10^2	
	Methyl methacrylate	46	
	Methyacrylic acid	50	

With $Fe^{3+}Cl^-$, polymer was obtained having two chlorine atoms per molecule indicating termination by combination. For this situation the following equation results for the number average chain length or degree of polymerization (D.P.).

$$\text{D.P.} = \frac{2k_2[M]}{k_4^{1/2}}\left(\frac{k_b + k_s}{k_s k_\epsilon I}\right)^{1/2}$$

In the case of methyl methacrylate reasonable agreement was observed between the chain lengths calculated by the above formula and those measured.

Bacon[129] has studied the effect of various reducing agents on persulfate polymerization, particularly the effect on acrylonitrile in aqueous solution.

Organic sulfides, hydrogen sulfide, and thiosulfate were effective activators. Nitrogen derivatives showing activity were hydroxyl amine and hydrazine, although the results obtained with these compounds depend on pH. Acid conditions were necessary for the former substance while basic conditions were required for the latter. Metal ions, ferrous, stannous, titanous, cuprous, silver, and finely dispersed metals, copper, silver and iron also activated the persulfate-acrylonitrile system.

Besides acrylonitrile, acrylic, methacrylic acids, and esters; vinyl halides, vinylidene chloride and vinyl esters are rapidly polymerized by these persulfate systems whereas styrene and butadiene polymerizations are least accelerated. These last two systems probably fail to accelerate because of their insolubility, since they respond quite easily to redox emulsion systems.

The mechanism of the persulfate-reducing agent initiated polymerizations is less firmly established than its analog, the ferrous ion-hydrogen peroxide reaction. This is partly due to possible side reactions and sensitivity to trace impurities[130]. With thiosulfate as the reducing agent the following reaction appears most likely as the first step.

$$S_2O_8^{=} + S_2O_3^{=} \rightarrow SO_4^{=} + SO_4^{-}\cdot + S_2O_3^{-}\cdot$$

The species $SO_4^{-}\cdot$ and $S_2O_3^{-}\cdot$ then add monomer and bring about the growth of polymer. There is also the reaction of such species with water molecules producing hydroxyl radicals which can add monomer.

$$SO_4^{-}\cdot + H_2O \rightarrow HSO_4^{-} + HO\cdot$$

In the absence of monomer the species having odd electrons probably undergo reactions of the type

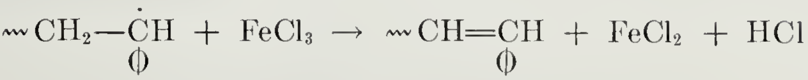
$$\left.\begin{matrix} SO_4^{-}\cdot \\ HO\cdot \end{matrix}\right\} + S_2O_3^{=} \rightarrow \left.\begin{matrix} SO_4^{=} \\ HO\cdot \end{matrix}\right\} + S_2O_3^{-}\cdot$$

Analogous reactions occur with any of the reducing agents described.

The persulfate-thiosulfate reaction can be made much more effective by the addition of cupric, ferrous or iodide ions. Very large increases in rate of polymerization and of persulfate decomposition occur when small amounts of either cupric or ferrous ion are added. For instance, a tenfold increase in the rate is obtained when 5×10^{-4} moles of cupric ion are added to the polymerization mixture of $0.05M$ ammonium persulfate, $0.01M$ sodium thiosulfate and $0.765M$ acrylonitrile in water. The results are interpreted to mean that the cupric ion, rapidly converted to cuprous by the thiosulfate, replaces the thiosulfate in reducing the persulfate. The reduction of the persulfate, of course, returns the copper to the cupric state and hence the system is a cyclic analog to the ferric ion-peroxide-sugar systems. Ferric ion can be substituted for cupric in the persulfate-thiosulfate reaction without any change in the mechanism.

With iodide ion the cyclic aspects are retained. The iodide ion reduces the persulfate and is regenerated by the thiosulfate. Without the thiosulfate the accumulation of iodine molecules would inhibit polymerization. The activation energies of these reactions range from 12 to 15 kcal, derived by studies carried out at temperatures of about 30 to 40°C.

Electron transfer processes between free radicals and cations of certain metals can also play a role in the termination of polymer chains. Various inorganic salts influence significantly the polymerization of vinyl monomers in nonaqueous solvents such as N,N′-dimethylformamide[130a]. A suggested mechanism for their influence is as follows:



$$\sim CH_2—\underset{\phi}{\dot{C}H} + FeCl_3 \rightarrow \sim CH{=}\underset{\phi}{CH} + FeCl_2 + HCl$$

Initiation of Polymerization by Electrolytic Processes

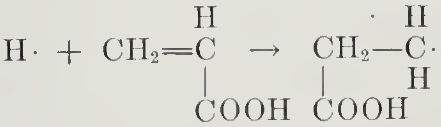
In the electrolysis of many organic compounds free radical intermediates have been postulated. In the presence of polymerizable monomers, such radicals might be expected to cause the formation of polymer. However, no published work has yet appeared where such systems, for instance, the electrolysis of organic acids, induced polymerization, although the results of such electrolysis indicate the following type of mechanism:

$$RCOO^- \rightarrow R\cdot + CO_2 + \bar{e}$$

$$R\cdot + R\cdot \rightarrow \text{Hydrocarbons}$$

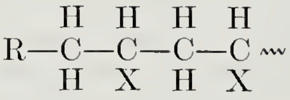
There are several other systems involving an electrolytic step which have been reported to initiate polymerization[131-133]. C. L. Wilson and co-workers[131, 132] found that acrylic acid, its methyl ester and methyl methacrylate polymerized when electrolyzed in sulfuric acid methanol solutions. Reduction to the saturated acid or ester was a competing process. The scheme believed to operate is as follows:

$$H^+ + \bar{e} \rightarrow H\cdot$$



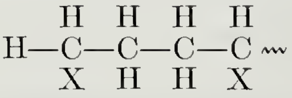
$$H\cdot + CH_2{=}\overset{H}{\underset{COOH}{C}} \rightarrow \underset{COOH}{CH_2}—\overset{\cdot\ H}{\underset{H}{C}}\cdot$$

The resulting propionate radical then adds to monomer. Dimer products were not formed in detectable amounts. The polymerization was established as being definitely the result of a cathodic process and was sensitive to the nature of the cathode. The metals which as cathodes produced polymerization are in the order of their effectiveness Pb, Sn, Hg, Pt, Bi, Fe, and Al whereas Cd, Ni, W, Ta, Mo, Cr, Ag, and Zn did not. This order is, except for the anomalous position of zinc and cadmium and of platinum and iron, quite compatible with an overvoltage sequence[134]. Wilson suggests that the initial radical is active in the beta position and propagates in the usual manner, hence there may be different terminal structures between a peroxide produced polymer



$$\mathrm{R{-}\underset{H}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}}\sim$$

where R = fragment of peroxide, and an electrolytic polymer



$$\mathrm{H{-}\underset{X}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}}\sim$$

which may be distinguishable by some determination of end group structure. Polymerization occurred only during the passage of current and could not be attributed to other factors such as peroxide formation. Hydroquinone did not inhibit the cathodic polymerization in the slightest degree. Wilson considers this as perhaps indicating that in ordinary polymerization this inhibitor reacts with the initiating peroxide radical and not with the growing chain. However, since electrolytic polymerization occurs at or near a metallic cathode and a considerable number of side processes are evidently occurring, this is hardly a firm conclusion. Apparently no attempts at inhibition using benzoquinone were made.

Crotonic acid did not polymerize during electrolysis, which is consistent with its known resistance to free radical polymerization. It is, however, reduced with difficulty to butyric acid, butyl alcohol and allyl alcohol, i.e., both olefinic and carbonyl reduction occurs.

Another possible method of employing electrolytic processes in polymerization is in the redox type of system to form the ferrous ion by electroreduction of the ferric thus:

$$\mathrm{Fe^{3+}} + \bar{e} \rightarrow \mathrm{Fe^{2+}}$$

$$\mathrm{Fe^{2+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{3+}} + \mathrm{HO\cdot} + \mathrm{OH^-}$$

A third possibility is the reduction of, in general, any oxidizing agent requiring more than one electron to reach a stable state. Intermediates active in polymerization should then occur after the first stage of reduction. The active intermediate, produced by the chemical reduction of persulfate has been used to initiate polymerization of various monomers[129]. The electrolytic reduction of the persulfate ion probably occurs in two stages.

$$S_2O_8^{=} + \bar{e} \rightarrow SO_4^{=} + SO_4^{-}\cdot$$

$$SO_4^{-}\cdot + \bar{e} \rightarrow SO_4^{=}$$

Kolthoff and Ferstandig[133] have succeeded in polymerizing aqueous acrylonitrile electrolytically in the presence of ferric compounds and oxidizing agents. Attempts to use the direct electro-reduction of organic peroxides

$$ROOR' + \bar{e} \rightarrow RO^{-} + R'O\cdot$$

$$R'O\cdot + \bar{e} \rightarrow R'O^{-}$$

as a means of initiating the polymerization of aqueous acrylonitrile were

Table 15. Cathodic Polymerization of Methyl Methacrylate Solutions at 24°C[135]

Cathode	Anode	Time for Polymer Formation (hr)	Hydrogen Overvoltage
Pt	Pt	>24	0.07
Pd	Pt	>24	
Ni	Pt	~18	0.74
Cu	Pt	~10	0.58
Zn	Pt	~6	0.75
Pb	Pb	2	1.09
Hg	Pt	1.5	

not successful as was the case of the inorganic persulfate, although there were some indications that a small number of free radicals were available as polymerization initiators. The authors[133] state that under proper conditions it is possible that the direct electro-reduction of the perdioxy-compounds may be a source of free radicals. Attempts to polymerize styrene and butadiene were not successful either in aqueous media in the presence of detergents or in methanol solutions. Acrylonitrile also failed to polymerize in alcoholic solutions and in systems containing dodecylamine hydrochloride.

Although the mechanisms have varied, polymerization as a result of electrolysis has thus far been confined to water-soluble monomers in aqueous systems.

In another study[135] the initiation of polymerization presumably by hydrogenation formed during electrolysis of aqueous solutions of methyl methacrylate was demonstrated and the results in Table 15 were obtained. It is seen that the efficiency of the process increases with the increasing over-voltage of the cathode. Metals such as platinum, palladium and nickel when loaded with hydrogen either by chemisorption or electrolytically also caused polymer formation in the absence of simultaneous electrolysis. The liquid from the cathode compartment was withdrawn after a brief electrolytic polymerization in which no turbidity had yet appeared, and added to more aqueous monomer solution. After a period of time polymer formation occurred in the absence of electrolysis and electrodes. These facts indicate apparently active hydrogen atoms on the metals, a small fraction of which initiate polymerization, the efficiencies of the processes being low. The solutions become activated by polymerization centers leaving the cathode. It is unlikely that these centers are hydrogen atoms but rather organic radicals formed by the reaction of absorbed hydrogen atoms with the monomer.

In the catalytic decomposition of hydrazine at palladium surfaces[136] and formic acid at platinum surfaces[137], the presence of free radicals has been indicated again by the initiation of polymerization of methyl methacrylate in solution, but not of acrylonitrile or methacrylonitrile. The nitriles were poisons for the catalytic decomposition of both the hydrazine and the formic acid. In the latter decomposition oxygen was necessary as neither decomposition nor polymerization occurred when the system was degassed. The rates of polymerization were in general proportional to the amount of metal catalysts, and the concentrations of monomer and decomposing substance. The degrees of polymerization were independent of catalysts and proportional to monomer concentration in both cases. The D.P. however was insensitive to hydrazine concentration in the one system although inversely proportional to formic acid concentration in the other. Active centers could also be shown to migrate away from the catalyst surfaces.

Polymerization Induced by Biological Systems

It has been reported[138] that washed suspensions of *B. coli* which are decomposing formic acid produce polymerization in methyl methacrylate solutions. This is evidenced by the development of turbidity after a period of several days at room temperature. The *B. coli* system was not studied extensively. The enzymatic dehydrogenation of formaldehyde by xanthine oxidase was, however, followed[138] in some detail. In degassed vessels this system was much more effective than the *B. coli* suspension in producing polymer. Oxygen was found to inhibit such polymerization. This work is a good illustration of the utility of polymer formation as a tool to indicate the presence of free radical species. At present there would seem to be no advantage to the employment of such systems in the production of polymers.

Emulsion Polymerization

Bulk polymerization is not rapid enough at reasonable temperatures nor is the product desirable from the point of view of rubber manufacture. Heat development during polymerization is also quite large and can lead to uncontrolled reaction. Better methods of polymerization were therefore required from the commercial viewpoint. Since natural rubber occurs in colloidal form the idea of emulsion polymerization must be attributed to nature. This type of system has been found to give much faster rates of reaction and higher degrees of polymerization than bulk at comparable temperatures. Reviews of the subject prior to 1946 have been given by Talalay and Magat[139] and by Hohenstein and Mark[140]. Since that time the work of Harkins[141] and of Smith and Ewart[142], has clarified the chief aspects of the emulsion system.

Besides the monomer and water, the minimum ingredients for emulsion polymerization are an emulsifying agent, i.e., soap, catalyst, and modifier usually a mercaptan. A typical laboratory recipe is as follows:

Monomer	100 g
Water	180
Sodium oleate	2
Ammonium persulfate	0.3
Isohexyl mercaptan	0.3

At 30°C the above system requires about two days in order to reach high conversion. With redox systems much faster rates are achievable at 0°C and below. Besides potassium and sodium persulfate benzoyl peroxide, cumene hydroperoxide, and *tert*-butyl hydroperoxide are commonly used catalysts. Provided there is sufficient agitation and a monomersoluble catalyst, suspension or pearl polymerization results in the absence of soap. This amounts to a water cooled bulk polymerization and is not of any particular fundamental interest. It is evident that Fikentscher[143], Fryling[144] and others had essentially correct views as to the initiation of emulsion polymerization in the aqueous phase. However, the mechanism of initiation and over-all reaction based on the soap micelle structure suggested by McBain[145] has been most clearly and adequately outlined by Harkins[141].

Such systems are naturally complicated in view of the numerous ingredients and their varying distribution among the two phases. Initially there exists, when monomer, soap and water are agitated, an aqueous phase containing emulsified monomer droplets about 1μ in diameter and soap micelles about 0.005μ. Most of the soap is in the form of micelles. Once polymerization occurs a new species appears known as the monomer-polymer particles, which according to Harkins are derived from the soap micelles. It is in these that the major amount of polymerization occurs. Small amounts of reaction can of course occur in all parts of the system since depending on its solubility monomer is distributed throughout the system. The aqueous phase is also probably a secondary locus for initiation. The mechanism involves the formation of radicals probably in the aqueous phases if persulfate catalysts are used; these radicals rather quickly enter a soap micelle and find there sufficient dissolved monomer for propagation. The monomer droplets then serve as reservoirs while the activated micelles grow into larger monomer-polymer particles, reaction continuing until depletion of the reservoirs. The locus of reaction cannot be the monomer droplet because it is experimentally found that these droplets are at least a thousand times the size of the polymer particles formed.

It has been demonstrated that in water saturated with monomer and containing catalyst, polymerization will occur, although at a relatively slow rate. A study[141] of the initial particle sizes in such a case versus that obtained when soap is added shows two quite different distributions. In the soap case almost all particles have diameters grouped around the value 1850Å while the soap-free system has a broad distribution from about 500 to 3000Å. The rate of reaction at low soap concentrations depends on the amount of soap, increasing initially as more soap is used. Both of these facts strongly support the theory that in emulsified systems reaction occurs mainly in the micelles initially and then in monomer-polymer droplets.

Although the production of high molecular weight polymer with a simultaneous rapid rate of conversion was attributed by some earlier authors[146] to a low termination rate due to high viscosity in the swollen polymer particles the most satisfying explanation arises from the theory developed by Smith and Ewart[142] based on the Harkins[141] model of the emulsion polymerization system.

The theory considers three special cases of free radical reactions in isolated loci:

1. The number of radicals per locus is much less than one,
2. The number of radicals per locus is approximately one half, and
3. The number of radicals per locus is much greater than unity.

The radicals are considered to originate outside the loci or from substances also diffusing into the loci. Case 1 and 3 do not in general apply to emulsion polymerization. In case 1, if termination is chiefly in the water phase, the rate law is similar to that for oil phase polymerization but the initiation and termination constants are those for the water solution. The ratio of radicals in the loci to those in the aqueous phase is important and the rate is independent of the size of the loci. If termination is in the reaction loci the rate behavior is again the same as in oil phase but now the termination constant becomes the rate of transfer out of the loci. This is due to the fact that one of two radicals must leave a locus in order to terminate with the other. Case 3 is equivalent to bulk polymerization.

Case 2 is the most interesting and is applicable to what is normally called emulsion polymerization. The rate in this case is simply determined by the rate of propagation and the number of reaction loci. Hence, from a knowledge of the number of particles, concentration of monomer in particles and overall rate, the propagation constants can be calculated. The necessary requirement for this case to occur is that the rate of escape of radicals from loci must be negligible and the rate of diffusion into a particle must be smaller than the rate of the oil phase termination. Then, on the average, one half of the loci contain one free radical and the rest none. For the overall rate per cc of water solution we then have:

$$-dM/dt = k_2\,(M)\,(N/2)$$

where N is the number of loci and M the concentration of monomer in the loci. Since it is possible to produce a very much larger number of particles per cc of solution in emulsion polymerization than there are free radicals in bulk systems a much faster rate of reaction in the former case can be attained. Moreover we have the following expressions for the number average D.P.:

$$\text{D.P.} = k_2\,(M)\,N/\rho = k_2\,(M)\,\tau$$

where τ is the average lifetime of a growing radical and ρ is the rate of free radical formation per cc of water solution. It can be seen from the above that the D.P. will increase with the number of particles as will the lifetime.

The rigorous calculation of the number of particles is rather involved. Hence, Smith and Ewart made two calculations based on two different assumptions. One assumption that only the very small soap micelles (containing dissolved monomer) capture free radicals as long as such species are present, gives too high a result. The other that a given interfacial area will always have the same effectiveness in capturing radicals gives too low a result. Neither assumption can be true but the actual situation is probably intermediate between the two. In both cases the soap present in other forms is neglected, and the interfacial area a_s as occupied by a gram of soap is considered the same whether on the soap miscelles or on the polymer particles, which of course are formed from the micelles. Both considerations lead to the equation:

$$N = k\left(\frac{\rho}{\mu}\right)^{2/5}(a_sS)^{3/5}$$

where S is the amount of soap per one cc and μ is the rate of increase in volume of a particle, except that k is 0.53 with one assumption and 0.37 with the second. The actual situation then requires an intermediate value for k. Fortunately the extreme k-values are not greatly different.

Smith[147] has presented considerable experimental evidence to substantiate the above theory for the emulsion polymerization of styrene using persulfate under conditions where case two is likely to operate. Utilizing the electron microscope for measurements of particle size he made a series of seeding studies in which the initial and final volumes of the particles were determined. The total polymer before and after was also measured. Table 16 summarizes the data.

It can be seen that the number of particles does not change greatly, if at all, even though the average particle size has increased 50 to 70 times. Under the typical conditions used, it is estimated[147] that particle formation from the micelles requires of the order of 10 to 100 seconds, if free radicals only enter the soap micelles during the initial period. For the number of particles when soap is no longer available to the micelles and hence no more particles can be formed, is about 10^{14}-10^{15} and the rate of free radical formation is 10^{13} per second. The actual time required will be longer, but it is clear that the majority of the soap micelles will be converted to monomer-polymer particles within the first few minutes of the reaction. The lifetime of a propagating radical in a particle is also about 10 to 100 seconds while the time for termination once a second radical enters a particle is estimated at 10^{-3} seconds. The time a given free radical remains in the aqueous phase is estimated at 10^{-5} seconds which is not sufficient to permit reaction with aqueous styrene or termination with another radical. This implies that practically all radicals enter the polymer particles before more than one or two additions to monomer.

TABLE 16. INCREASE IN POLYSTYRENE PARTICLE SIZE DURING POLYMERIZATION[147]

Average initial volume of particles = 0.618×10^{-16} cc

$\frac{\text{Final polymer}}{\text{Initial polymer}}$	2.09	2.2	3.57	4.86	9.6	17.3	17.9	32.7	70.5
$\frac{\text{Final volume}}{\text{cc} \times 10^{-16}}$	2.11	1.77	3.72	3.25	5.98	8.27	17.1	14.9	32.8
$\frac{\text{Final no. of particles}}{\text{Initial no. of particles}}$	0.62	0.77	0.60	0.94	0.99	0.29	0.65	1.35	1.33

On the basis of the above theory, calculation of the propagation constant for styrene gives[147]:

$$k_2 = 3.5 \times 10^{10}\, e^{-11{,}700/RT} \text{ l/mole/sec}$$

This result is reasonable in view of the complexity of emulsion studies and is comparable with those obtained by rotating sector experiments[148].

Thus in systems where case 2 of Smith and Ewart's is valid the measurement of absolute propagation rates is feasible. For several monomers, rates have been determined in this manner[149-151]. In order to obtain precise data one must use an emulsion recipe which gives linear rates of polymerization over the range of conversion (30 to 60 per cent) where the number of particles is essentially constant. Addition of catalysts in this region of conversion should not change the rate of polymerization indicating that a maximum number of particles are formed and active. Not all catalysts systems give the desired behavior[149]. In Table 17 values for the rate constants obtained in emulsion systems are shown and compared with rotating sector results. The catalysts systems used are given in the table and all presumably behaved satisfactorily. The results appear to be remarkably consistent.

The high molecular weights found in the emulsion reaction may indicate fewer transfer processes than in the bulk systems. It is quite likely, however, that viscosity effects found at high conversion in bulk are operating within the monomer-polymer particles.

TABLE 17. ABSOLUTE PROPAGATION RATE CONSTANTS

Monomer	Catalyst System	E	$A_2 \times 10^{-7}$ (l/mole/sec)	k_2 (60°C) (l/mole/sec)	Ref.
Styrene	Persulfate	7.4	4.1	277	151
Styrene	Cumene hydroperoxide triethylenetetramine	8.4	3.3	221	151
Styrene	Photo-initiation	7.8	2.2	176	46
Styrene	Rotating sector	6.5	0.102	57	148
Styrene		9.0	38.0	510	148
Butadiene	Peroxamine	9.3	12	100	142
Isoprene	Diisopropylbenzene monohydroperoxide Tetraethylene pentamine	9.8	12	50	151

Although the Smith-Ewart treatment certainly applies when the catalyst is soluble in the aqueous phase it is also evident that similar effects will occur with an oil-soluble catalyst. For if two radicals are formed within a particle by the decomposition of an oil-soluble catalyst they would certainly be able to diffuse or transfer out of a locus as easily as they could enter one, providing they did not propagate to any great extent.

Haward[127] has also treated theoretically polymerization in discrete particles, obtaining much the same result as Smith and Ewart in the case of one radical per active particle. Where two radicals are completely isolated in a given particle the rate of polymerization will decrease with decreasing size of particle and would presumably be negligible under emulsion conditions. This follows from the fact that the lifetime of the radicals would approach zero.

The fundamental reason for the enhanced rate of reaction and simultaneous large molecular weights in emulsion systems is the isolation of the growing chains once they attain an appreciable size (5 to 10 monomer units), and hence cannot leave a monomer-polymer particle. The number of growing radicals is then of the same order as the number of particles, which can be much greater than the number of free radicals in the bulk polymerization. It is probably true that even two large radicals in the same particle would have a decreased probability of termination due to viscosity effects such as are found in the high conversion bulk reaction[146] but this is of secondary importance. It has also been observed[152] that in the benzoyl peroxide catalyzed polymerization of methyl methacrylate small amounts of water decreased the induction period and this effect may be significant in emulsion polymerization.

In emulsion copolymerization there is no apparent difference in the composition of the product from that obtained in bulk or solution systems as long as the solubility properties of the two monomers are similar. In the styrene-acrylonitrile copolymerization a small difference is observed[153] which is adequately explained by the larger water solubility of acrylonitrile over styrene. With itaconic acid and styrene as comonomers a very marked difference appears[154] which evidently results from the very high solubility of the acid in water.

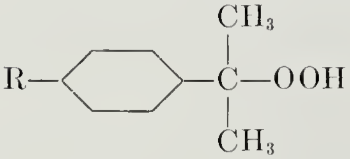
A decrease in pH usually occurs during emulsion polymerization and it has been found advantageous to buffer the emulsion. The factors causing variations in pH are quite complex. Initially the pH is on the alkaline side due to the hydrolysis of the soap which factor is reversed at appreciable conversion due to the absorption of the emulsifier at the polymer interface. Most catalysts also produce by-products which are acidic, lowering the pH. Frying and Harrington[144] have studied the rather complicated fashion in which the pH varies when neutral organic liquid is added to a soap solution. Initially the pH drops, due to the removal of soap by inclusion in micelles with the solubilized organic liquid, i.e., monomer. With the appearance of a distinct oil phase the pH rises because the hydrolysis equilibrium is shifted by the solubility of the fatty acid in the organic phase. In polymerization the organic phase decreases and eventually disappears, hence the pH drops. The over-all pH change will depend on the importance of the various factors in a given case.

With the redox system (see pp. 227–233 on redox polymerization) polymerizations are now carried out at temperatures near 0°C and below. For such systems several additional ingredients in the emulsion recipe are required, chiefly ferrous sulfate, dextrose and, where temperatures below 0°C are used, an antifreeze substance. In the redox emulsion polymerization cumene hydroperoxide[155] is commonly used as the catalyst. Several studies[156, 157] on the effectiveness of various hydroperoxides as low temperature initiators have shown considerable dependence on structure. Furthermore, the amount which gives optimum results varies for different hydroperoxides and appears to depend somewhat on molecular weight. In general, a higher amount of ferrous ion per mole hydroperoxide is required in order to attain the maximum rate of polymerization as the molecular weight of the catalyst increases. The presence of impurities in the hydroperoxides does not alter the results greatly, although purified samples always give somewhat better results. The relative efficiencies of some initiators are presented in Table 18[157]. Many of the compounds were oxidized mixtures containing the parent compound, but presumably the active ingredients contained hydroperoxy-groups where the parent compound possessed a *tert.*-hydrogen

TABLE 18. ORDER OF EFFECTIVENESS OF VARIOUS HYDROPEROXIDES AS INITIATORS FOR EMULSION POLYMERIZATION AT 5°C[157]

Hydroperoxide	Conversion (%)/hr
Chlorodiisopropylbenzene hydroperoxide	15.8
Di-*tert.*-butylisopropylbenzene hydroperoxide	14.7
Cyclohexylbenzene hydroperoxide	14.3
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene hydroperoxide	13.2
tert.-Butylisopropylbenzene hydroperoxide	13.1
Chloroisopropylbenzene hydroperoxide	11.1
Triisopropylbenzene hydroperoxide	10.2
(1-Methylhendecyl)-toluene hydroperoxide	9.8
Diisopropyltoluene hydroperoxide	9.4
Isopropyl-1,2,3,4-tetrahydronaphthalene hydroperoxide	9.1
o-, *m*-, *p*-Diisopropylbenzene hydroperoxides	8.8
(1-Methylhendecyl)-isopropylbenzene hydroperoxide	8.7
m-Diisopropylbenzene hydroperoxide	8.6
1-Methyl-1,2,3,4-tetrahydronaphthalene hydroperoxide	8.3
5-(4-Isopropylphenyl)-2-pentenehydroperoxide	8.2
1,2-Bis-(dimethylphenyl)-butane hydroperoxide	8.0
1,2-Diphenylbutane hydroperoxide	7.7
2,2,5-Trimethylhexane hydroperoxide	7.7
p-Cymene hydroperoxide	7.5
o-, *m*-, *p*-Cymene hydroperoxides	7.3
Hydroperoxide from aliphatic alkylate	6.5
(1-Methylbutyl)-isopropylbenzene hydroperoxide	5.9
Cumene hydroperoxide	5.8
Methylcyclohexane hydroperoxide	4.6
1,2,3,4-Tetrahydroperoxide	4.0
2,3-Dimethylbutane hydroperoxide	3.3
sec.-Butylbenzene hydroperoxide	2.2
5-Phenyl-2-pentene hydroperoxide	2.0

atom. The rate of conversion is based on the time required for 60 per cent polymerization and on the optimum results obtained for each substance. There are probably several factors involved besides the actual rate of hydroperoxide decomposition upon which the effect of structure is decisive as has been shown previously. The concentration of hydroperoxide in the aqueous phase is believed important[156]. The diffusion rate in the aqueous phase of the catalyst may influence its activity[156] since the fastest rates were associated with substituted aromatic hydroperoxides of the cumene type where the substitutent groups contain more than 3 carbons but less than 15. In comparing the rates of Table 18 for the structures of the type[157]



we find the following decreasing order of effectiveness of the substituent R: *tert.*-butyl > chloro > isopropyl > *sec.*-dodecyl > methyl > *sec.*-amyl > hydrogen. However, no exact correlation with structure should be made because of the superimposed factors of solubility and molecular weight.

An interesting point is the fact that styrene ozonide will function in redox emulsion systems to give 60 per cent conversions in about 1 hr at 40°C[158]. It has also been shown that molecular oxygen can be substituted for the oxidizing substance in redox systems[159]. It is of course well known that oxygen normally inhibits many bulk and emulsion systems.

Certain organic polyamines have been shown[160] to be effective as reducing agents in the activator systems for emulsion polymerization, replacing both the iron or other heavy metal salts and the sugar. However, the rate of polymerization in these recipes is influenced by the presence of traces of iron and can sometimes be enhanced by the presence of sugar[161]. The concentrations of these materials, giving optimum rates, vary with the nature of the polyamine and the temperature. The structure of the monomer will also influence the operation of an activator mixture. For instance, the usual polyamine systems that are effective for butadiene-styrene copolymers are not effective for butadiene-acrylonitrile copolymers[162].

The possible combination of reducing and oxidizing agents which can conceivably act as activators for polymerization, especially emulsion polymerization, is unlimited. The mechanism involved in these systems is obviously complex and very few attempts at elucidating such processes have been made. One interesting study[163] of the reaction between cumene hydroperoxide and ferrous iron complexes of the polyamines shows that the process is first order with respect to hydroperoxide and dependent on the pH of the medium. The primary step is believed to be:

$$ROOH + RNH_2{:}A \rightarrow RO\cdot + RNH\cdot + A + H_2O$$

where A may be Fe^{2+}, $FeOH^+$ or $Fe(OH)_2$. It was also demonstrated that with the polyamines $H_2N(CH_2CH_2NH)_xH$ an increase in size, (larger x in the above formula), led to more rapid reaction.

The action of mercaptans in emulsion polymerization is essentially, as in the bulk or solution reaction[126], that of a transfer agent, although they also function as reducing agents and lead to some increase in rate of polymerization[164]. It is rather well established that through the transfer reaction, mercaptans serve to control the molecular weight of the final polymer and to delay the formation of gel. Smith has presented experimental evidence establishing the nature of the factors controlling mercaptan efficiency in emulsion systems similar to the studies of Mayo[11, 165] on bulk systems. In conditions usually employed, the polymer is found to contain one mercaptan unit per molecule, hence it is evident that:

$$\text{No. Av. D.P.} = dm/dM$$

Table 19. Transfer Constants 60°C[126]

System		C
Styrene	*tert.*-butyl mercaptan	4
	n-butyl mercaptan	22
	n-amyl mercaptan	20
Methyl methacrylate	*n*-butyl mercaptan	0.67
	n-amyl mercaptan	0.8

where dm/dM is the mole ratio of monomer consumed to mercaptan consumed. This can be rewritten[11] as:

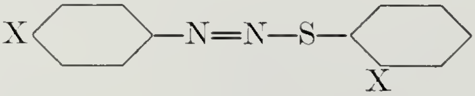
$$\frac{d \ln M}{d \ln m} = \frac{k_3}{k_2} = C$$

where the transfer constant k_3/k_2 is the ratio of the elementary transfer rate constant to the propagation. Determination of the polymer yield versus mercaptan reacted for various starting mixtures should then give sufficient data to calculate C. In practice rather good straight lines are obtained when $d \ln M$ is plotted *vs.* $d \ln m$ the slope of which is C. Table 19 gives some of these results. Smith found little effect due to temperature and no difference between emulsion and bulk polymerization in the cases of *tert.*-butyl and *n*-amyl mercaptans in styrene and *n*-amyl in methyl methacrylate.

In studies of the action of *n*-alkyl mercaptans in the emulsion polymerization of butadiene it was found that where the alkyl group ranged from C_5 to C_{10} the mercaptans were equally effective in oil phase and in emulsion polymerization. Mercaptans from C_{11} to C_{14} were increasingly less active in the emulsion system than in the bulk. With the higher mercaptan it then appears that the rate of diffusion through the aqueous phase is a controlling factor in determining the rate of their reaction. The rate of reaction of the higher mercaptans could also be increased by increasing the pH of the emulsion. At high pH more mercaptan is soluble in the aqueous phase and hence diffusion into the monomer-polymer particles is more rapid.

Smith also derived the relationship between the transfer constant of a copolymerizing mixture and the transfer constant of each individual monomer with the same mercaptan and found good agreement in the case of styrene-methyl methacrylate mixtures. Since only two transfer steps were assumed, i.e., the radical ending in styrene unit plus the mercaptan and the radical ending in a methyl methacrylate unit plus the mercaptan, the result indicates quite clearly that the rate of transfer depends only on the terminal structural of the radical chain end.

An interesting series of compounds which are useful initiators for polymerization and which are also capable of regulating, i.e., reducing the molecular weight of the resulting polymers, are the diazothiolic esters or diazo thioethers[166]. These compounds have the following type of structure:



and, depending on the nature of the group X, may be either oil or water soluble. They are easily prepared by coupling diazotized aromatic amines with aliphatic or aromatic mercaptans. The activity of a series of diazo thioethers in emulsion polymerization is demonstrated in Table 20. The first column shows their relative effectiveness as initiators and the second column gives an index of their modifying ability. A value less than one in the second column indicates increasing polymerization rates with increasing DTE concentrations, while values greater than one imply an increase in modifier action with increasing concentrations. The diazo thioethers are assumed to initiate polymerization by a unimolecular decomposition into nitrogen and radicals of the types R• and RS• which then react with monomer. Their modifying action is considered to result from the reaction of a growing chain with a diazo thioether molecule, setting free another small free radical and terminating the growing chain. This amounts to the induced decomposition of the ether and has no effect on the net number of free radicals. The most active diazo thioethers have little modifying action since chain initiation predominates. The two functions, initiation and modifying action, are nicely balanced for ethers of moderate activities which are nearly independent of concentration. In the less active substances the modifying action predominates and initiating ability decreases with concentration.

Gel Point. In emulsion polymerization the formation of infinite molecular networks called gels occurs at conversions >60 per cent. This results in insoluble materials which are intractable in milling. Presence of relatively small amounts of mercaptan or other transfer agents is known to delay the appearance of gel which is indicative of a reaction linking together polymer molecules. Since gel formation is highly characteristic of diene polymerization, the most logical conception of this process is the propagation of growing radicals through the olefinic groups which are part of the polymer molecules. On this basis the theoretical treatment has been carried out[167] and a relationship obtained:

TABLE 20. EFFECT OF DIAZO THIO ETHER CONCENTRATION ON EMULSION POLYMERIZATION RATES AT 50°C[166]

Diazo thio ether	Polymerization Rate*	Ratio Rate**
2-(2,4-Dimethylbenzenediazomercapto) naphthalene	16.5	0.55
2-(4-Methoxybenzenediazomercapto) naphthalene	10.0	0.92
2-(4-Methylbenzenediazomercapto) naphthalene	9.7	0.97
2-(2-Methylbenzenediazomercapto) naphthalene	9.4	0.94
2-(3-Methylbenzenediazomercapto) naphthalene	7.5	1.13
2-(2,5-Dimethoxybenzenediazomercapto) naphthalene	7.1	1.10
4-(2,4-Dimethoxybenzenediazomercapto) toluene	6.0	1.20
4-(2-Naphthalenediazomercapto) anisole	5.3	1.64
tert.-(4-chlorobenzenediazomercapto) octane	5.3	1.65
2-(Benzenediazomercapto) naphthalene	5.0	1.65
2-(4-Acetylaminobenzenediazomercapto) naphthalene	3.7	1.83
2-(2-Naphthalenediazomercapto) naphthalene	3.7	2.00
2-(4-Sulfobenzenediazomercapto) benzothiazole	3.4	1.40
2-(1-Naphthalenediazomercapto) naphthalene	2.7	2.30
2-(4-Chlorobenzenediazomercapto) naphthalene	1.7	1.92
2-(5-Quinolinediazomercapto) naphthalene	1.5	2.15
2-(2-Quinolinediazomercapto) naphthalene	1.1	2.78
2-(4-Nitrobenzenediazomercapto) naphthalene	0.4	1.44

* Polymerization rate, per cent/hour for DTE concn. of 10 millimoles/100 g monomer.

** Ratio of rate at 1 millimole/100 g. Monomer to rate at 10 millimoles/100 g monomer.

$$\frac{d\nu}{d\alpha} = \frac{2k_c}{k_2}\frac{\alpha}{1 - \alpha}$$

where ν is the number of moles of cross-linked units per mole of initial monomer, α the fractional conversion, k_c the rate constant for cross linking, i.e., the propagation through the unsaturation in dead polymer, and k_2 has its usual significance. The gel point occurs, according to random statistics when ν/α is equal to the reciprocal of the weight average degree of polymerization. The size of the "primary" molecules, that is, those which would result if cross-linking was nonexistent, determines the point at which gel formation will occur. It is easily visualized that the larger the "primary" molecules the more probable the production of networks and, hence fewer cross-links are needed to form gel. Transfer agents then act merely to reduce the size of the "primary" molecules[167].

The application of this theory enables one to measure the ratio k_c/k_2 by measuring rate of mercaptan consumption, and the conversion at which gelation occurs. This measurement has been reported[168, 169] for two monomers, butadiene and isoprene. The values obtained at 60°C for the ratio k_c/k_2 were, respectively, 20×10^{-5} and 3.4×10^{-5}, l/mole/sec. Since the propagation constants are known (see Table 17) the cross-linking constants can be obtained and are summarized below:

$$\text{(Butadiene) } k_c = 1.9 \times 10^9 \, e^{-16{,}800}/\mathrm{RT}$$

$$\text{(Isoprene) } k_c = 8.5 \times 10^6 \, e^{-14{,}800}/\mathrm{RT}$$

The lower pre-exponential factor in polyisoprene seems explainable on the basis of steric factors due to the presence of the methyl group in the isoprene unit and also, perhaps, the smaller number of pendant vinyl groups, which result from 1,2 polymerization, in this polymer. The lower activation energy seems reasonable in terms of the possible effects of the methyl group on the double bond in the polymer.

Initiation by Atomic Radiations

Here we discuss the induction of polymerization by means of neutrons, β- and γ-rays, as well as secondary effects arising from the primary radiations. During the last thirteen years or so, that is since World War II, a number of investigations have been undertaken which deal with the general production of free radicals by the above high energy sources. Some of these are specifically concerned with polymerization of vinyl compounds.

Early qualitative work indicated the possibility of producing polystyrene and polymethyl methacrylate by neutrons[170, 171] γ-rays[170, 172] and x-rays[172]. More recently Dainton[173] studied quantitatively the polymerization of acrylonitrile in dilute aqueous solutions irradiated with γ-rays and x-rays as an indicator of free radical formation. A series of extensive investigations covering several polymers and solvents, and various radiations has been carried out in the laboratory of M. Magat. Prevot[174] examined the possibility of characterizing x-ray dosage by polymerization effects and added vinyl acetate to the previously used three polymers.

The use of slow neutrons has the advantage that the number of free radicals directly initiated can be evaluated. The production of activated molecules occurs in this case by the Szilard-Chalmer mechanism[175]. The capture of a thermal neutron is followed by the emission of one or more high energy quanta. Their emission in turn produces a recoil in the nucleus. It is so intense (see Table 20) that the bond linking the atom to the rest of the molecule is broken and furthermore the ejected atom has such a high kinetic energy that secondary active atoms and radicals are produced by collision. Actually it turns out that the secondary centers are primarily responsible for the polymerization[176]. Thus the initiation by attack on a molecule RN, where N contains the capturing nucleus, and the subsequent process may be written as:

TABLE 21. CAPTURE CROSS-SECTION PERTINENT ENERGIES AND LIFE TIMES OF SOME ELEMENTS[176]

Elements	$\Sigma 10^{-8} \text{Å}^2$	E (recoil) × 10^{-3} kcal mole^{-1}	E^a kcal mole^{-1}	Half life
H_1	0.31	38	83	Stable
Cl_1	38.5	13	—	37.5 min.
Br_{35}	6.6	4	64	18 min. 4.5 hr 33.6 hr
I_{53}	6.5	2.2	50	25 min.

[a] Bond to carbon.

$$R\ {}^{A}_{Z}N + {}^{1}_{0}n \rightarrow R\ {}^{A+1}_{Z}N + h\nu \rightarrow R. + {}^{A+1}_{Z}N^*.$$

$$N^* + RN \rightarrow R\cdot + N\cdot + N^*\cdot$$

$$R\cdot + CH_2CHX \rightarrow RCH_2CHX\cdot$$

$$N^*\cdot + CH_2CHX \rightarrow N^*\,CH_2CHX\cdot$$

Since $N^*\cdot$ is radioactive, a corresponding activity in the chains bound by primary radicals is to be expected. Table 21 shows some cross-sections for neutron capture $\sum$, recoil energies, bond energies referred to the bond with carbon, and the half lifes of the radioactive atoms N^*. It is assumed that the γ-emission occurs in a single quantum.

In order to produce radioactive atoms, necessary for a quantitative determination, ethyl bromide was chosen[177] because of its relatively stable isotope and reasonably large cross section. Polymerization takes place in pure styrene, due to a Szilard-Chalmers effect with hydrogen. In the presence of bromide, radioactive material with a half life of 33.6 hours appears. At room temperature and in a period in which no polystyrene is formed in the absence of catalyst, conversions of a few per cent are possible.

The authors[177] carried out a kinetic analysis for styrene in terms of the usual chain mechanism including transfer with solvent and monomer. Taking into consideration the initiation of primary radicals by a Szilard-Chalmers effect on (1) the hydrogens in the monomer and solvent and (2) a nucleus X (e.g., Br) in the solvent, one has for the rate of initiation I per unit volume:

$$\mathrm{I}/N_nA = f_{\mathrm{H}} \sum_{\mathrm{H}} [n_H^M \mathrm{M} + n_H^S S] + f_X \sum_X n_X^S SF$$

Here N_nA is the neutron flux through the surface A per unit volume, $n_{\mathrm{H}}^{\mathrm{M}}$, $n_{\mathrm{H}}^{\mathrm{S}}$, n_X^{S} are the respective number of atoms H and X in monomer and solvent, and f_{H}, f_{X} efficiency factors, for instance $f_{\mathrm{H}} \geq 2$, since each H attacked leads to an active atom (D) as well as a residual radical. The factor $F \leq 1$ is introduced to account for the probability $1 - F$ of recombination of active atoms and radicals. For pure C_2H_5Br, $F = 0.25$[178] and recombination decreases with increasing concentration M. The following interpolation formula is suggested:

$$F = a + bM^z$$

From the over-all kinetics as a function of composition and assuming various values of the constants a, b, and z one deduces $f_{\mathrm{Br}}/f_{\mathrm{H}}$ to be 0.38 to 0.47.

Assuming the value of the kinetic chain length determined from thermal polymerization at the same temperature[17], one can calculate from the rate of conversion the rate of production of active centers (see pp. 192–196). It turns out that the primary effect makes only a small contribution, about 1 per cent of the total. The other sources are (1) the γ photons emitted on capture, (2) β- and γ-radiation of the radioactive Br atoms, and (3) collisions with high energy Br- and D-atoms. In a series of ingenious experiments, the parts contributed by photons and electrons of known number and intensity similar to that in the original experiments, and by primary Szilard-Chalmers particles were separated. Preliminary results gave the following orders of magnitude for the percentage contributions to the total production of polymer:

	Per cent
Primary	8
β	4
γ	4
High energy collision	84

We now turn to a consideration of the effects of γ-radiation as obtained from a radium source. Initially high energy electrons are produced. These interact with a molecule in four possible ways: (a) simple ionization, (b) ionization accompanied by decompositions yielding at least one free radical with each ion, and (c) decomposition into free radicals. For our purposes step "b" is most important, since in the liquid state recombination of the radicals formed by mechanism "c" is favored.

In his study of the system acrylonitrile-water at a molar concentration of about 0.1, Dainton[173] actually found an enhanced polymerization at room temperature. For example, about 20 per cent conversion occurs in 20 cc of solution after 20 hr of irradiation by a source of 0.6 g Ra. This is due to the presence of H· and OH· species, the latter being shown to be incorporated in the polymer. Furthermore, the over-all rate of reaction is proportional to the first power of intensity I of radiation, and to the square of the monomer concentration. Mutual termination of growing radicals would require a one-half power dependence on the intensity. Therefore the results indicate that the primary radicals participate in the initiation and the termination as well.

This may be compared with the results in the French laboratory[177, 179]. The progress of the polymerization was followed by dilatometry, the temperature varying between 11 to 16°C. The over-all rate may be judged from the results: A radium source of 0.4 g was placed at a distance of 4.5 cm from the sample. It is noteworthy that correcting for the differences in intensity and taking account of the induction period of an hour, found by Dainton, one finds that the rate of polymerization of pure acrylonitrile is only a small fraction, of the order of $1/10$ to $1/20$, of that observed in aqueous solution. Thus the presence of a suitable diluent is important and makes a study of a number of monomer-solvent combinations desirable. In these experiments the rate turns out to be proportional to $I^{1/2}$. Thus the growing radicals terminate each other. The most general kinetic scheme allows for a rate of initiation

$$I(\varphi_M M + \varphi_S S)$$

where the φ's are the probabilities of producing a radical by irradiation of monomer M and solvent S, respectively. There follows a transfer step in which both M and S participate:

$$k_{3\text{M}} M(M\cdot + SM\cdot) + k_{3S} S(M\cdot + SM\cdot)$$

The dots indicate, as usual, radicals, SM· being those originating from the solvent. Together with propagation k_2 and termination k_4 (not distinguishing between $SM\cdot$ and $M\cdot$ radicals) one finds for the over-all rate:

$$-dM/dt = \frac{k_2(I\varphi_M)^{1/2} M^{3/2}}{k_4^{1/2}} \left[1 + \frac{\varphi_S}{\varphi_M} \cdot \frac{S}{M}\right]^{1/2}$$

and for the number average D.P., $\bar{P}$:

$$\bar{P}_0/\bar{P} = \frac{\bar{P}_0 k_{3S}}{k_2} \frac{S}{M} + \left[1 + \frac{\varphi_S}{\varphi_M} \cdot \frac{S}{M}\right]^{1/2}$$

where $\bar{P}_0$ refers to the pure monomer system. The term containing the ratio $K' = \varphi_S/\varphi_M$ is the only one characteristic for the solvent and can be determined from either of the two equations, once the undiluted system has been analyzed. It represents a relative quantum efficiency of solvent and monomer and determines the solvent effect on the rate. For we have for a given M and t:

$$\mathrm{d}[(-1/M)\cdot(dM/dt)]/d\mathrm{S} \begin{array}{ll} > 0 & K' > 1 \\ = 0 & K' = 1 \\ < 0 & K' < 1 \end{array}$$

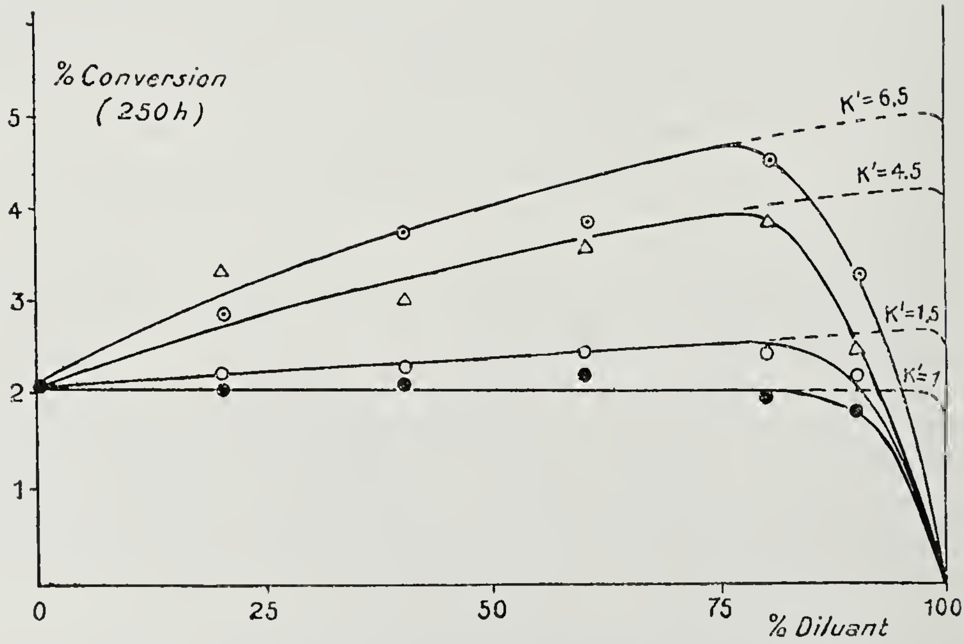


Figure 3. Polystyrene formation induced by γ-radiation in the presence of aromatic solvents. ● Benzene; ○ Toluene; ⊙ Ethyl benzene; △ *m*-Xylene.

and the same holds for the moderate degrees of conversion involved here. For pure styrene one has under such conditions approximately $(-d\mathrm{M}/dt)_{\mathrm{S}=0} = 2 \times 10^{-7}$ mole/l/sec, corresponding to 2.06 per cent conversion after 250 hr.

We illustrate the application of the above equations by showing a few graphs due to Chapiro[179]. Figure 3 shows the conversion of styrene as a function of solvent concentration for four benzene derivatives. The agreement with theory is satisfactory up to dilutions of 80 per cent and more. The proportionality of the rate with $I^{1/2}$ however remains preserved at greater dilutions. Whether the discrepancy is only apparent, due to low molecular weight polymer which is not precipitated, or has kinetic reasons, remains unsettled.

The behavior of halogenated compounds and amines is different and exemplified by Figure 4. This might be due to the formation of HCl or of unreactive radicals, such as CCl_3. An estimate of the K'-numbers can nevertheless be made at high monomer concentrations. It is noteworthy that amines, known to act as inhibitors[180], act as accelerators under γ-radiation, due to their ease of breakdown.

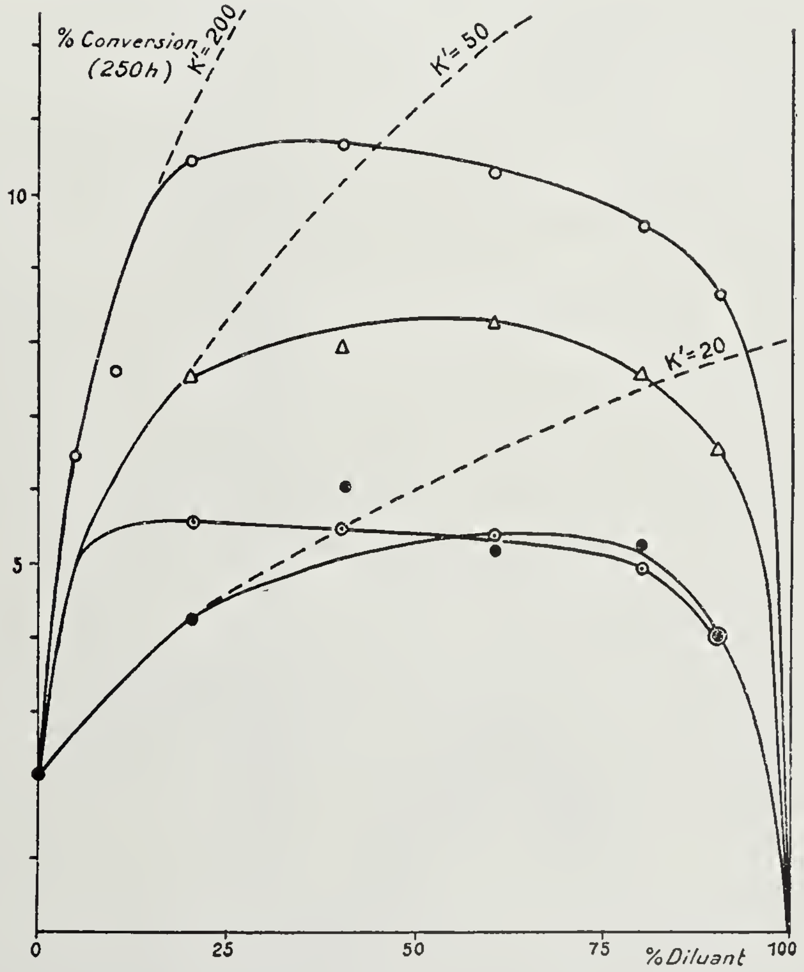


Figure 4. Polystyrene formation induced by γ-radiation in the presence of diluents. ● Ethyl bromide; △ Chloroform; ○ Carbon tetrachloride; ⊙ Diphenyl methane.

The behavior of alcohols as shown in Figure 5 is again different, due to the fact that the polymer becomes insoluble beyond a certain alcohol content. The initial portions of the curves represent the usual trend, and the K'-values are high, indicating that radicals are readily produced. The maximum occurs just prior to the precipitation region. The subsequent decrease in rate is paralleled by that of the molecular weight and is caused by an increase in the probability of termination in the coagulating mass. The interesting phenomenon is the second increase beyond 70 per cent which may be caused by the difficulty of strongly coiled molecules terminating each other. Furthermore at high dilution a "dark" reaction, that is polymerization, is observed. Benzyl alcohol, which is a solvent, behaves as the previously shown diluents up to about 60 per cent. Results for a series of other poor solvents are exhibited in Figure 6.

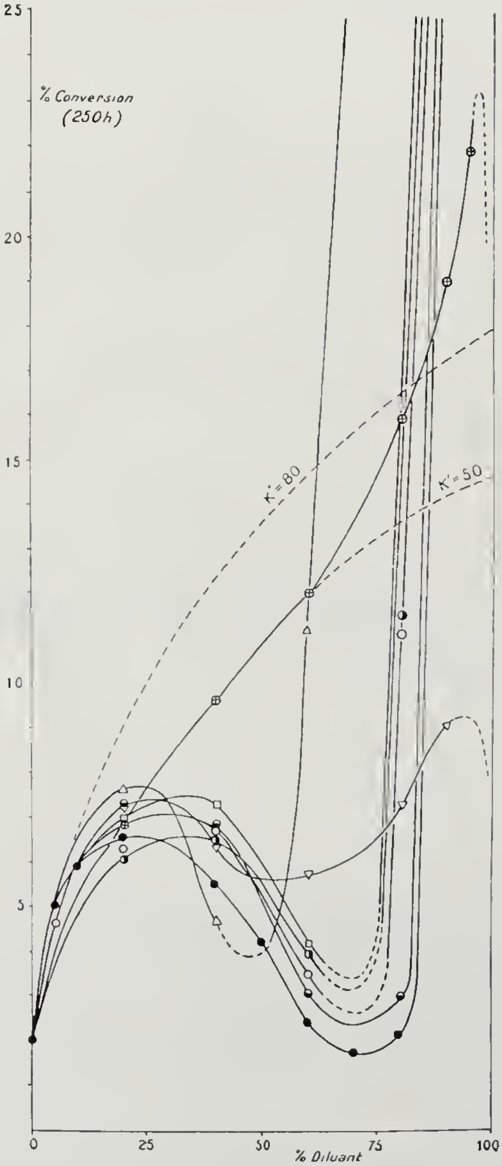


Figure 5. Polystyrene formation induced by γ-radiation in the presence of alcohols. ● Methanol; ○ Propanol-1; ◒ Propanol-2; □ Butanol-1; ◑ tert-Butanol; △ Octanol-1; ▽ Octanol-2; ⊕ Benzyl alcohol.

The comparative rates for different pure monomers may be judged from Figure 7. From the initial slopes of these curves the product

$$\varphi_M^{1/2}(k_2/k_4{}^{1/2})$$

(see the rate equation, p 255) can be determined and φ_M found whenever $k_2 \cdot k_4{}^{1/2}$ is independently known. This involves a determination of the over-all rate and life time of growing radicals in photopolymerization as indicated previously. In cases where this information is not available, a value φ_M relative to another monomer, say styrene, can be found if K' relative to the reference monomer and to the monomer in question is known. In this manner the approximate values given in Table 22[179, 181], column 3 were obtained, based on φ (benzene) = 1. The molecules most stable toward radioactive attack are the hydrocarbons, and among these the aromatics predominate in agreement with the findings of Schoepfle and Fellows[182] and also reported by Burton[183]. This is due to the nonlocalized

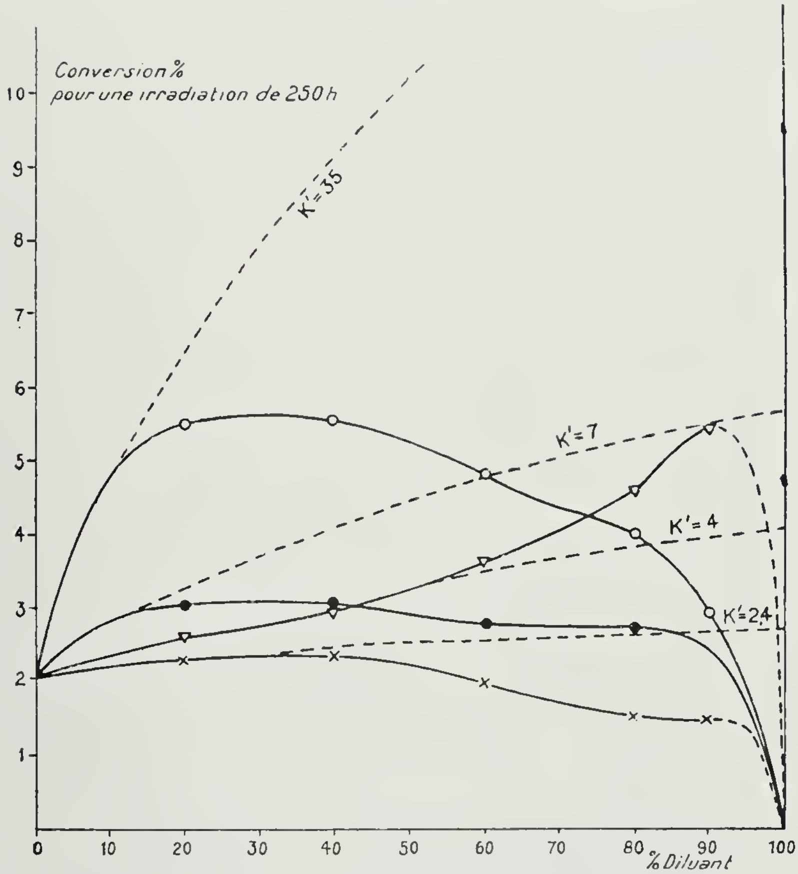


Figure 6. Polystyrene formation induced by γ-radiation in the presence of solvents. x Heptane; ○ Acetone; ● Ether; ▽ Cyclohexane.

electron structure in the benzene ring. Among the alcohols and amines the φ-value is more or less independent of the nature of the hydrocarbon portion of the molecule. What is involved here is the splitting off of OH and NH_2 groups, probably as negative ions. At the bottom of the hierarchy is CCl_4 suggesting as a factor the electronegativity of Cl and consequent ease of forming negative chlorine ions and radical fragments.

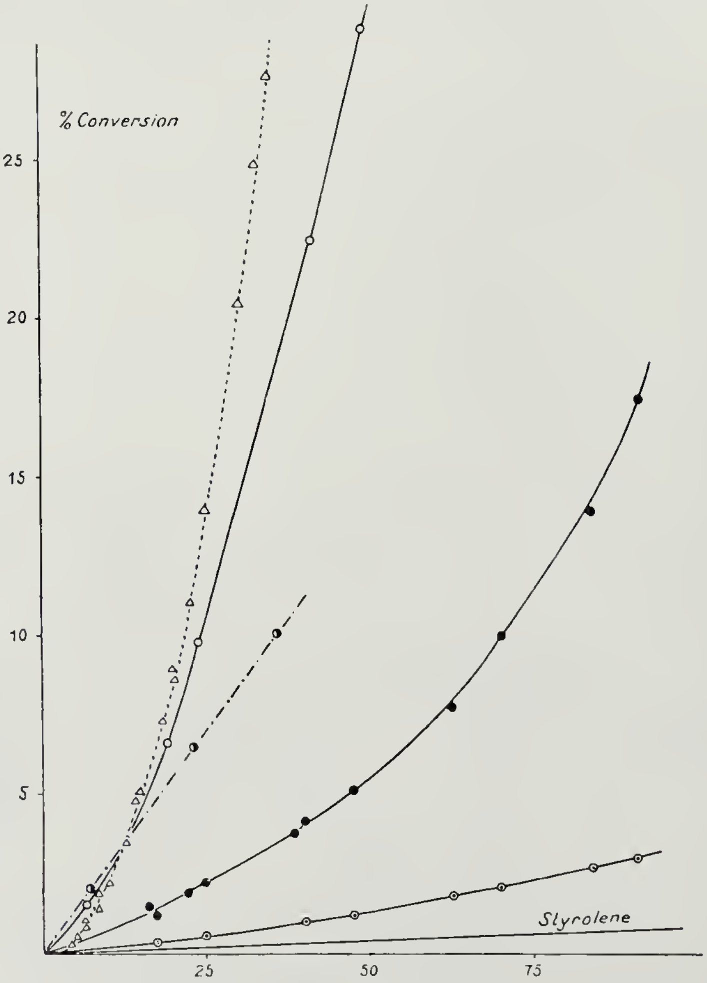


Figure 7. Polymer formation induced by γ-radiation for a series of monomers. △ Vinyl acetate; ○ Methyl acrylate; ◑ Vinyl chloride; ● Methyl methacrylate; ⊙ Acrylonitrile; — Styrene.

In Table 22, column 2, are shown results based on the reaction of diphenyl picryl hydrazyl (DPPH) with free radicals. The extent of reaction is measured by the disappearance of the DPPH color. There is satisfactory agreement between the two methods. The values in the parentheses are considered uncertain due to secondary effects, precipitation of the poly-

Table 22. Production of Free Radicals by γ-Irradiation of Organic Liquids[181]

Compound	Relative Number of Free Radicals Produced per cm^3 per Unit Dose		G_R (number of free radicals produced per 100 eV)	Y Energy Yield in %
	DPPH	Polymerization		
Inorganic				
Carbon disulfide	0.7	1.0	0.85	—
Aromatic				
Benzene	1.0	1.0	1.8	3.0
Styrene	—	0.9	1.6	2.8
Toluene	1.75	1.45	3.1	5.3
m-Xylene	—	3.8	6.3	11.0
Ethylbenzene	—	5.5	9.0	15.0
Nitrobenzene	3.5	—	4.5	7.8
Halogenated aromatic				
Chlorobenzene	12.4	13.0	17.5	26.0
ortho-Dichlorobenzene	25.4	—	30.0	45.5
Aliphatic				
Acrylonitrile	—	1.1–1.4	2.7	4.6
Propionitrile	2.0	—	3.9	6.8
n-Heptane	4.4	(1.7)	9.9	17.0
n-Octane	5.2	—	11.4	20.0
Cyclohexane	7.4	(3.9)	14.3	24.5
Perdeuteromethanol	13.0	—	23.0	39.0
Methanol	12.5	(10–20)	24.0	41.5
Propanol	15.0	(50–80)	30.0	51.5
Ether	11.2	(7.2)	24.5	42.0
Dioxane	13.2	—	20.0	34.0
Methyl acrylate	—	13.6	23.5	40.5
Methylmethacrylate	—	15.0	27.5	47.5
Ethyl acetate	18.4	—	32.0	55.0
Vinyl acetate	—	18.7	33.0	57.0
Acetone	25.5	(50.0)	50.0	87.0
Halogenated aliphatics				
Ethyl bromide	25.6	27.0	28.0	39.0
1,2-Dichloroethane	33.0	—	41.0	61.5
Chloroform	57.0	65.0	59.5	88.4
Bromoform	107.0	—	57.0	80.0
Carbon tetrachloride	(72.0)	(200.0)	(70.0)	(105.0)

mer in polymerization or unusual behavior in the DPPH reaction with time.

Recently, with small β-sources, a similar study has been carried out using some of the same organic liquids listed in Table 22[184]. The relative sensitivities of the liquids towards β-radiation were found to be similar to those reported for γ-radiation. The absolute values of the yields of free radicals per 100 ev, however, were found to be considerably lower.

Further work[184a] with γ-rays has produced G values for radicals from the radiolysis of styrene and methyl methacrylate close to those obtained with β-rays[184]. It appears that the discrepancies arose from the use of different values for the propagation and termination constants for polymerization by the different investigators. The efficiency of radical production is then essentially the same regardless of whether γ- or β-radiation is used.

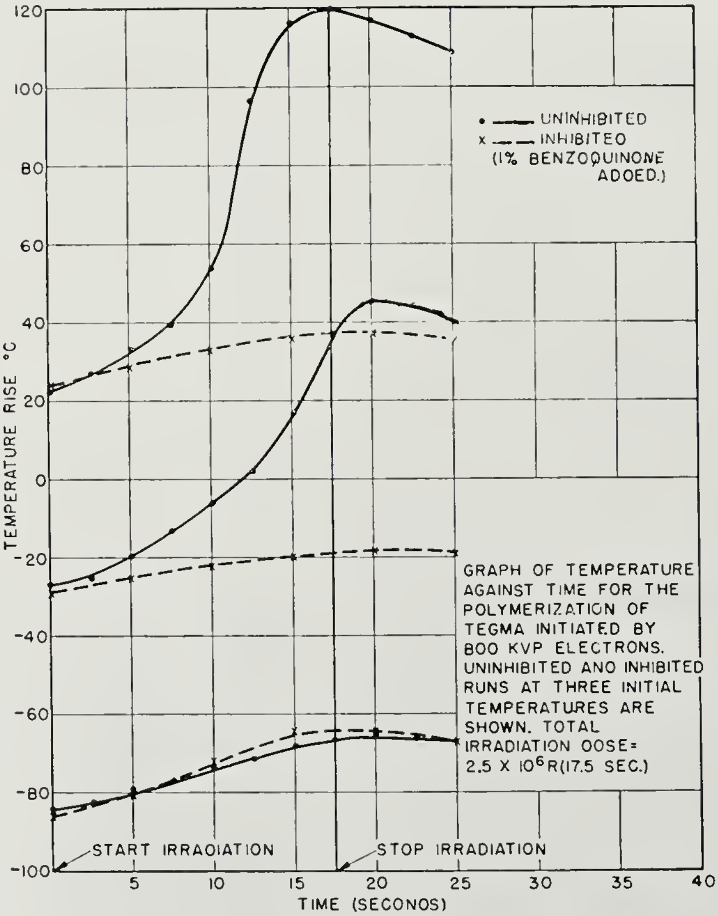


Figure 8. Temperature *vs.* time plots for 800 KV electron initiated polymerization of tetraethylene glycol dimethacrylate with three initial temperatures. ● —— Uninhibited; × – – – Inhibited with 1 per cent benzoquinone.

A closer study[184b, 184c] of radical production with γ-rays reveals that the efficiency of radical production depends on the concentration of diluent in the monomer. It should be mentioned that the term "radical" in these polymerization studies refers to any species which initiates the formation of a polymer molecule. Excited states which function as initiating species are thus included.

Polymerization with high energy β-radiation was first undertaken by Coolidge[185] and resumed in the same laboratory by Schmitz and Lawton[186]. A cathode ray generator operating at 800 kv was used. Acrylates, methacrylates, styrene and acrylonitrile polymerize in the order indicated which follows more or less the one shown for γ-ray initiation in Figure 7. Data for a difunctional monomer, tetraethylene glycol dimethyacrylate are presented in greater detail. Whereas in methyl methacrylate ten double bonds disappear per ion pair created, five hundred participate in the latter monomer. In the runs indicated in Figure 8[186], it will be noted that the time of irradiation was only 17.5 seconds. The differences in the temperature increments between the inhibited and uninhibited process are due to the polymerization reaction. It is completely suppressed at $-80°C$ and is estimated by the authors to require a minimum temperature of $-55°C$. From the length of the induction periods observed in the presence of benzoquinone, it is concluded that at room temperature about 5×10^{12} radicals per cc are produced by one roentgen (the dosage which produces a change of one electrostatic unit in 1 cc of air). Thus the yield is approximately 3 radicals per ion pair in the difunctional monomer. In the experiments with styrene and γ-radiation, previously discussed, the yield was of the same order of magnitude, about 0.5[180]. In both cases it is assumed that one inhibitor molecule reacts with one radical.

Polymerization with Preformed Polymers

Polymerization in the presence of polymer is at present a rapidly developing field. Two aspects are worth noting: (1) polymers as initiators, and (2) polymers which are reacted further with their own or different monomers, producing new and different structures with perhaps unique properties. The first aspect provides a means for detecting and for obtaining a better knowledge of the presence and structure of groups on the polymer, occurring in minute quantities. The second involves the possibility of grafting on branches of like or different structure to a given chain, producing graft polymers, or reactivating a polymer at its ends so that in the presence of monomers of a different type further growth occurs. This produces so-called "block" polymers. The two aspects are intimately related.

Polymer Induced Polymerization. It has been reported[187] that polymethyl methacrylate induces polymerization of its own monomer and also, contrary to normal polymerization behavior, the molecular weight of the polymer obtained in this manner increases with increasing temperature. In this work the effect appeared to be specific for methyl methacrylate, other monomers failing to show more rapid initial rates in the presence of polymethyl methacrylate.

These results led to the speculation[188] that the presence of polymer causes some orientation of the monomers to give an array of units which could produce diradicals of degree of polymerization, n, greater than two, but presumably less than ten. Energetically, large diradicals are favored, the reaction which is endothermic for $n = 2$, quickly becomes exothermic with $n = 4$ or 5. In brief, an initiation reaction was postulated with a molecularity, n, larger than two but less than 10.

Other workers[189, 190] have studied this process and found no increased rate of polymerization when the polymer used was first heated to 65 to 100°C for 40 to 24 hr. Also with untreated polymer, induced polymerization of styrene was achieved. The conclusion was that peroxide groups in the polymer were responsible for the induced polymerization.

Polymerization induced by polymer can be used as a test for active groups in the polymer. With this tool a study of polymethyl methacrylate irradiated with gamma rays has been carried out[97]. Evidence indicative of immobilized free radicals was obtained from the observation that initial polymers irradiated and manipulated under vacuum gave initially much faster rates of polymerization than when not irradiated. Inhibitor studies strengthen this conclusion. The time between irradiation and polymerization ranged from days to weeks. The effect appears slight presumably because it is over rapidly, the polymerization then returning to a more nearly normal behavior. The concentration of free radicals in the polymer was estimated to be about 10^{-5} moles/liter.

Polymer irradiated in air gave greater effects since peroxides were presumably formed. Polymer irradiated in vacuum but subsequently exposed to air showed intermediate activity possibly due to peroxide formation after irradiation caused by reaction of oxygen with immobilized radicals. Ultraviolet irradiation of polystyrene[191] in air also produces polymer which causes polymerization of other monomers. Again peroxidic groups are probably the active agents. With methyl methacrylate monomer an insoluble gel was obtained pointing to the linking together of polystyrene chains by polymethyl methacrylate chains.

Graft Polymers. We shall restrict the term graft polymers to those products where a previously formed mainly linear polymer is reactivated at certain sites along the chains. There branches grow or become attached, usually composed of monomer units structurally different from those of the original linear polymer. With polystyrene peroxides groups can be formed along the chain and this effect produced[191] as noted above. However, several workers[192, 193] reported little success along these lines. An alternative procedure[192] is to alkylate styrene on the ring with isopropyl groups and oxidize the alkylated portion of the polymer. Several hydroperoxide groups per 100 monomer units can be obtained and this oxidized polymer used to polymerize a different monomer, forming a graft polymer.

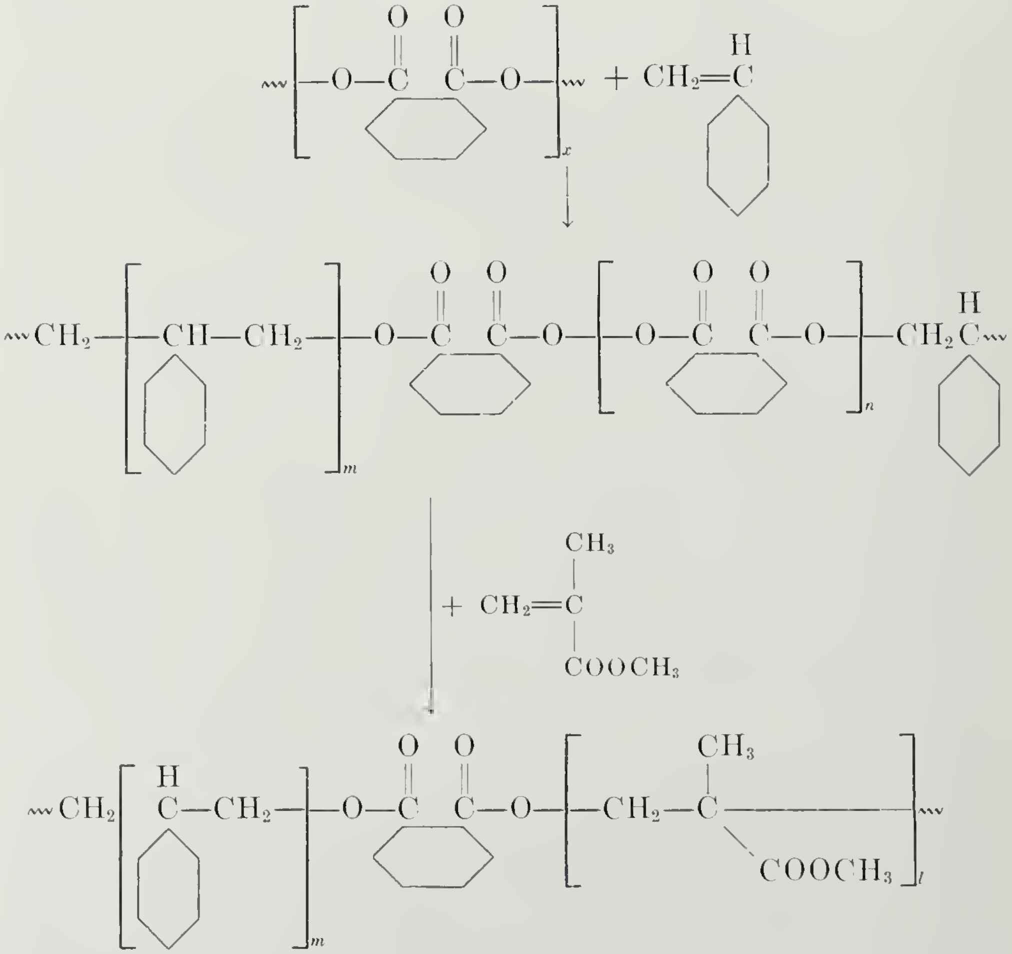
Another procedure[193] is to partially brominate polystyrene and then photolyze the brominated polymer in the presence of another monomer. In this case it was considered advantageous to have present a small amount of transfer agent, carbon tetrachloride, to prevent the branches from linking up with other chains thereby producing gels.

With diene polymers a natural approach to graft polymers is the polymerization of vinyl monomers in the presence of such polymers. Attack on the double bonds in the diene polymer chains by growing radicals will lead to branched or cross-linked polymers. Several studies[194, 195] of this kind have been carried out.

Another extremely interesting approach[196] involved the photolysis of polymethyl vinyl ketone in acrylonitrile. Here it was found that, as in the gas phase photolysis of ketones, free radicals were formed together with carbon monoxide. These free radicals, some of which were associated with the polymer chain, reacted with the acrylonitrile to form branches of this monomer. Scission of the polymer chain was also indicated, in which case these radicals can presumably also grow by acrylonitrile addition and we would have essentially linear chains of methyl vinyl ketone units attached end to end to chains of acrylonitrile units. Such structures which may be symbolized as $(A)_m(B)_n$ or $(B)\ (A)_m(B)_n$ are designated as block polymers. In the literature the two terms are sometimes used interchangeably. In the case of the polymethyl vinyl ketone and acrylonitrile system there would probably be a mixture of both graft and block polymers.

Block Polymers. Several methods[197-200] for preparing block polymers have been proposed and studied. Polymer with terminal bromine atoms can be prepared by polymerization in the presence of a bromine containing transfer agent such as carbon tetrabromide. Subsequently, this polymer can be photolyzed in the presence of another monomer to produce a block polymer. The styrene and methyl methacrylate system has been rather well explored[197]. Important problems in such syntheses are the choice of wave lengths of light specific for the photolysis of the terminal group and a primary homopolymer which is stable to light. The second monomer will also homopolymerize and the result is a mixture of block polymer and homopolymer of the second monomer. Conditions are usually such that the latter polymer is of lower molecular weight and by means of fractionation it can be separated from the block polymer. Also unreacted initial polymer, i.e., of the first monomer, must be removed by some method. In the reported study[197] this was low molecular weight polystyrene which was soluble in ether while the block copolymer of styrene and methyl methacrylate and the polymethyl methacrylate were insoluble.

Another method[198] for preparing block polymers utilizes the polymeric peroxide, phthalyl peroxide. The procedure described[198] was to polymerize styrene in the presence of this initiator without completely consuming the peroxide. The polystyrene containing peroxide links is then recovered and polymerized in the presence of a second monomer, methyl methacrylate. The synthesis is depicted by the following scheme:

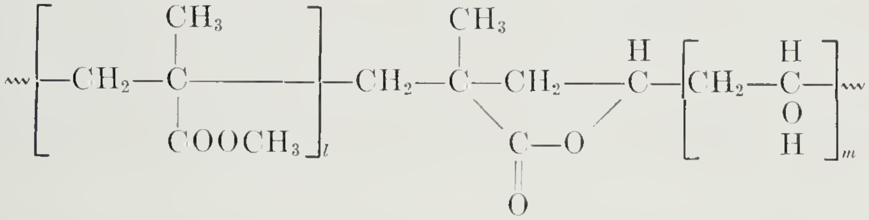


Depending on whether polymer growth was terminated by transfer, disproportionation, or combination processes the resulting block polymers would have the structures:

$$(A)_l(B)_m \text{ or } (A)_l(B)_m(A)_n$$

or a mixture of the two.

Emulsion systems also offer an opportunity to prepare block structures[199, 200]. This method makes use of solubility differences between monomers. Water-soluble and oil-soluble monomers are polymerized by the usual emulsion technique, precautions being taken to insure that initiation or small radical formation occurs in the aqueous phase. The mechanics of the situation is then such that growth of polymer starts in the aqueous phase and continues to appreciable size before diffusing into a micelle where oil-soluble monomer is located. Further growth is then with the second monomer. Studies with the acrylic acid-styrene[199], the methacrylic acid-styrene[199], and the methacrylic acid-vinyl acetate[200] system have been reported. The latter system can produce the block polymer of methacrylic acid-vinyl alcohol by alkaline hydrolysis of the final block polymer. Further reactions can produce only lactone rings at the junction of the two homo sequences, viz.



Hence the production of lactone rings should be the smaller, the better the block structure that is achieved. Considerable success is indicated by the reported results. Due to some solubility of both monomers in both phases the results showing some lactone formation in the emulsion prepared copolymers would be expected.

A more novel procedure for producing block polymers has been described[201]. The first monomer containing a suitable photosensitizer is passed through a capillary at a rapid calibrated rate into a reservoir containing the second monomer. A portion of the capillary is illuminated with very intense ultraviolet light, producing a concentration of radicals up to 10^{-4} moles per liter (in normal polymerization 10^{-8} moles per liter usually are obtained). These radicals grow as they traverse the capillary by addition to the first monomer. At the end of the capillary they are injected into the second monomer, which is then in excess, and hence grow mainly by addition to second monomer. The result is a block polymer having $(A)_l(B)_m$ or $(A)_l(B)_m(A)_n$ structures depending again on the method of termination occurring. Although the analysis of the products is difficult, the results[201] indicate formation of block polymers with butyl acrylate-styrene and acrylonitrile-styrene systems.

Mixed Block and Graft Polymers. The possibility of activating polymers by means of high energy radiation and simultaneously or subsequently obtaining a reaction with added monomer has received considerable attention[184a, 201a]. Ionizing radiation is not particularly selective and the indications are that main chain scissions occur together with rupture of pendant groups. Hence various radical sites of differing structures are probably formed. Subsequent reaction with monomer then leads to a mixture of block and graft polymers.

There are essentially two procedures for obtaining graft polymers with ionizing radiation. In one, polymer and monomer are in contact. Here the polymer should be most sensitive to radiation. For the best results, moreover, the polymer should be partially swollen with monomer. In such a viscous mass termination of polymer radicals is retarded and the rate of polymerization is increased. As polymerization proceeds, monomer is continuously added in order to maintain the reaction. In this manner any ratio of original to final polymer can be achieved[201a]. In this procedure oxygen-free conditions are maintained.

In the second procedure polymer is irradiated in the presence of oxygen prior to contact with the monomer. During the irradiation period peroxide and hydroperoxide structures become incorporated in the polymer molecules. Upon addition of monomer and heating, polymerization of the added monomer occurs[97, 201a].

IONIC POLYMERIZATION

There are essentially two groups of compounds other than the peroxide type (i.e., free radical sources) which readily bring about polymerization, the Friedel-Crafts catalysts, which, in addition to being alkylation and isomerization agents, are effective catalysts for polymerization, and the alkali metals or their organic derivatives. In recent years the latter two categories of initiators have become the object of numerous studies of mechanism and kinetics. Several reviews of the subject have been published[202-205]. The most striking method for demonstrating that there are fundamental differences in the action of various catalysts and that there are essentially three different mechanisms is a copolymerization[206] in which an equimolar mixture of styrene and methyl methacrylate is polymerized. The results of this type of experiment are presented in Table 23. It is seen that the initial polymer is almost pure polystyrene when acid catalysts are used, whereas the alkali metals produce almost pure polymethyl methacrylate. Catalysts normally considered to produce free radicals give 50:50 copolymers. Thus this type of experiment offers an excellent test for the nature of the polymerization mechanism. However, for heterogeneous reactions it is conceivable that this technique could be unsuccessful if configurational restrictions of catalyst surfaces favored the polymerization of one monomer more than the other.

The acid type reagent, the best example of which is boron trifluoride, polymerizes olefins most effectively at low temperatures and is believed to act through the production of carbonium ions. The alkali metals are believed to operate via a carbanion intermediate and will be considered in detail later. Thus, although the details of the various mechanisms are in many respects controversial, we appear to be dealing, in addition to radical polymerization, both with the propagation of positive ions by the addition of monomer units and the propagation of negative ions.

Whether these ions, both positive and negative, are really free, i.e., highly dissociated, is an apparently open question. Obviously they must be subject to some influence from their counter ions in both ionic types of systems and may be very closely associated or complexed. Ion pair is a common term used for the description of ionic intermediates[202], in which a cationic species is in the field of a given anion. For ionic polymerization the counter ions may be necessary for reaction. The fact that polymerization produced by atomic radiation appears to be of the free radical type may be pertinent in this respect since these radiations presumably produce considerable quantities of ions and ion pairs. In other words the reaction probably depends specifically on the structure of both types of ions.

TABLE 23. EFFECT OF CATALYST ON COMPOSITION OF POLYMER PRODUCED FROM 1:1 STYRENE-METHYL METHACRYLATE MONOMER MIXTURES[206]

Catalysts	Temp. (°C)	Per cent styrene in initial polymer
Benzoyl peroxide	60	51
None	60	51
None	131	51
Stannic chloride	30	>99
Boron trifluoride etherate	30	>99
Sodium	30	<1
Potassium	30	<1
Light	60	51
Thymol	131	49.5
Magnesium perchlorate	30	50

Cationic Polymerization

The action of anhydrous aluminum halides, in particular aluminum chloride, on organic compounds has been known for many years. The variety of applications to small molecules is enormous and has been described in detail some years ago[207]. Another Friedel-Crafts catalyst of importance is boron trifluoride and descriptive information as to its properties and uses can be found in at least one text[208].

A large amount of patent literature exists on the polymerization of isobutylene by boron trifluoride to oils, high polymers, and to copolymers with a few per cent isoprene or butadiene. This system is perhaps the best known commercial application of acid catalysis to polymerization. Our discussion will be restricted to nonpatent literature.

The above and related compounds cause, under many conditions, a great diversity of reactions[209], notably with unsaturated materials. Low temperatures and relatively small amounts of these agents, however, lead to the production of linear polymers by an addition process, often with such rapidity, as to invoke the use of the term explosive.

Until recently few fundamental studies had appeared in the field, principally because of experimental difficulties and the sensitivity of the reactions to impurities and moisture. An additional problem in the study of the kinetics is the fact that these systems are usually heterogeneous and special care and precautions are required in order to confine an investigation to a single phase.

Catalysts and Co-catalysts. The Friedel-Crafts catalysts are acids in the generalized sense (Lewis acids), that is, they are electrophilic and form strong coordinate or dative bonds with molecules having exposed and available electron pairs, for instance the etherate of boron trifluoride. Their activity can be regulated by such complex formation.

Pepper[202] classifies known cationic catalysts in three groups:

Hydrogen acids:	H_2SO_4 , H_3PO_4 , $HClO_4$, $HClSO_3$, HCl, HBr, HF
Lewis acids:	$BeCl_2$, $CdCl_2$, $ZnCl_2$, BF_3 , BCl_3 , BBr_3, $AlCl_3$, $AlBr_3$, $GaCl_3$, $TiCl_4$, $TiBr_4$, $ZnCl_4$, $SnCl_4$, $SnCl_2$, $SnBr_4$, $SbCl_5$, $SbCl_3$, $BiCl_3$, $FeCl_3$, UCl_4
Substances forming cations other than protons:	$AgClO_4$, I_2 , Ph_3CCl.

Recently the three chloroacetic acids[210] have been found to cause the polymerization of styrene and α-methyl styrene, provided large quantities are used and water is present.

The general order of activity for a series of such catalysts in forming polymers from isobutene at low temperatures, −78°C, has been given by Fairbrother and Seymour[211]. The compounds studied are listed below in the order of their decreasing activity:

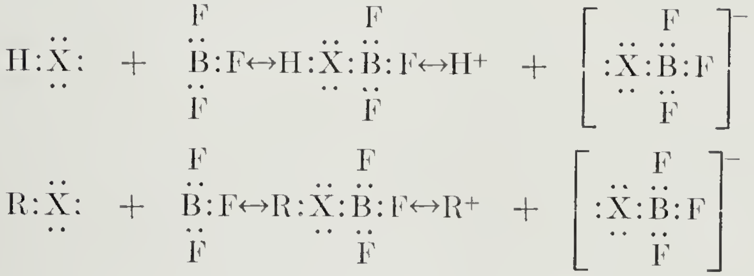
$$BF_3 > AlBr_3 > TiCl_4 > TiBr_4 > BCl_3 > BBr_3 > SnCl_4$$

Recently Polanyi, Plesch, Evans, and others[212-214] have demonstrated that the erratic behavior in the low temperature polymerization of diisobutene and isobutene by $TiCl_4$ in hexane at −80°C is due to the requirement of a third substance which is called a "co-catalyst." Water is usually very effective and has been found necessary for the formation of polyisobutene by BF_3[215]. In the gaseous polymerization of isobutene at room temperature with BF_3 , *tert.*-butanol and acetic acid are, in addition to water, co-catalysts.

In the polymerization of ethylene by aluminum chloride Ipatieff and Grosse found that traces of water or hydrochloric acid are required[216]. Hydrogen chloride, however, is found to inhibit in the case of the styrene-stannic chloride system[217] and to be without any effect in the reactions of titanium tetrachloride with isobutene[212] and of boron trifluoride with diisobutene[213].

As Plesch[204] points out, the dangers of generalizing the results obtained for one set of conditions and reagents can be illustrated by the fact that acetic acid and *tert.*-butanol are co-catalysts for the room temperature polymerization of isobutene by BF_3 but act as inhibitors for the low temperature polymerization of the same monomer by $TiCl_4$. Co-catalysts for the latter reaction are sulfuric and trichloroacetic acid.

At the present time the co-catalyst concept appears to be generally accepted and required for the over-all unification of the mechanistic and kinetic data in the field. These co-catalytic systems are believed to result in the following type of reactions:



$$\mathrm{H}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{X}}}{:} + \underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{B}}}{:}\mathrm{F} \leftrightarrow \mathrm{H}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{X}}}{:}\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{B}}}{:}\mathrm{F} \leftrightarrow \mathrm{H}^+ + \left[{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{X}}}{:}\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{B}}}{:}\mathrm{F}\right]^-$$

$$\mathrm{R}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{X}}}{:} + \underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{B}}}{:}\mathrm{F} \leftrightarrow \mathrm{R}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{X}}}{:}\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{B}}}{:}\mathrm{F} \leftrightarrow \mathrm{R}^+ + \left[{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{X}}}{:}\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{B}}}{:}\mathrm{F}\right]^-$$

Here X may be OH, OR, halide etc. It is seen that the co-catalyst is a source of cations. It may be preferably present in trace quantities as in the isobutene-boron trifluoride case, in amounts comparable to catalyst or in excess of catalyst, there being cases where the solvent plays such a role[218, 219]. It is also easy to visualize monomers which could act as their own co-catalysts[220, 221]. Too much co-catalyst can presumably retard polymerization, as for instance, in the case of the water-BF_3 system, by producing an inactive dihydrate.

The hydrogen containing catalysts do not necessarily require a co-catalyst since they contain a potential cation. However, they are often very effective co-catalysts.

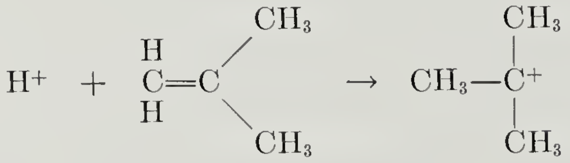
The third somewhat miscellaneous group of catalysts listed above consists of special cases. The silver perchlorate presumably produces an active silver cation. There is, of course, considerable suspicion arising from the oxidative nature of the anion that the polymerization observed is due to free radicals. However, there is an effect of the dielectric constant of the reaction medium and this catalyst is capable of polymerizing the vinyl ethers which are not very responsive to free radical initiators. These facts suggest an ionic mechanism[222]. Iodine polymerizes vinyl ethers[223] and the production of ions results from the reaction: $2I_2 \rightarrow I^+ + I_3^-$. The triphenyl methyl chloride is an example of a highly ionic organic compound capable of dissociating into a carbonium and chloride ion in polar solvents.

Evidence for the ionic character of polymerization by the above catalysts is found in the enhanced rates observed when the reactions are carried out in polar solvents[224, 219]. This correlates favorably with the increased ionization found for triphenyl methyl chloride in solvents of increasing dielectric constant[225]. However, as pointed out by Pepper[202], it is not always clear whether the solvent has a polar or a co-catalytic effect. In some cases the two modes of action appear to be linked together as in the stannic chloride polymerization of styrene which fails to occur in carbon tetrachloride but does occur in ethyl chloride, and even more rapidly in ethylene dichloride[202]. The reaction rate follows the order of increasing dielectric constant although the co-catalytic effect would not be expected to be greatest in the last named solvent.

Mechanism. At the present time the most probable mechanism for the formation of polymer by Lewis acids or Friedel-Crafts catalysts from olefins entails as the basic feature the propagation of positive ions as is implied in the term cationic polymerization. A terminology greatly facilitating discussion has developed along the pattern of that for free radical polymerization with analogous postulated reactions carrying the same descriptive terms. An important difference in ionic mechanisms is the generally found absence of square root dependence of rate on catalyst concentration. Although the catalyst entity is, in view of the co-catalytic phenomenon not always known with certainty, this leads to the assumption of an unimolecular termination step. With regard to the propagation step the similarity between radical and ionic mechanisms is evident.

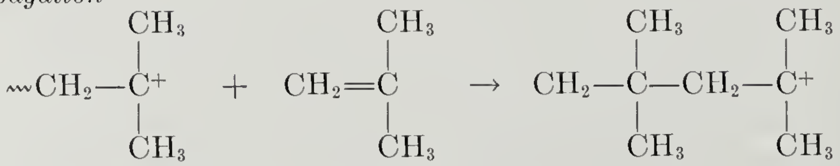
The process is started by some source of cations such as the hydrogen acid or some complex with the metal halides as described above. The subsequent reactions for isobutene are as follows[214]:

Initiation



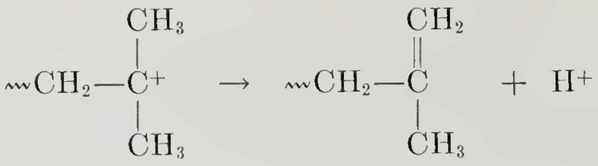
$$H^+ + H_2C{=}C(CH_3)_2 \rightarrow CH_3{-}C^+(CH_3)_2$$

Propagation



$$\sim CH_2{-}C^+(CH_3)_2 + CH_2{=}C(CH_3)_2 \rightarrow CH_2{-}C(CH_3)_2{-}CH_2{-}C^+(CH_3)_2$$

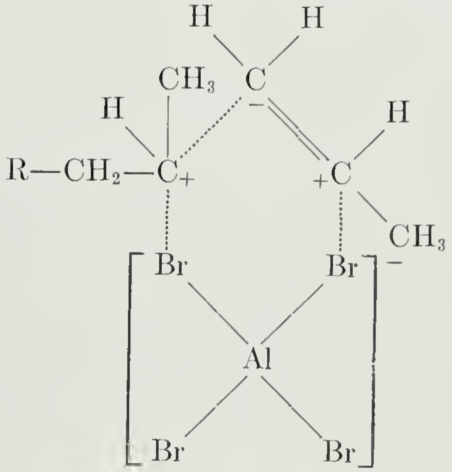
Termination



$$\sim CH_2{-}C^+(CH_3)_2 \rightarrow \sim CH_2{-}C({=}CH_2)(CH_3) + H^+$$

Although the above processes are written with free ions for convenience it must be remembered that these are closely associated with an anion of the catalyst, or catalyst-co-catalyst complex which may play an important role in these reactions. Due to the relatively unknown role of the anion the factors influencing the propagation are perhaps the least understood. Evidence for the presence of carbonium ions is cited from spectral data[226].

The transition state for propagation has been pictured in one case[227], i.e., the propene $AlBr_3$-HBr system, as involving the six-membered ring:



Here the anion is depicted as aiding the propagation step.

It might be expected that if the growth step occurred as depicted above, copolymerization would depend on the nature of the anion which varies with the catalyst. In other words, copolymer composition which is determined by the competition of propagation steps could conceivably be a function of the type of catalysts. Several studies[228-233] of cationic copolymerization have been carried out and tabulation of reactivity ratios may be found in a review of Pepper[202]. In one case[229], variation in copolymer composition with catalyst was apparently found for styrene-3,4-dichlorostyrene in carbon tetrachloride. Studies on styrene-*p*-chlorostyrene have shown no dependence of copolymer composition on dielectric constant, temperature, or catalyst type[231-233]. It is suggested[233] that the variation in the above case may be the result of the heterogeneous systems employed, in which surface effects may be significant.

The most general feature of ionic copolymerization is the fact that, roughly, the reactivity ratios reported are related reciprocally, i.e., the r_1r_2 product is approximately unity indicating little alternating tendency[230] in the reaction which is in contrast to free radical results. This implies that the nature of the growing cation is not important for the reaction rates. The net result of these studies then seems to indicate in general quite large separation of the ion-pairs and to point to the nature of the monomer as the most crucial factor in the propagation reaction. This is borne out by the fact that reasonable correlation of Hammett's σ values with relative propagation rates is obtained[232].

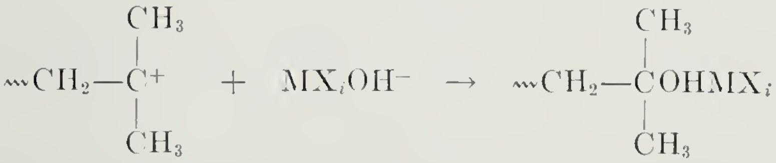
The initiation by proton addition seems on firm ground in view of the detection of C—D bonds in polymers formed with D_2O as the co-catalysts[234]. The conversion of the heavy water to light water during the course of the reaction and the fact that the number of polymer molecules formed exceeds the number of co-catalyst molecules present, supports the proton expulsion termination mechanism which may perhaps be more accurately designated as a transfer reaction. The reassociation of the expelled proton with the anion may more accurately depict the termination reaction. In this scheme there is in a sense no termination process, the reaction only stopping when monomer is depleted.

Initiation via carbonium ion has also been demonstrated in some systems. For instance, polystyrenes, prepared with $TiCl_4$ in alkyl bromide solvents, have incorporated alkyl groups[218]. Triphenyl methyl chloride in *m*-cresol polymerizes octyl vinyl ether implying initiation via the triphenyl methyl carbonium ion[235]. The effect of dielectric constant of the reaction medium is generally attributed to an enhancement of the initiation process by the more polar solvents[224]. The use of electrical conductivity in the investigation of cationic polymerization mechanisms has been recently described[235a, b, c]. The molecular weights of the polymer formed in the system isobutylene-$AlCl_3$-C_2H_5Cl with a series of weak Lewis acids, exhibit maxima when the molar ratio between base and acid reaches unity. At this point the conductivity is at a minimum. With acetic and chloroacetic acids, the extreme occurs at higher values of this ratio. Special acid-based equilibria are invoked in this case. With diethyl ether the above minimum in specific conductivity is accompanied by maxima at molar ratios of approximately 0.5 and 2. Correspondingly there are additional minima in molecular weight. The D.P. of polyisobutylene formed in C_2H_5Cl or CH_3Cl depends on the catalyst concentration. To explain this, termination with the base is suggested and expressions for the number average molecular weight in terms of the various equilibrium constants involving the acid and base co-catalyst are derived

The influence of the dielectric properties of solvents are well illustrated by the HBr and HCl catalyzed polymerization of styrene. Recently the production of high polymers by these simple acids has been reported[236]. It is well known that these acids hydrohalogenate olefins through cationoid addition, but it has now been observed that in solvents of high dielectric constant they will initiate polymerization. The molecular weights range from $\approx$5,000 to 10,000. Very likely the polarity of the medium stabilizes the ions so that recombination to give the monomeric derivative is retarded, hence allowing many further additions of olefin before combination of ions.

Several studies with radioactive metal halides have been made in order to determine the fate of the catalyst. With $SnBr_4$ composed of radioactive bromine, polystyrenes were prepared which contained one catalyst molecule for every three polymer molecules[237]. This rather high value for incorporated catalyst may have resulted from bromination of the polymer by side reactions and since bromine was the radioactive atom in the catalyst the results have been questioned[238]. An experiment with $SbCl_5$ containing radioactive antimony led to the conclusion that no catalyst was incorporated in the chains[238]. This result lends support to the proton or carbonium ion initiation and a termination step, such as proton expulsion, in which no metal halide combines with the growing polymer chain. Much earlier, in the simple Friedel-Crafts alkylation or acetylation of benzene with $AlCl_3$ and alkyl or acetyl chloride it had been demonstrated that the evolved HCl contained 75 per cent of the radioactive chlorine, originally in the $AlCl_3$[239]. This is good evidence for the existence of the $AlCl_4^-$ type anion in these reactions and probably also in polymerization reaction.

Proton expulsion has been suggested[240], on energetic considerations, to be a rather improbable termination step, at least in solvents of low dielectric constant. Another alternative termination process would be:

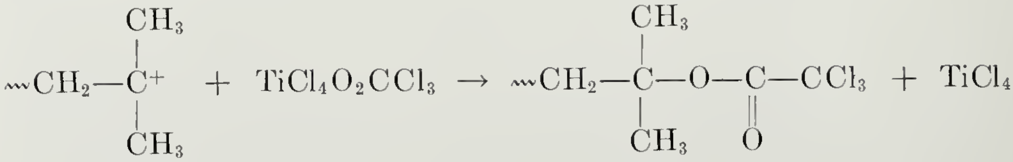


$$\sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}} + MX_iOH^- \rightarrow \sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}OHMX_i$$

The metal halide presumably remains bound to the *tert.*-butanol type end group and with $TiCl_4$ as catalyst, this would be a "true" termination process since *tert.*-butanol does not act as a co-catalyst for the $TiCl_4^-$ isobutene system[241]. With the BF_3-isobutene system *tert.*-butanol is a co-catalyst[214] and hence this step would not be a termination. In fact this system appears to lack a kinetic termination[240]. A variation of the above reaction is:

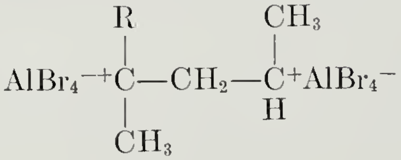
$$R_3C^+ + MX_iOH^- \rightleftarrows R_3CX + MX_{i-1}OH$$

which may also act as a termination depending on the position of the equilibrium[240]. This possibility is suggested as an explanation of the halogen content of polymers formed with systems which contain halogen only in the catalyst[242] and would seem to be indicated by the radioactive studies[237, 238]. Another analogous reaction of this type is on much firmer footing. In the system isobutene-$TiCl_4$-CCl_3COOH in hexane solution it is found that the co-catalyst is consumed during polymerization and infrared evidence indicates trichloroacetate end groups[243]. The mechanism of termination in this case is presumably:



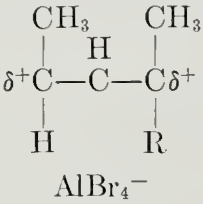
$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}} + TiCl_4O_2CCl_3 \rightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O-\underset{O}{\underset{\|}{C}}-CCl_3 + TiCl_4$$

A more complicated termination step has been visualized for the system propene-$AlBr_3$-HB_2Br in which the reaction stops due to the consumption of the catalyst[227]. A hydride ion transfer (this mechanism will be mentioned later) in the vicinity of a carbonium ion may give rise to the structure,



$$AlBr_4^{-}\,{}^{+}\overset{R}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{CH_3}{\underset{H}{\overset{|}{C}}}{}^{+}AlBr_4^{-}$$

which by the expulsion of a proton to another monomer unit leads to a resonance stabilized allylic cation complexed strongly with one anion.

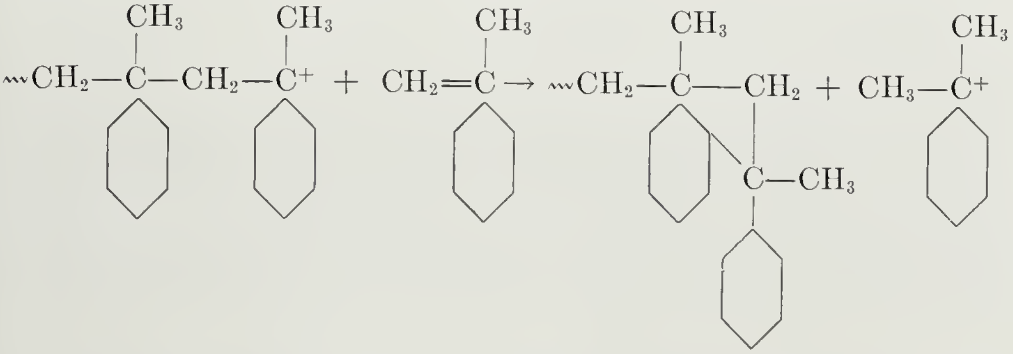


$$\delta^{+}\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{C}-\overset{CH_3}{\underset{R}{\overset{|}{\underset{|}{C}}}}\delta^{+} \quad AlBr_4^{-}$$

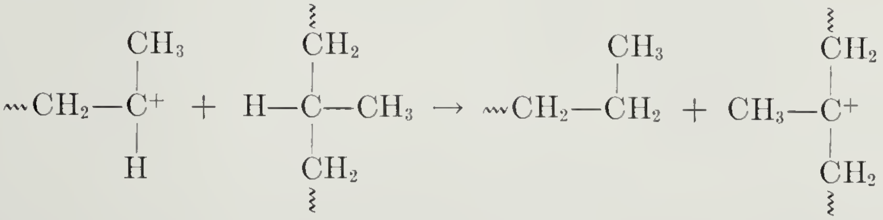
This species presumably is too inactive to cause further polymerization and hence inactivates one catalyst molecule. This reaction may occur with all 1-olefins[209]. Consumption of catalyst has also been observed in the styrene-$AlCl_3$ system[244] and may result from a similar reaction[240]. However, with styrene-$TiCl_4$ in dichloroethylene no catalyst consumption is noted. It is found instead that successive portions of styrene added to the same solution of $TiCl_4$ all polymerize at the same rate[245], indicating the continual presence of the catalytic species and an absence of a kinetic termination step. There is an implication in these facts of a fundamental difference between catalysts which seems to depend on whether they are halides of groups three or four of the periodic table[240].

Transfer Reaction

Proton expulsion from a growing cation is, as has been mentioned earlier, more accurately described as a transfer process although some authors classified it as a termination. In the polymerization of alkenes this step accounts for the terminal unsaturation usually found. However, with aromatic monomers such double bonds are often lacking. The evidence in the α-methyl styrene case points to an intramolecular attack on the phenyl group producing an indane structure with loss of a proton from the ring[246, 247]

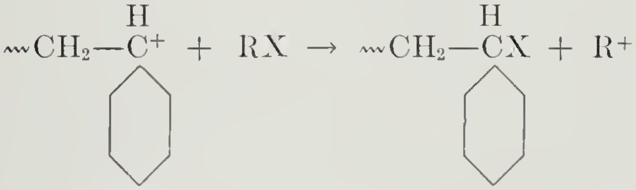


In the propene-$AlBr_4$-HBr system transfer of a hydride ion has also been postulated to explain the broad distribution of molecular weights observed. This mechanism which would produce branched polymers presumably is[227]:

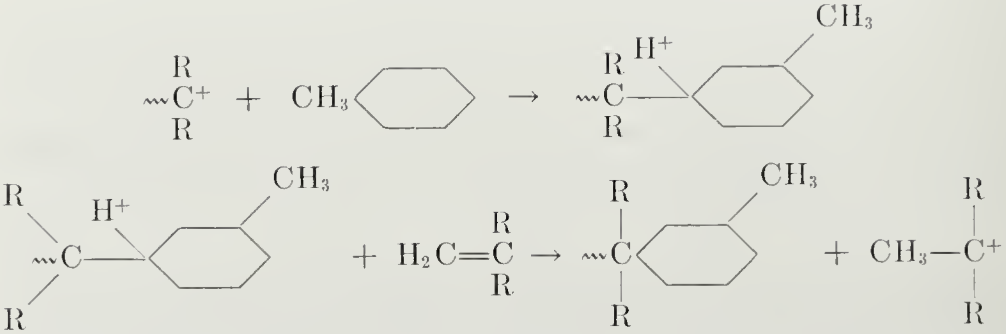


$$\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^+}} + H-\overset{\displaystyle \wr\,CH_2}{\underset{\displaystyle CH_2\,\wr}{C}}-CH_3 \rightarrow \sim CH_2-\overset{\displaystyle CH_3}{CH_2} + CH_3-\overset{\displaystyle \wr\,CH_2}{\underset{\displaystyle CH_2\,\wr}{C^+}}$$

This reaction is exothermic by about 17 kcal since a *tert.*-carbonium ion is formed from a secondary one[248]. If isobutane is a solvent for the reaction, the molecular weight of the polymer is lower implying the same type reaction with the isobutane[227]. Other transfer reactions with solvent have been suggested[240]. With alkyl halides the transfer of a halide anion is reasonable.



With toluene solvents tolyl groups have been reported as part of the polymer[218]. In this case the growing carbonium ion probably attacks the ring which then loses a proton to another monomer molecule.

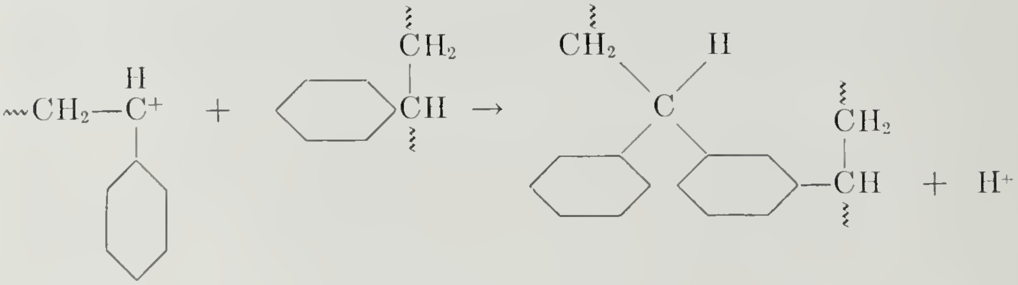


Aromatic solvents have been studied[249] with the styrene-stannic chloride-carbon tetrachloride nitrobenzene system and a decided effect on molecular weight is observed. The application of the relation (Eq. 4) from which solvent transfer constants can be calculated led to the values in Table 24 for the cationic transfer constant.

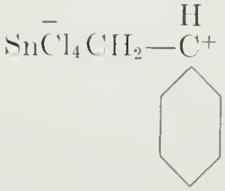
Table 24. Transfer Constant in Cationic Polymerization[249]

Substance	Transfer Constant
p-Cymene	0.0044
p-tert.-Butyl toluene	0.0062
p-Chloroanisole	0.0082
p-Xylene	0.0105
Thiophene	0.98
Anisole	1.62

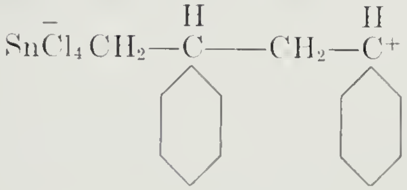
This type of reaction can also produce branches in polymers with aromatic groups along the chain. It has been mentioned that the reaction in which a growing cation attacks an aromatic nucleus of another chain, is quite probable[250].



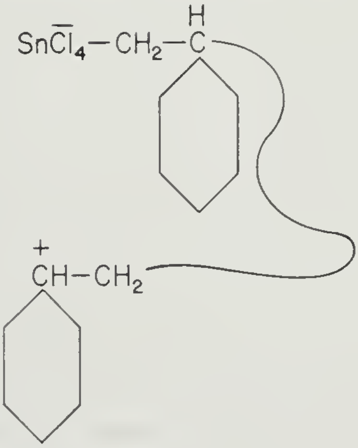
Alternate Mechanism. Prior to the development of the co-catalyst concept which allows one to visualize a connection between the action of hydrogen acids and that of the metal halides, it had been postulated that the Friedel-Crafts catalysts complexed with monomer to form a polar molecule[100, 251]. With stannic chloride and styrene the initial process would be the formation[100] of



and this species then adds styrene units at the positive site. Consequently, one is required to visualize either a larger separation of charge



or a molecule coiled[252] in a fairly specific manner:



Both situations appear unreasonable thermodynamically. This type of mechanism also does not make any provision[202] for the co-catalytic effect.

General Kinetic Features. Cationic polymerization differs considerably from the radical process. The outstanding differences are the absence of a square root dependence of rate on catalyst concentration and negative activation energies for the overall rate in some systems. In other words, lower temperature produces faster rates. Higher molecular weights also occur at lower temperature, as is ordinarily found in radical polymerization. The lack of square root dependence implies that the over-all rate constant, k_0, is given by

$$k_0 = k_2 \frac{k_1}{k_4} \quad \text{and} \quad E_0 = E_1 + E_2 - E_4$$

The activation energy for propagation is probably even lower than in radical polymerization since it involves the approach of an ion to a polarizable molecule, and is believed to be approximately zero[214]. Therefore, if $E_1 < E_4$ negative activation energies for the rate will occur. The same type of argument holds for the molecular weight variations which are functions of the ratios k_2/k_3 or k_2/k_4. Hence $E_{MW} = E_2 - E_{3 \text{ or } 4}$ and since $E_2 \approx 0$ it is seen that molecular weights would increase the lower the polymerization temperature. With the vinyl ethers positive activation energies for the rate of about 10–16 kcal/mole occur, implying that E_1 is somewhat greater than this value. Altogether, activation energies for the rates in cationic polymerization have been observed to range from about +16 to −8 kcal per mole. Although some systems are believed to be homogeneous, in many ionic systems the catalyst is not soluble and heterogeneous complications in the kinetics appear[253, 254]. The possibility also exists that many systems are not amenable to steady state assumptions for the reactive intermediates. In certain systems[255, 246] there is no apparent termination step, polymerization continuing upon further addition of monomer. These facts suggest reversible reactions for some of the steps in the polymerization process[202, 255].

Inhibition. The chain reaction character of these cationic processes is indicated by the demonstration of inhibition. In general one would expect bases to inhibit acid catalyzed polymerization and it is true that amines are effective inhibitors[224]. However, the mechanism of inhibition seems to involve more than just neutralization of the catalyst. It is believed that they may stabilize the carbonium ion by converting it into a nonreactive ammonium ion

$$\sim\!\!\sim R^+ + R_3N \rightarrow \sim\!\!\sim R\overset{+}{N}R_3$$

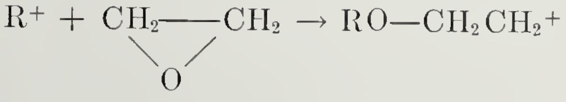
This seems reasonable in view of experimental evidence demonstrating that the stannic chloride dibutylamine complex is as good an inhibitor as the amine itself in the stannic chloride polymerization of styrene[224]. Chloride ions are also inhibitors in this system. Ethers and alcohols impede the polymerization of isobutene[212] and vinyl ethers[256]. Hydrogen chloride was previously mentioned as an inhibitor for the polymerization of styrene by stannic chloride[217]. Thus inhibition mechanisms seem to be quite varied and it is suggested, in view of the co-catalyst mechanism, that not only can inhibition occur by formation of stable catalyst-inhibitor complexes incapable of producing sufficient or sufficiently active cations, but that altered anions may impede polymerization.

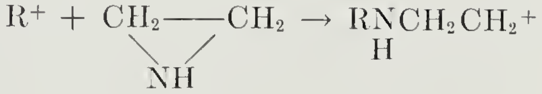
Another effect can be seen from the result that diisobutene inhibits isobutene polymerization. This probably results from the fact that cations containing terminal diisobutene groups are completely hindered from propagating by steric effects[257].

Quinone has been observed to lower the rate and molecular weight in chloroacetic acid polymerization[210]. This effect is, however, interpreted as due to an ionic rather than a free radical mechanism.

Ionic Polymerization Not Involving Double Bonds

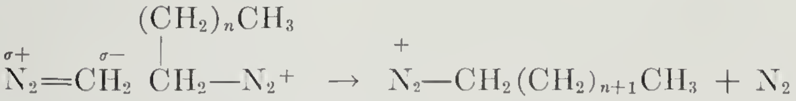
Polycondensations producing polyesters or polyamides are of course more or less obvious examples of ionic polymerization. Such polymers can be produced from diacids and dihydroxy alcohols or diamines, their cyclic salts, lactones, lactams with common acids or bases. More interesting reactions are the formation of polyethers or polyamines by the action of acid or base on ethylene oxide and ethyleneimine-type compounds. The polymerization of ethylene oxide has been known for some time[210]. Free radical systems are not effective but Friedel-Crafts catalysts such as stannic chloride are[260]. Other, and milder polymerizing agents, are glycols, amines, mercaptans, and common acids or bases. Similar reactivity is found for ethyleneimine[258]. These reactions presumably occur via the propagation reaction:





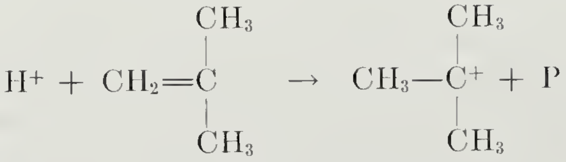
Similar reactions can be visualized involving negative ions. The over-all mechanism leads to sharp molecular weight distributions[259] and presumably no true termination or initiation steps.

The production of very high molecular weight linear hydrocarbon, of the order of 10^6, from diazomethane in ether solution upon the addition of boron trifluoride has been observed recently[261]. Nitrogen gas is evolved during the process. Several mechanisms have been suggested. One involves the propagation of carbonium ions[261] the other the propagation of diazonium ions[262]. In the latter case water co-catalyst is assumed. One can also speculate that carbonium ions from the solvent may be the initiating agent. The carbonium ion mechanism is not favored because of its high reactivity and instability[262]. The diazonium mechanism is written[262] as:



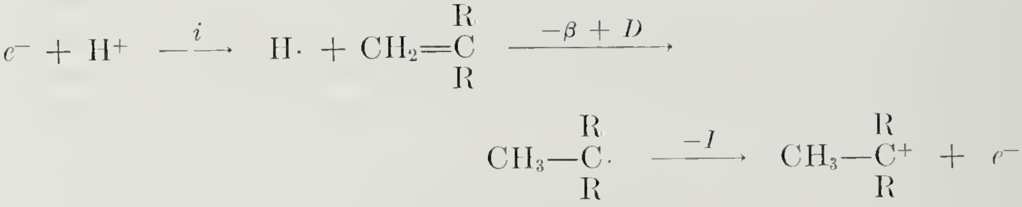
$$\overset{\sigma+}{N_2}{=}\overset{\sigma-}{CH_2}\;\overset{(CH_2)_nCH_3}{\overset{|}{CH_2}}{-}N_2^+ \rightarrow \overset{+}{N_2}{-}CH_2(CH_2)_{n+1}CH_3 + N_2$$

Energetics. In contrast to radical propagation, carbonium ion propagation on theoretical grounds requires no activation energy[214], and the reaction should go at all temperatures. The analogous radical reaction involves an activation energy and will not occur appreciably at sufficiently low temperatures. It is logical then to discuss the energetics of cationic polymerization in terms of the heats of reaction. The pertinent step with which we are concerned is:



$$H^+ + CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} \rightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C^+}} + P$$

The heat of this reaction, P, called the proton affinity[214] is then the critical quantity and should run approximately parallel with the carbonium ion affinity. This reaction can be equated to the following steps:



$$e^- + H^+ \xrightarrow{i} H\cdot + CH_2{=}\overset{R}{\underset{R}{C}} \xrightarrow{-\beta + D} CH_3{-}\overset{R}{\underset{R}{C}}\cdot \xrightarrow{-I} CH_3{-}\overset{R}{\underset{R}{C^+}} + e^-$$

It is seen that $P = i - \beta + D - I$ where i is the ionization potential of hydrogen atoms, β the energy difference between a double and single bond, D the carbon hydrogen bond strength, and I the ionization potential of the radical. The results for three olefins are:

PROTON AFFINITIES AT INDICATED SITES IN KCALS

Olefin 1 2 ($CH_2{=}CR_2$)	P_1	P_2
Ethylene	152	152
Propylene	175.5	168.5
Isobutylene	189	168

These values are for the gaseous state. In polar solvents the solvation energy for protons is very large, 282 kcal, and hence proton affinities ≈ −20 to −30 kcals result[263]. The larger the proton affinity the more favorable the process. Therefore, the above values would indicate an increasing ease of cationic polymerization down the table and preferential formation of the tertiary carbonium ion with isobutene and the secondary one with propylene which is of course in accordance with Markownikoff's rule.

Radical affinities show similar variations except that they range around the rather low value, compared to proton affinities, of about 40 kcal[214]. Thus even though free cations are not necessarily involved in acid polymerization, we see that the cationic reaction is more favored energetically and hence can overcome greater steric effects and produce polymers from monomers such as isobutene, and α-methyl styrene where radical polymerization fails to give high polymers. Since there is an appreciable difference in the proton affinities for the two carbon atoms of the monomeric double bond we would expect head to tail arrangement of the units and this is the case in isobutene. For isobutene the head to tail structure should theoretically have, in an unstrained condition, a heat of polymerization of 19.5 kcal, but is found to be 12.8 kcal[214]. This difference results from the steric repulsion between the methyl groups of the adjacent units. On the other hand, the head to head, tail to tail structure is less strained. The heat of reaction for the tail to tail step is estimated as 40 kcals, the head to head step is slightly negative or endothermic. The former is then much more favored than the head to tail while the latter is much less so. Since these two processes must alternate to produce a polymer it follows that the unfavorable endothermic step bars such a formation.

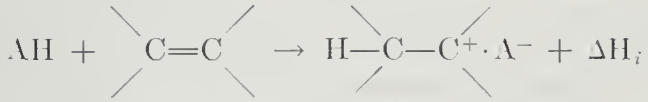
The acid catalyzed addition of alcohols to a series of olefins has been investigated[263]. Presumably the rate determining step in these reactions is the addition of a proton to the olefin which is also the step defining the proton affinity. In polar solutions this reaction is endothermic hence it is reasonable to correlate the activation energy or heat content for the transition state of the alcohol-olefin reaction with the thermochemical heat of reaction for the proton addition step. That is, $\Delta H^{\ddagger} = -P_{(\text{solution})} = 23.2$ kcal (isobutene); 22.6 (α-methyl styrene); 29.1 (styrene)[263]. Hence styrene would be expected to be the slowest of the three monomers to propagate in cationic polymerization.

A comprehensive analysis of the energetics of the various cationic steps in polymerization has been carried out by Plesch[262], who has found it useful to introduce the quantity θ, the heterolytic dissociation energy of various bonds, defined as the endothermicity of the process:

$$\mathrm{RX} \rightarrow \mathrm{R}^{+} + \mathrm{X}^{-} + \theta$$

Then $\theta(\mathrm{R{-}X}) = D(\mathrm{R{-}X}) + I(\mathrm{R}) - E(\mathrm{X})$, where D denotes the homolytic dissociation energy, I the ionization potential, and E the electron affinity.

The initiation step, assumed to be:



where AH refers to catalyst-co-catalyst complex or simple hydrogen acid, then has the endothermicity ΔH_i which can be equated as follows:

$$\Delta H_i = \theta(\mathrm{A{-}H}) - P(\mathrm{C{=}C}) - [e^2/rD]_{\mathrm{R^+A^-}}$$

Here P refers to the proton affinity previously defined and the last term to the coulombic energy of the resulting ion-pair. Since the entropy is negative, ΔH_i must be negative and further since θ for "strong" acids is in excess of 200 kcals while the largest known value for P is $\approx$200 kcals, it follows that the coulombic energy must be the determining factor for the existence of this reaction. In polar solvents, solvation energies of the ions will partly replace the coulombic energy. Possibly, recombination of the ions will also depend on the magnitude of solvation and/or coulombic energies.

The superiority of the Friedel-Crafts complexes, i.e., $H^+BF_3OH^-$ or $R^+\overline{AlCl_4}$ as polymerization catalysts may be related to the fact that in these complexes, combination of ions to form covalent bonds is not possible or, in others words, $\theta(H—BF_3OH)$ is zero. The simple chloride ion however can and does combine with a carbonium ion.

In addition to the possibility of hydride ion transfer evidence exists for carbanion transfer in the fact that in the polymerization of various alkenes low polymers are sometimes formed with nonintegral number of monomer units[209]. In Table 25 heterolytic dissociation energies pertinent to this point are presented. The values show, even though considerable uncertainties may exist in the estimates, that dissociations forming the methide ions are preferred. Hence it seems on these grounds that carbanion transfer is quite as likely as hydride ion transfer.

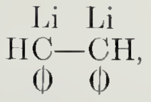
TABLE 25. HETEROLYTIC BOND DISSOCIATION ENERGIES FOR HYDROCARBONS (kcal/mole)[262]

R	θ(R—H)	θ(R—CH_3)
CH_3	317	287
C_2H_5	281	257
RCH_2CH_2	266	237
R_2CH	249	221
R_3C	232	209

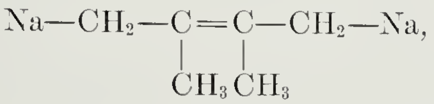
Anionic Polymerization

The first synthetic rubber produced on a commercial scale was that used by Germany in the period 1914–1918. A polymer (the so-called methyl-rubber), was formed by the action of metallic sodium on 2,3-dimethyl-1,3-butadiene. This type of polymerization agent is believed to act through negative ions (carbanions) which are, however, closely associated with the metallic cation. A free radical mechanism has been suggested[264] for the case of butadiene polymerized by sodium. However, evidence derived from copolymerization studies[206] in the presence of different catalysts, indicates a mechanism distinct from both the free radical and the cationic types when sodium or potassium is used with monomer mixtures containing styrene. It is well known that the alkali metals form alkyl derivatives of various degrees of stability, which decreases as the atomic weight of the metals increases, lithium derivatives being in general most stable.

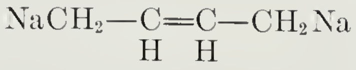
The formation of alkali metal adducts with diene monomers or aromatic substituted ethylenes has been demonstrated. For instance such complexes as



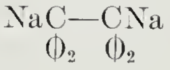
$$\begin{array}{cc} \mathrm{Li} & \mathrm{Li} \\ \mathrm{HC} & \!\!-\!\!\mathrm{CH}, \\ \phi & \phi \end{array}$$



$$\mathrm{Na{-}CH_2{-}}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}{=}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{{-}CH_2{-}Na},$$



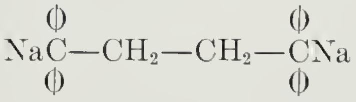
$$\mathrm{NaCH_2{-}}\underset{\mathrm{H}}{\mathrm{C}}{=}\underset{\mathrm{H}}{\mathrm{C}}\mathrm{{-}CH_2Na}$$



$$\mathrm{Na}\underset{\phi_2}{\mathrm{C}}{-}\underset{\phi_2}{\mathrm{C}}\mathrm{Na}$$

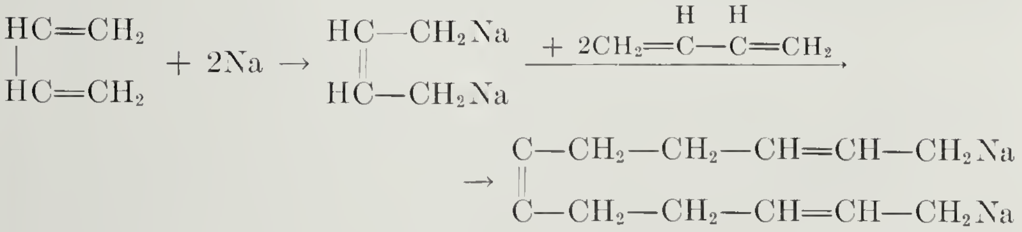
have been shown to exist. By further reaction with water or carbon dioxide the sodium atoms are replaced by hydrogen or carboxyl.

In the case of $\phi_2C{=}CH_2$ reaction with sodium produced a dimer adduct:



$$\mathrm{Na}\overset{\phi}{\underset{\phi}{\mathrm{C}}}\mathrm{{-}CH_2{-}CH_2{-}}\overset{\phi}{\underset{\phi}{\mathrm{C}}}\mathrm{Na}$$

These facts and the general features of the polymerization kinetics for butadiene have been interpreted[265] in terms of a mechanism involving a slow build up of the sodium adduct which proceeds to add monomer units in an essentially step-wise fashion.



$$\begin{array}{l} \mathrm{HC{=}CH_2} \\ \quad | \\ \mathrm{HC{=}CH_2} \end{array} + 2\mathrm{Na} \rightarrow \begin{array}{l} \mathrm{HC{-}CH_2Na} \\ \quad \| \\ \mathrm{HC{-}CH_2Na} \end{array} \xrightarrow{+\ 2\mathrm{CH_2{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2}}$$

$$\rightarrow \begin{array}{l} \mathrm{C{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na} \\ \| \\ \mathrm{C{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2Na} \end{array}$$

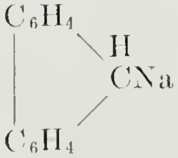
The activation energy was found to be 7300 cal while the preexponential factors are of the order of 5×10^3 and depend on the specificity of the reaction media. The reaction is probably heterogeneous.

Polymerization can also be initiated by various alkyls or aryl compounds of the alkali metals. One of the first reported was 2-phenylisopropyl lithium[266] which induced the formation of a polybutadiene in ether solution.

Recent work[267] indicates considerable specificity in regard to polymer formation by various mono-alkali metal compounds. It seems well established that the compounds are highly ionic and are essentially salts $\overset{+}{Na}\ \overset{-}{C}H_2R$. A number of such systems in certain solvents have shown a moderate degree of conductance. Morton[268] estimates the activity of sodium salts from data on the replacement of hydrogen by the sodium from a salt of a weaker acid, including hydrocarbons.

In order of decreasing activity we have:

$$C_5H_{11}Na > C_6H_5Na > C_6H_5CH_2Na > (C_6H_5)_3CNa$$

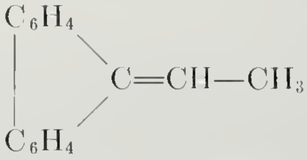


$$> C_2H_5ONa > HONa > C_6H_5ONa > CH_3COONa$$

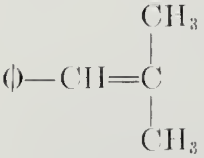
The reactions of alkali metal akyls with olefins involve both substitution and addition. The former will compete with the polymerization process. Ziegler[269] compared the action of phenylisopropyl potassium with various olefins and found that

$\phi-CH=CH_2$, $\phi_2C=CH_2$, $\phi CH_3C=CH_2$, $\phi-CH=CH-CH_3$,

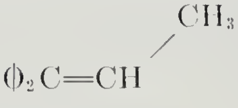
and



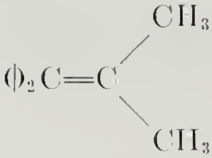
reacted predominantly by addition, whereas



$\phi-CH=C(CH_3)_2$,



,



,

$\phi_2C=CHCH_2CH_3$, and $\phi_2C=CHCH_2-C_6H_5$

reacted by substitution. Substitution occurred at the alkyl hydrogens beta to the double bond. It also is apparent that the compounds reacting by addition are those which more readily polymerize.

The action of various sodium derivatives is quite specific. For instance, amyl, benzyl, and cyclohexyl sodium add one or two butadiene units while phenyl, furyl, and *p*-phenylphenyl sodium form compounds of high molecular weight[267] under similar conditions. The sodium salts of these hydrocarbons are insoluble in the usual polymerization reaction media of low dielectric constant. The polymerizations are then heterogeneous and proceed in the presence of disperse clusters of ions. The general view would then be that the anion propagates in steps while the cation remains closely associated. The nature of the cation as well as the structure of the anion will determine the efficiency and mode of reaction. Another factor is the presence of inorganic salts in solutions of the alkyl derivatives. The method of preparation involves the reaction:

$$2Na + RCl \rightarrow NaCl + RNa$$

This may be followed by a replacement reaction to produce other alkyl derivatives.

$$RNa + R'H \rightarrow RH + R'Na$$

In any case, whether direct or indirect methods of preparation are used, an equal quantity of highly dispersed inorganic salt is present together with the organic derivative.

In the polymerization of butadiene[270], for example, the inorganic salt has a great influence on the activity of the catalysts. Phenyl sodium prepared from chlorobenzene was very active and produced high polymers of butadiene while the same catalyst prepared from bromobenzene showed little activity. The same effeet was observed between catalysts prepared from bromo and chloro-isopropylbenzene. The effect of salts on the catalysts are shown in Table 26. Certain specific instances of solvent action have been observed[265]. Phenyl sodium in benzene produces polymer of intrinsic viscosity 0.16 compared to 0.69 when pentane is the solvent. Triethylamine accelerates the addition polymerization of butadiene by amyl sodium but changes the phenyl sodium process from the catalytic production of high polymer to a step-wise addition reaction which produees low molecular weight materials.

Two mechanisms are thus distinguishable, a step and a chain process, which presumably differ mainly in the rapidity of the growth reaction. Probably neither mechanism operates exclusively. Morton suggests, on the basis of the results mentioned, that the polymerizing activity is determined by complexes of the inorganic and organic salts of the type $\overset{-}{[C_6H_5NaX]}\overset{+}{Na}$ where X is Cl, OH, or OCH_3. Such complex anions are believed to be the active species in the catalytic reaction whereas the step process is ascribed to the action of cation complexes.

A very effective catalyst for polymerization of dienes consists of a complex of sodium alkyl and sodium isopropoxide which is usually formed by the addition of propylene and isopropyl alcohol to amyl sodium[271]. The effect was discovered when studies were carried out using diisopropyl ether as a solvent. The amyl sodium reacted with the ether to give the two required sodium salts. This polymerization initiator has been called the alfin catalyst since it is a complex of the sodium salts derived from a secondary alcohol and an olefin.

TABLE 26. EFFECT OF SALTS ON THE POLYMERIZATION OF BUTADIENE BY PHENYLSODIUM AND *p*-ISOPROPYLPHENYL SODIUM[270]

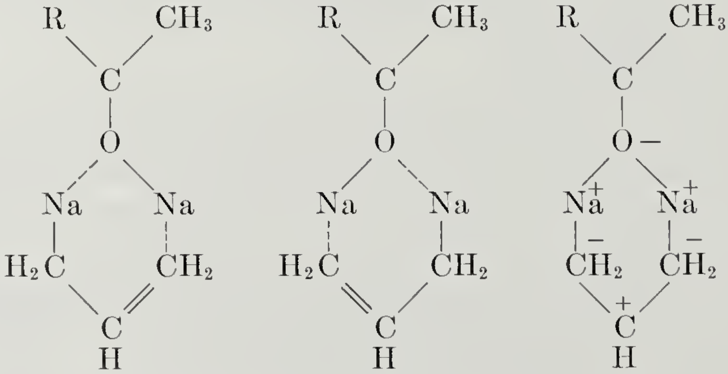
RCl Used to Prepare RNa	Salt Formed from Halide	Salt Added to the Reaction	Butadiene Conversion (%)	Polymer (n)	Acid Recovered (%)
C_6H_5Cl	NaCl	None	60	0.69	70
C_6H_5Br	NaBr	None	22	.19	53
C_6H_5Br	NaBr	None	20	.21	57
C_6H_5Br	NaBr	NaCl[a]	22	.22	62
C_6H_5Br	NaBr	NaCl[b]	23	.36	65
C_6H_5Br	NaBr	NaCl[c]	73	.57	53
C_6H_5Br	NaBr	$NaOC_6H_5$	Trace	—	65
C_6H_5Br	NaBr	$NaOCH_3$	34	.49	61
C_6H_5Br	NaBr	NaOH	51	.52	50
$i\text{-}C_3H_7C_6H_4Cl$	NaCl	None	47	.26	56
$i\text{-}C_3H_7C_6H_4Br$	NaBr	None	8	Low	74

[a] One-third equivalent of ordinary dry sodium chloride finely powdered.

[b] One equivalent of sodium chloride as in a.

[c] One-half equivalent of sodium chloride prepared *in situ* by the addition of the required quantity of amyl-chloride to the phenylsodium so that sodium chloride would form from the second stage of a Wurtz reaction.

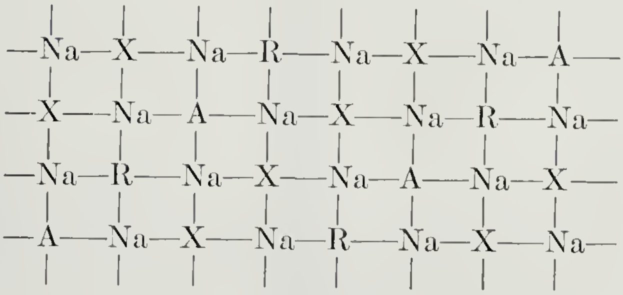
The structure suggested[271, 272] for this complex is stabilized by several resonance forms:



The alfin catalyst apparently acts by enhancing the relative rate of propagation, perhaps by hindering termination processes, and 1,4 addition leading to high intrinsic viscosities. In other words the alfin catalyst induces a chain type of process.

Again the alfin catalysts are usually prepared in such a way as to contain sodium chloride. Little catalytic activity is observed when the salt is not present. When sodium chloride is added to a catalyst mixture originally free of sodium chloride, activity is restored, and the finer the salt is dispersed the greater the activity. This of course indicates again an inhomogeneous reaction in which the surface of the salt crystals plays a role. Morton and Bolton[273] have also tested salts other than sodium chloride. All of the halides of the common alkali metals except the fluoride, chloride, and bromide of lithium and the fluorides of sodium and potassium could serve as catalyst components. Pseudohalides such as sodium cyanide and thiocyanate were also active.

Thus it is found that for the alfin catalyst three components are equally important[274]; sodium allyl, sodium isopropoxide, and a salt, normally sodium chloride. The active agent is an insoluble cluster of ions in the usual nonpolar pentane medium in which polymerization is carried out. This ternary mixed salt may be visualized as shown below:



$$\begin{array}{l}
-\mathrm{Na}-\mathrm{X}-\mathrm{Na}-\mathrm{R}-\mathrm{Na}-\mathrm{X}-\mathrm{Na}-\mathrm{A}- \\
-\mathrm{X}-\mathrm{Na}-\mathrm{A}-\mathrm{Na}-\mathrm{X}-\mathrm{Na}-\mathrm{R}-\mathrm{Na}- \\
-\mathrm{Na}-\mathrm{R}-\mathrm{Na}-\mathrm{X}-\mathrm{Na}-\mathrm{A}-\mathrm{Na}-\mathrm{X}- \\
-\mathrm{A}-\mathrm{Na}-\mathrm{X}-\mathrm{Na}-\mathrm{R}-\mathrm{Na}-\mathrm{X}-\mathrm{Na}-
\end{array}$$

Alfin Catalyst

X = halide, A = alkoxyl, R = alkenyl. The reaction is obviously heterogeneous and presumably involves adsorption of the monomer units on the crystals where strong electrical forces can induce polymerization. As would be expected, a high degree of specificity is observed. Butadiene reacts by far the best and at about the fastest rate known for polymerization, styrene and isoprene less efficiently and 2,3-dimethylbutadiene hardly at all. It appears then that the butadiene molecule fits nicely on the surfaces of these dispersed ion clusters.

The properties of alfin produced polybutadiene are also remarkably different. For one thing, the weight average molecular weight is about 7×10^6 or greater without the occurrence of cross linking. This may be compared to natural rubber, about 3×10^6, or to sodium or emulsion polymerized butadiene prepared without allowing cross linking, about 10^5. Also the alfin polymer has 70 to 80 per cent incorporated 1,4 units, similar to free radical produced material. Sodium produced polymer has around 30 to 40 per cent 1,4 units[275]. This difference in mode of addition suggests that free radicals may be involved. However, it is not unreasonable that the surface nature of the process in which spatial arrangement is involved may account for this result.

The reactions so far discussed were usually carried out in nonpolar media and exhibited heterogeneous characteristics. In more polar materials such as liquid ammonia or ether homogeneous systems exist in which basic reagents produce polymerization by anionic mechanisms. Beaman[276] induced the polymerization of methyl acrylonitrile at room temperature and −75°C in ether by the addition of butyl magnesium bromide, phenyl magnesium bromide, and triphenylsodium in ether solutions.

With the Grignard reagents the molecular weights were about 8,000 while with the sodium compound it was near 20,000. Sodium in liquid ammonia at −75°C produces immediately and quantitatively polymer of over 100,000 molecular weight. In the sodium-liquid ammonia system isobutylene and butadiene failed to polymerize, vinyl acetate and ethyl acrylate yielded viscous oils, and methyl methacrylate formed polymer of molecular weight, 16,500 or higher.

TABLE 27. AMIDE ION POLYMERIZED POLYSTYRENE MOLECULAR WEIGHT DATA[278]

Percentage N Found	Molecular Weight from N Content	Viscometric Molecular Weight
0.995	1410	1500
0.645	2180	2200
0.500	2800	2200
0.706	1980	2300
0.645	2180	2300
0.422	3320	3200
0.378	3700	3200
0.411	3400	3600
0.464	3020	3600

This type of reaction has been also studied by others[277, 278] in particular the polymerization of styrene, methyl methacrylate and acrylonitrile in the temperature range of −30 to 70°C induced by the amide ion. The reaction occurs within a few seconds or minutes.

Relatively low molecular weight material is found. The system is unlike those described above, apparently homogeneous, has a positive temperature coefficient and the molecular weight increases with decreasing temperature. The lowest molecular weight reported[278] was 1400 produced in 26.5 per cent yield when 0.0645 mole/l $NaNH_2$ and 0.0845 mole/l styrene were reacted. A molecular weight of 3600 in 75.7 per cent yield occurred in the reaction of 0.0064 mole/l $NaNH_2$ and 0.282 mole/l styrene. From the nitrogen content of the polymer (see Table 27) it is apparent that each polymer molecule contains one NH_2.

Further evidence on this point is that an increase in molecular weight is found upon reaction of the polymer in xylene solution with phosgene, a process which couples amine groups.

The mechanism[278, 279] used to describe this system is:

$$N\bar{H}_2 + CH_2{=}CHX \xrightarrow{k_1} NH_2{-}CH_2{-}C\bar{H}X$$

$$NH_2CH_2{-}C\bar{H}X + CH_2{=}CHX \xrightarrow{k_2} NH_2CH_2{-}CHXCH_2C\bar{H}X$$

$$NH_2(CH_2CH\bar{X})_i + H - NH_2 \xrightarrow{k_4} NH_2(CH_2CHX)_iH + N\bar{H}_2$$

This scheme and the steady state assumption lead to the following over-all rate equation:

$$\frac{-dM}{dt} = \frac{k_2k_1}{k_4}\,\frac{[M]^2[\overline{NH_2}]}{[NH_3]}$$

The weight average DP_w for complete conversion is given by:

$$DP_w = \left(1 + \frac{k_2M_0}{k_4[NH_3]}\right)$$

Although there is considerable scatter, the data and the above expression have at least the same general trend. Since with potassium amide under the experimental conditions used, $[NH_2^-]^2 \approx K_d[KNH_2]$, where K_d is the dissociation constant for KNH_2, the over-all rate may be written:

$$\frac{-dM}{dt} = \frac{k_1k_2}{k_4}K_d^{1/2}\,\frac{[M]^2[KNH_2]^{1/2}}{[NH_3]}$$

From the rate and molecular weight dependence on temperature the following energy values result[279]: an over-all activation energy, E, of 9 ± 2 Kcal/mole, and a quantity $E_2 - E_4$, of -4 ± 1 kcal/mole. It is estimated that ΔH for dissociation of KNH_2 is 0 ± 2 kcal/mole. Thus since: $E = E_1 + E_2 - E_4 + \Delta H$, E_1 is 13,000 kcal/mole.

Potassium alone in liquid ammonia causes the polymerization of styrene with reaction characteristics similar to the use of potassium amide[280]. For one thing the polymer was found to contain nitrogen, indicating reaction with the solvent. It is suggested[280] that the amide ion is responsible for the polymerization and is formed in this system on reduction of the monomer by the potassium as follows:

$$2K + CH_2CHPh + 2NH_3 \rightarrow 2K^+ + CH_2CH_2Ph + 2NH_2$$

A survey of the polymerization activity of various organic bases has been carried out[281]. The qualitative results are listed in Table 28. It is seen that the order of polymerizability of the monomers is: acrylonitrile > methyl methacrylate > styrene > butadiene, as previously found[206]. Also the activity of the catalysts correlates reasonably well with the base strength as seen from the acid pK's which are given. The same trends are seen for both ethereal at 20°C and liquid ammonia solutions at −33.5°C. Probably a more quantitative correlation is not feasible since other factors such as steric effects will exert appreciable influence.

TABLE 28. POLYMERIZABILITY OF MONOMERS AND ANIONIC SYSTEMS[281]

Acid	pK (ether)	Color of Anion	Monomers			
			Acrylonitrile	Methyl Methacrylate	Sytrene	Butadiene
(Ethereal solution; 20°C)						
Methanol	17	Colorless	+	—	—	
Ethanol	18	Colorless	+	—	—	
Acetophenone	19	Yellow	+	—	—	—
Triphenylcarbinol	19	Green	+	—	—	
Indene	21	Yellow	+	+	—	—
Phenylacetylene	21	Colorless	+	+	—	—
Diphenylamine	23	Colorless	+	+	—	—
Fluorene	25	Red	+	+	—	—
Aniline	27	Colorless	+	—	—	—
p-Methoxyaniline	27	Colorless	+	—	—	
Xanthen	29	Red	+	+	+	+
Triphenylmethane	33	Red	+	+	+	+
(Liquid-ammonia solution; −33.5°C)						
Ethanol	18	Colorless	+	—		
Acetophenone	19	Yellow	+	—		
Triphenylcarbinol	19	Green	+	—		
Indene	21	Yellow	+	—		
Phenylacetylene	21	Colorless	+	—	—	
Diphenylamine	23	Colorless	+	+	—	
Fluorene	25	Orange	+	—	—	
Acetylene	26	Colorless	+	+	—	
Aniline	27	Colorless	+	+	+	
Xanthen	29	Red	+	+	+	
Triphenylmethane	33	Red	+	+	+	
Ammonia	36	Colorless	+	+	+	—

+ Indicates formation of polymer.
− Indicates absence of polymer.

In liquid ammonia, chloride, iodide, and hydroxide ions did not initiate the polymerization of styrene or methyl methacrylate. The anions from diphenylamine, aniline, triphenyl methyl and ammonia, i.e., the amide ion, all were effective in causing the polymerization of the methyl methacrylate while only the latter two ions were effective toward styrene. It was also observed that α-methyl styrene and 1,1-diphenylethylene, although failing to polymerize, apparently reacted to form negative addition complexes with the amide ion which were intensely red-colored.

These results have been discussed[278] in terms of the energetics of the reaction scheme postulated. The heat of reaction Q_a of an ion X with the ammoniated solvent and the heat of reaction Q_i of an ion with the monomer can be estimated from the following relations:

Table 29. Energies for Anionic Polymerization Processes in kcal/mole[278]

X	$(E + S)$	D_{X-H}	D_{X-C}	Q_a	Q_i
Cl	150.4	102.7	82	−57	−35
$B\bar{r}$	138.4	87.3	70	−60	−35
I^-	118.9	71.4	55	−57	−30
$\bar{O}H$	147.4	120	92	−36	−22
$\Phi_3\bar{C}$	82	65	51	−26	+3
$\Phi_2\bar{C}H$	78	71	57	−16	+13
$N\bar{H}_2$	95	104	80	0	+19
$\Phi C\bar{H}_2$	72	77	63	−4	+25
$C\bar{H}_3$	67	102	88	+26	+55

$$Q_a = -(E + S)_X + D_{X-H} + (E + S)_{NH_2} - D_{N-H}$$

$$Q_i = -(E + S)_X + D_{X-C} + (E + S)_R - D^{\alpha\beta}_{C=C}$$

where $(E + S)_X$ is the sum of the electron affinity of the species X and the solvation energy of its ion, $(E + S)_R$ the corresponding quantity for the radical $-\dot{C}HR$ and its anion $-\bar{C}HR$, D_{X-H}, D_{N-H} and D_{X-C}, are the dissociation energies of the indicated bonds, and $D^{\alpha\beta}_{C=C}$ is the energy to open the double bond to a single bond. Table 29 lists the values used for the above terms and the results obtained. There are considerable uncertainties in some of these numbers, however. Nevertheless it is felt that they show the general trend of the various energy factors and warrant discussion. The values are reasonable judging from observations on the equilibria of the reactions between the various phenyl substituted methyl carbanions and ammonia.

The first group of substances are unlikely to effect polymer formation, as seen from their Q_i values. This is obviously a consequence of their high electron affinity and solvation energies. The second group should be active towards monomers unless, as in the first two, large steric effects interfere. The substances at the bottom of the list can readily initiate polymerization. However, in liquid ammonia, they also react rapidly to produce the amide ion. In the light of this, it is readily apparent that in ether they would be good initiators as found by Beaman and Ziegler[276, 282, 283].

In general, one deduces a plausible reactivity series for the amide ion towards the following olefins, ethylene being the least active.

$$\mathrm{CH_2{=}CH_2} < \mathrm{CH_2{=}CCH_3\Phi} < \mathrm{CH_2{=}CH\Phi} < \mathrm{CH_2{=}C\Phi_2}$$

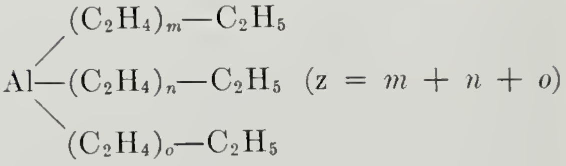
The heat of reaction for the termination step in the styrene system is about -4 kcal, i.e., approximately equal to Q_a for the phenyl methyl carbanion in Table 29. From the Q_a's for $\overset{-}{\mathrm{C}}\mathrm{H_3}$, $\overset{-}{\mathrm{C}}\mathrm{H_2\Phi}$, and $\overset{-}{\mathrm{C}}\mathrm{H\Phi_2}$, it is evident that the tendency for solvent termination will decrease in the order:

$$\mathrm{R{-}}\overset{-}{\mathrm{C}}\mathrm{H_2} > \mathrm{R{-}}\overset{-}{\mathrm{C}}\mathrm{H\Phi} > \mathrm{R{-}}\overset{-}{\mathrm{C}}\mathrm{\Phi_2}$$

In the case of diphenylethylene steric hindrance prevents polymerization, and reasonably high concentrations of the latter type ion can occur to give highly colored solutions.

An interesting new catalyst for polymerization has resulted from researches on lithium aluminum hydride and aluminum hydride[284]. Both substances have been found to add to ethylene and 1-olefins to form alkyl derivatives. For these reactions to occur it is essential for the hydrides to be ether-free. Since ether is normally used as a solvent for preparing these compounds and complexes with aluminum derivatives, this entails certain precautions. Using ethylene as an example, the following reactions occur when the gas is reacted with aluminum hydride, possibly in hydrocarbon solvent and under pressure:

$$\mathrm{AlH_3} \xrightarrow{\mathrm{C_2H_4}} \mathrm{AlH_2C_2H_5} \xrightarrow{\mathrm{C_2H_4}} \mathrm{Al(C_2H_5)_2} \xrightarrow{\mathrm{C_2H_4}} \mathrm{Al(C_2H_5)_3} \xrightarrow{\mathrm{z\ C_2H_4}}$$



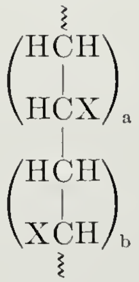
$$\mathrm{Al}\begin{cases}\mathrm{(C_2H_4)}_m\mathrm{{-}C_2H_5}\\ \mathrm{(C_2H_4)}_n\mathrm{{-}C_2H_5}\\ \mathrm{(C_2H_4)}_o\mathrm{{-}C_2H_5}\end{cases} \quad (\mathrm{z} = m + n + o)$$

The first additions occur readily at 60 to 80°C. Further reaction requires high temperature, owing to differences between the hydride bond and the alkyl bond. Extensive reaction of this type can lead to high molecular weight polyethylenes which are presumably completely linear in contrast to free radical prepared material which is highly branched. Temperatures around 200°C are required for production of long chain derivatives. The aluminum can be removed by hydrolysis leaving pure paraffinic materials.

An extension of the above work led to the discovery that aluminum alkyls in combination with metal halides, particularly titanium tetrachloride, polymerize ethylene at normal pressures and temperatures to very high molecular weight and at a high rate of conversion[284a]. The resulting polymer is linear and readily crystallizes to give a highly crystalline material. It is more dense than the older commercial polyethylene, a less crystalline substance; hence the term, high density polyethylene. Sometimes the terms "high pressure" and "low pressure" polyethylene are used respectively for the two types. The older material is ordinarily prepared at several thousand atmospheres pressure while the new one is obtained at one atmosphere.

Crystallizable Polymers and Method of Polymerization. Few polymers are "normally" found to be highly crystalline. Free radical prepared polystyrene and polymethyl methacrylate are completely amorphous materials which do not show any tendency to crystallize. On the other hand, polytetrafluoroethylene readily crystallizes and is normally in a crystalline condition. Natural rubber, however, exists ordinarily in an amorphous state; but will crystallize on stretching or at low temperature. Often quite strenuous conditions are required to achieve crystallinity in polymers. Special treatment and extremes of pressure and temperature may be necessary, even when complete structural regularity exists. An ordered macroscopic structure, i.e., a crystalline material, is in general the result of a high degree of uniformity in the molecular structure. Polymers, owing to their molecular size, offer considerable opportunity for the occurrence of structural imperfections or irregularities. Two factors or structural effects, which mitigate against uniformity or order, and which often occur as a result of the method of polymerization, are: (1) random branching and (2) randomness of the asymmetry of the carbon atoms in the chain. Homogeneous free radical polymerization at fairly high temperatures favors both effects.

The operation of the first effect is fairly clear. The second may require some explanation. In the linear carbon chains of monomers of the type CH_2—CHX, every other carbon is asymmetric, hence stereoisomerism is possible. The various possibilities have been discussed in some detail[285a]. This means that several different arrangements may exist. Using the same method of presentation common in carbohydrate chemistry, some possible structures are shown below:



A

B

C

The most unfavorable molecule from a crystallinity viewpoint is structure A where the right and left X groups are randomly put together, i.e., the probability of sequences of i right X groups is $(\frac{1}{2})^i$. However, structures B and C are highly uniform, X's being always on the right or alternating. The enantiomorph of B, i.e., X's always on the left is, of course, another possibility. If all polymers could be made in these various arrangements one might expect to have two or three forms of all polymers of this type unit with considerable differences in properties. One might expect that with heterogeneous systems of solid catalysts, where steric effects controlled the mode of growth, such results could be obtained, and indeed results along this line have recently been reported[285, 286]. In a rather epic-making work, polypropylene, poly-1-butene and polystyrene have been made in highly crystalline forms. The workers[285, 286] favor a structure such as B above and point out that a helical configuration probably results when crystallization occurs. These investigators have coined the names atactic, isotactic, and syndyotactic, respectively, for the above structures A, B, and C, while eutactic has been used as a general term[285c] for structures B and C. The catalysts system used in preparing these highly crystallizable materials was that developed by Ziegler[284a] which results in a linear polyethylene. There, of course, no asymmetric carbon atoms are present and hence a highly linear structure suffices for crystallization to occur. Several reviews of these developments have appeared[285b, c, d]. Further investigations have produced many crystallizable hydrocarbon polymers. In Table 30 several of these are listed.

Simultaneously with the above work numerous developments along the same line were reported by other workers. However, a much earlier investigation[287] of the polymerization of vinyl isobutyl ether showed that amorphous or noncrystallizable and crystallizable polymer could be formed from the same monomer depending on the manner of polymerization. If polymerized rapidly (actually a flash polymerization) in liquid propane at about −40°C with boron trifluoride, vinyl isobutyl ether forms an amorphous rubber-like polymer. On the other hand, if boron trifluoride etherate is used dropwise at −60 to −80°C, the polymerization is quite slow and the polymer formed is nontacky and crystalline. Definite x-ray patterns are obtained on the latter and the properties of the two forms differ considerably. This difference is not due to molecular weight or distribution differences between the two types of polymer. The explanation of this phenomenon appears to be that steric effects are more important in the slow process and presumably lead to a considerable amount of structure C in the polymer. In the fast process the steric effect is overcome or absent for some reason or another, possibly the lack of time for orientation of the reacting monomer units.

TABLE 30. PROPERTIES OF EUTACTIC HIGH POLYMERS[285c]

Polymer	Type of Order	Melting Point (°C)	Specific Gravity
Polypropylene	Isotactic	160	0.92
Polybutene-1	do	125	0.91
Polypentene-1	do	70	0.87
Polyhexene-1	do	55	
Polyheptene-1	do	40	
Polyoctene-1	do	38	
Polydodecene-1	do	45	
Polyoctadecene-1	do	10	
Poly-3-methyl-butene-1	do	300	0.90
Poly-4-methyl-pentene-1	do	235	0.83
Poly-4-methyl-hexene-1	do	190	0.86
Poly-4,4-dimethyl-pentene-1	do	>320	
Polybutadiene-1,3	1,2 isotactic	120	0.96
	1,2 syndyotactic	154	0.96
	1,4 trans	135	1.01

Another recent example of what is now called stereospecific catalysis is the preparation of crystallizable polystyrene by the use of the alfin catalyst system[285e]. Also propylene oxide has been prepared in a crystallizable form[285f] with ferric chloride catalysis. Several oil companies have patents for solid catalysts which can polymerize olefins to crystallizable polymers. Molybdena and nickel on alumina[285g] and chromia-alumina on silica[285h] have been described.

Most of the above systems polymerize isoprene to give essentially "natural" rubber, i.e., an all *cis*-1,4-polyisoprene. However, another catalyst which accomplishes this is simple lithium metal[285i] which was used to polymerize isoprene over forty years ago[285j].

Conceivably, much simpler methods of polymerization for crystallizable polymers may yet be developed. For instance, liquid ethylene polymerizes readily to high molecular weight at 0°C when gamma-rays are used to initiate polymerization[285k]. No methyl groups are found in the infrared spectra. Furthermore, it has recently been reported that a low temperature (-78°C) isobutylene is polymerized[285l] by gamma-rays to give high molecular weight ($M \approx 10^5$), polymer. Although this may indicate ionic polymerization with gamma-rays, the low efficiency of the process and other characteristics suggest a free radical process. Assuming this to be the case, one must conclude that monomer transfer producing allylic radicals is reduced relative to chain growth at the low temperature in order for high polymer to result. On this basis then, propylene and other alkenes should also form high polymers under the action of ionizing radiation at -80°C. There is also the possibility that these and other polymers prepared at such temperatures by means of free radicals would be eutactic.

In some recent Russian work on organometallic catalyst systems it was reported that isobutylene polymerized by $Al(C_2H_5)_3$ and $TiCl_4$ gave polymers with CH_3/CH_2 ratios of 1:1 instead of the usual 2:1 for polyisobutylene[284b]. One suspects that such a result may be caused by incorporation of hydrocarbon material from solvent or catalysts in the polymer. In another recent Russian study of copolymerization as a function of catalyst composition, the alfin catalyst is classified with butyl lithium while the Natta-Ziegler system is classified with the acid type[284c].

DEGRADATION OF POLYMERS

The previous pages in this chapter were devoted to a discussion of polymerization processes. The kinetics and mechanisms of these reactions have been studied extensively and a firm foundation of knowledge accumulated. Absolute rate constants have been measured and broad generalizations made, which on the whole appear successful. Knowledge of the reverse process, i.e., depolymerization, or more broadly speaking, polymer decomposition or degradation has been rapidly advancing during the past ten years. This appears to be partly due to the close relationships between depolymerization and polymerization processs and to the importance of the stability of polymers in their application. Several reviews[45, 288] on polymer degradation have been published recently.

As before, we wish to consider methods of inducing the reaction and to show how experimental conditions determine the final result. Certain limitations will be imposed at the outset. Hydrolytic and enzymatic breakdown of polysaccharides and proteins are considered outside the scope of this chapter. We shall be concerned with thermal, radiation, and oxygen induced processes, with particular attention to bulk polymers mainly of the vinyl type. The ensuing reactions all involve free radical intermediates.

Thermal Decomposition

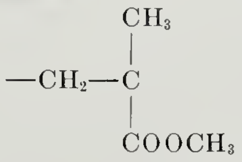
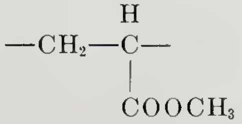
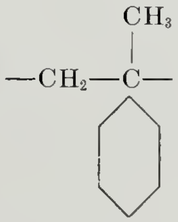
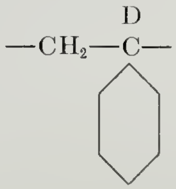
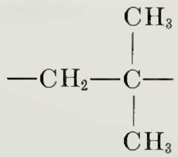
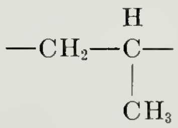
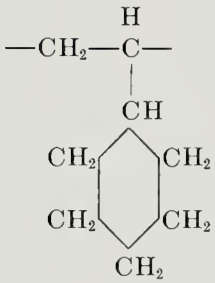
It is striking that in a process which leads, after all, to the same end product, namely small molecules, such pronounced differences[289] in the reaction pattern can occur, as are observed for instance between polymethylene and polymethyl methacrylate. It will be one of our main purposes to discuss such differences quantitatively.

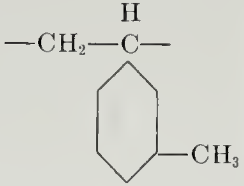
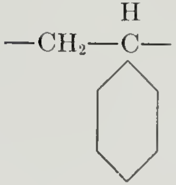
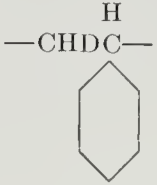
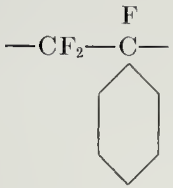
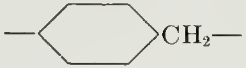
Clearly, in order to study the primary breakdown and reaction products it is desirable to work under high vacuum conditions, that is, 10^{-4} to 10^{-6} mm. There are three convenient quantities, characteristic for each polymer, to be investigated. These are[290]: (1) the over-all rate of volatilization, (2) the rate of decrease of the average molecular weight, and (3) the yield of pure monomer. Analysis of the volatiles for most polymers, so far studied, shows only a fraction to be pure monomer. The molecular structure of the polymer has a profound influence on these yields. This is shown in Table 31[291].

These polymers are grouped according to structure into five groups: acrylates, styrenes, aliphatics, fluorine-containing compounds and those with aromatic rings in the chain. It is seen that methyl substitution in the α-position of the monomer units results in higher yields; compare, for example, styrene vs. α-methyl styrene, methyl acrylate *vs.* methyl methacrylate and even propylene *vs.* isobutylene. Recently reported results establish this comparative behavior also for the pair acrylonitrile[291a] *vs.* methacrylonitrile[291b], their respective monomer yields being $\sim$1 and $\sim$100 per cent. The substitution of deuterium in the α-position in styrene also increases the monomer yield whereas in the β-position no effect is seen. Earlier results of this type, although meager, suggested that the mechanism of thermal decomposition of polymers should involve both a depropagation step[292] producing pure monomer and a step analogous to transfer in polymerization producing nonmonomeric compounds such as dimers, trimers, and other derivatives, etc. Inspection of Table 31 readily supports this conclusion. Structures which have only limited possibilities for transfer in thermal depolymerization produce high monomer yields. The data in Table 31 do raise some questions. For instance, higher monomer yields might have been anticipated in the case of polyisobutene and polytrifluorostyrene. We shall revert later to this point.

The molecular weights of the decomposing polymers also follow different patterns. In polymethylene a very rapid decrease in molecular weight occurs before more than 1 or 2 per cent of the material volatilizes[293]. On the other hand, for polymethyl methacrylates of molecular weights $\leqq 10^5$ no significant decrease in the degree of polymerization (DP) occurs until 20 to 40 per cent[294] of the polymer has been completely degraded. Polystyrene occupies an intermediate position, the DP decreasing rapidly but not as drastically as in polymethylene[295, 296]. Although molecular weight studies,

Table 31. Monomer Yields[291]

Polymer		Wt. %
Methyl methacrylate	 $-CH_2-\underset{\underset{COOCH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}$	95
Methyl acrylate	 $-CH_2-\underset{\underset{COOCH_3}{\vert}}{\overset{H}{C}}-$	2
α-Methyl styrene		95
α-Deuterostyrene		70
Isobutylene	 $-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-$	20
Propylene	 $-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{H}{C}}-$	2
Vinyl cyclohexane		.1
Ethylene, branched	$-CH_2-CH_2-$	.025
Ethylene, linear (methylene)	$-CH_2-CH_2-$	.1
Tetrafluoroethylene	$-CF_2-CF_2-$	95

m-Methyl styrene		45
Styrene		42
β-Deuterostyrene		42
Trifluorostyrene		75
Trifluorochloroethylene	$—CF_2CFCl—$	28
Trifluoroethylene	$—CF_2CFH—$	1
Vinylidene fluoride	$—CH_2CF_2—$	1
Vinyl fluoride	$—CH_2CHF—$	1
p-Xylene		0
Benzyl		0
Phenyl		0

particularly of number averages, are very important for a complete understanding of the decomposition mechanisms, such data have been reported on only relatively few polymers.

Rates of volatilization also show large differences, depending on the type of polymer. It has been customary to plot the rate as per cent or fraction of original sample weight evaporated per unit time versus per cent volatilized[290, 294]. These rates again exhibit two general types of behavior. The initial values are high and decrease thereafter monotonically, sometimes with constant slope but more often with downward curvature, or alternatively, they start low and pass through a maximum[297].

These then are the essential facts theory must account for quantitatively. In considering the possibilities of decomposing a long chain molecule, the simplest assumption is that all force constants and dissociation energies of the bonds to be attacked are equal. On the basis of classical statistics which should be adequate, this has the consequence that all links are equally likely to break, regardless of the chain lengths and of their position[298]. Indeed this assumption of a random degradation explains in the main the nonbacterial hydrolysis of linear polysaccharides. It also yields a molecular weight curve quite similar to polymethylene and describes the molecular weight distribution of the volatiles, provided one properly accounts for the fact that large fragments, of the order of 70 methylene units, can evaporate[299]. Such a mechanism obviously gives a low yield of small species, and preferentially intermediate sizes, until the last stages of the reaction.

In attempting an explanation of the slow molecular weight drop and rapid evolution of volatiles observed in other polymers, one of the present authors suggested some fifteen years ago a preferential or exclusive breaking of terminal bonds[300]. This results in a linear decrease of molecular weight with conversion but is not sufficient to describe all possibilities. Formally, one might introduce a whole spectrum of decomposition probabilities. This, however, is not satisfactory. It is true that a consideration of the zero point energies in low molecular weight hydrocarbons gives different decomposition rates for ethanes and for example propane and butanes[301]. The latter two actually pyrolyze more rapidly than the former to an extent[302] which may be indicative of real differences in the bonds. With increasing size, however, the differences decrease, and should become unimportant in very long chains. Even accepting the picture of a distribution of bond strengths, the differences in monomer yield still remain to be explained.

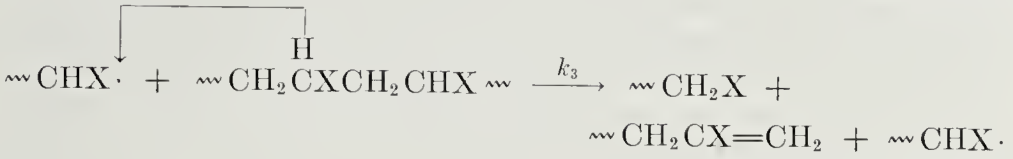
So far, we have discussed the problem on the basis of a step reaction, consisting of the iteration of a single step, the rupture of a bond. It is well known that the thermal decomposition of low molecular weight hydrocarbons can proceed by a chain mechanism and be catalyzed by free radicals[303]. Furthermore, we must be able to establish a bridge between the reactions which form and destroy the molecule. A chain theory, which accounts for the above facts and avoids the above difficulties of interpretation, has been developed[304] and extended[290]. We might mention that the chain mechanism leads naturally to a spectrum of rate constants, however, only as a purely statistical effect, which has nothing to do with weak links. The elementary acts of the chain reaction postulated are as follows·

$$\sim CH_2-CHX-CH_2-CHX\sim \xrightarrow{k_1} \sim CH_2CHX\cdot + \sim CHXCH_2\cdot$$

initiation

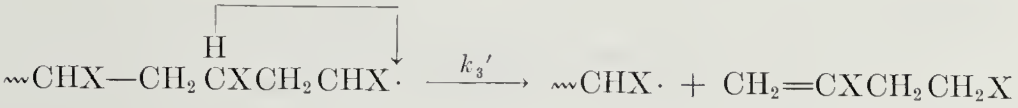
$$\sim CH_2CHXCH_2CHX\cdot \xrightarrow{k_2} \sim CH_2HX\cdot + CH_2=CHX$$

propagation



$$\sim CHX\cdot + \sim CH_2\overset{H}{C}XCH_2CHX\sim \xrightarrow{k_3} \sim CH_2X + \sim CH_2CX=CH_2 + \sim CHX\cdot$$

intermolecular transfer



$$\sim CHX-CH_2\overset{H}{C}XCH_2CHX\cdot \xrightarrow{k_3'} \sim CHX\cdot + CH_2=CXCH_2CH_2X$$

intramolecular transfer

$$2 \text{ radical} \xrightarrow{k_4} 2 \text{ polymer}$$

termination

For extremely pure polymers it is natural to assume that the initiation act involves the rupture of a C—C bond. Two important types of initiation are suggested by experimental data[294, 295], namely, random and terminal initiation. With most polymers it is also likely that initiation may result from impurities or peroxidic groups which are part of the polymer molecule. These can arise either by the oxidation of the polymer, normally occurring under most storage conditions, or by the reaction of small amounts of oxygen with the growing radicals during the polymerization process. Such alternatives can be easily taken into account by suitably defining the rate constant k_1 for initiation.

The propagation step is the reverse of radical growth in polymerization. The transfer processes depicted consist actually of two elementary acts, hydrogen abstraction followed by decomposition of the resulting radical. These are combined for mathematical convenience. Further refinement of the treatment may require the separation of these acts. Intermolecular transfer contributes a random component to the over-all process. Intramolecular transfer, on the other hand, enhances effectively, as far as the formal kinetics is concerned, the propagation step. Product analysis should aid in separating the two transfer steps. Finally, a termination step must occur. The high temperatures required for depolymerization processes suggest disproportionation as the preferred process. Combination may occur but would be difficult to distinguish from disproportionation if the over-all reaction had a long kinetic chain length. A more pertinent possibility is the evaporation of small radicals[305, 306]. If predominant, this would mean an apparent unimolecular termination.

It may seem at first sight that the kinetics ensuing from the above scheme is merely the reversal of the simple polymerization kinetics. This is not the case. It is more complicated because of the production of intermediate species which can be reactivated. In polymerization on the other hand, a stable chain, once formed, is usually assumed to remain dead, except in graft polymerization. In addition, the initial size of the degrading molecules imposes a natural boundary condition as will be seen below.

Assuming the existence of a steady state in respect to radical concentration, R, as we have done previously, the theory introduces two characteristic parameters, ϵ and σ.

Defining:

$$1/\epsilon - 1 = \frac{\text{probability of propagation}}{\text{probability of termination} + \text{transfer}}$$

one has

$$1/\epsilon - 1 = \frac{k_2}{k_4R(1 + \sigma/2)}; \qquad \text{random initiation}$$

$$1/\epsilon - 1 = \frac{k_2}{k_4R\left[1 + \dfrac{k_3}{k_4R}\sum iQi - \dfrac{3\sigma}{2}\right]}; \qquad \text{initiation at ends}$$

$$\sigma = \frac{\text{probability of transfer}}{\text{probability of initiation}} = \frac{k_3R}{k_1}$$

The rate equations resulting from the above mechanism for all depolymerizing species Q_i, with i the number of units in the molecule, assume the following form, where $N - 1 \approx N$ denotes the initial number of carbon atoms in the main chain or an upper limit of the initial chain length distribution, and $\tau = k_1t$.

(a) *Initiation at random:*

$$dQ_n/d\tau = -(1 + \sigma)(n - 3)Q_n + 2(k_0 - \sigma/4)Q_{n+2}$$

$$+ 2\sum_{i=1}^{(N-n-3)/2} K_iQ_{n+2i+2} \qquad 4 \leqq n \leqq N - 3, \qquad n \text{ even} \qquad (10a)$$

$$dQ_{N-1}/d\tau = -(1 + \sigma)(N - 4)Q_{N-1}$$

with $K_i = (2 + \sigma)[1 - (1 - \tfrac{3}{4}\epsilon)(1 - \epsilon)^i] + \sigma$

(b) *Initiation at ends:*

$$dQ_n/d\tau = -[2 + (n-3)\sigma]Q_n + 2(K_0 - \sigma/4)Q_{n+2} + 2\sum_{i=1}^{(N-n-3)/2} K_i Q_{n+2i+2}\,; \qquad 4 \leqq n \leqq N-3 \quad (10b)$$

$$dQ_{N-1}/d\tau = -[2 + (N-4)\sigma]Q_{N-1}$$

with $K_i = \sigma[1 - (1 - \frac{3}{4}\epsilon)(1-\epsilon)^i] + \sigma + \epsilon(1-\epsilon)^i$

To clarify the physical significance of the parameter ϵ, we consider that after initiation has taken place, the propagation will consume a number of monomer units by "zipping" down the chain. All zip lengths are possible, although the average will be larger, the larger the propagation at the expense of transfer and termination. The probability p_i of consuming i monomers in one zip equals: $p_i = \epsilon(1-\epsilon)^i$ and the number average zip,

$$Z = \sum_{i=1}^{i=\infty} ip_i \text{ is } 1/\epsilon - 1.$$

It is the analog of the number average DP in polymerization and hence is not identical with the kinetic chain length unless transfer is zero.

Equations (10a, b) are formally equivalent to a step degradation with rate constants K_i which depend on the position i of the bond to be broken. Provided initiation occurs at the chain ends, interior bonds are less likely to be reached by the zip than those near the end. If the initial break occurs at random, the situation is reversed[304]. This, although equivalent to a spectrum of rate constants, is a purely statistical effect. It will be noted also that the transfer parameter σ occurs as a factor in K_i since it effectively increases the rate of initiation of radicals. It also appears as an additive term independent of i, giving rise to a random scission of chains.

The essential consequences of these equations[290a] can be seen intuitively without recourse to the solution. If σ is negligible, the critical quantity is the ratio $(\epsilon N)/2$ between initial DP and the zip length. When it is large, the features of a chain reaction are lost and the process degenerates into a step process which amounts to exclusive breaking of terminal bonds or a random degradation depending on the mode of initiation. In the former instance the rate remains constant until nearly the end, because the number of chain ends remains constant and the reaction is of zero order with respect to the mass of the decomposing material.

In random degradation no simple reaction order occurs. However, there is a maximum rate of conversion when the total number of chain ends reaches a maximum. This can be shown to occur at ≈25 per cent conversion, practically independent of the size of the evaporating fragments[290].

When the ratio $(\epsilon N)/2$, is very small, a radical once initiated, is completely destroyed. The initiation is the rate determining step, monomer comes off rapidly, and the reaction is practically of first order. As first pointed out by Grassie and Melville[294], the molecular weight remains constant. For intermediate values of $(\epsilon N)/2$ and finite σ the picture is modified within the two extremes.

The present discussion indicates the reasons for the observed parallelism between monomer yield, Y, molecular weight decrease $(-dM/dC)$ and over-all rate dC/dt and the connection with the parameters ϵ and σ. Namely:

$$\text{large } 1/\epsilon \longrightarrow \text{small } \sigma \longrightarrow \text{large } Y \longrightarrow \text{small } (-dM/dC) \longrightarrow \text{large } dC/dt \text{ (initial).}$$

This is exemplified by polymethyl methacrylate. The reverse applies to polymethylene while polystyrene is intermediate.

The magnitude of ϵ can be estimated from the monomer yield. At complete conversion the molar ratio r between pure monomer and all nonmonomeric products should be a measure of the relative probabilities of propagation and termination plus transfer. Thus:

$$r = \tfrac{1}{2}(1/\epsilon - 1)$$

This is strictly valid only when intramolecular transfer, which increases kinetically the propagation and at the same time decreases the monomer yield, is zero. Moreover, initially present impurities are disregarded. The zip lengths, $Z = 1/\epsilon - 1$ so calculated, represent minimum values. Results on several polymers are presented in Table 32. The relative position of the three polymers referred to above should be noted. If intramolecular transfer is operative, the above equation becomes[290a]:

$$r = \tfrac{1}{2}(1/\epsilon - 1)\{1 + [s + \tfrac{1}{2}(1/\epsilon - 1)]k_3'/k_2\}^{-1}$$

Here s represents the size of the fragment severed in the k_3' step. The definition of $(1/\epsilon - 1)$ now contains an additional term $k_3' \cdot s$ in the numerator. This can considerably affect the minimum zip-values of Table 32. For example, if radicals depropagate twice as often on the average as they abstract intramolecularly, $k_2/k_3' = 2$, and $s = 2$ or 3, the value for styrene is increased from 3 to 30.

The numerical evaluation of the theory, Eqs. (10a, b), for intermediate values of Z involves the solution of a linear set of order N and hence is feasible only by means of electronic computers. Such a program is now in progress. In Figure 9 there is presented the molecular weight decrease for several polymers. The points and dashed line are experimental while the full lines are theoretical. It is seen that in polymethyl methacrylate the D.P. does not drop sharply. Even so, the theoretical line, which is for $\sigma = 0$, fits the points imperfectly. The sharper decrease observed suggests the presence of some transfer as indeed is found in photo induced depolymerization studies[307]. In polymethylene the experimental values are reasonably close to those predicted by a random process[293], but are consistently higher. The experimental curve for polystyrene to which no theoretical line can as yet

TABLE 32. MONOMER YIELDS AND "ZIP" LENGTHS $1/\epsilon - 1$[315]

	Monomer Yield, Wt (%)	$1/\epsilon - 1$
Ethylene or methylene	0.025	0.01
Acrylonitrile	1	<0.5
Methyl acrylate	2	<1
Isobutylene	20	3.1
Styrene	42	3.1
m-Methyl styrene	45	3.7
α-Deuterostyrene	70	11.8
α-Methyl styrene	>95	>200
Methyl methacrylate	>95	>200
Tetrafluoroethylene	>95	>200

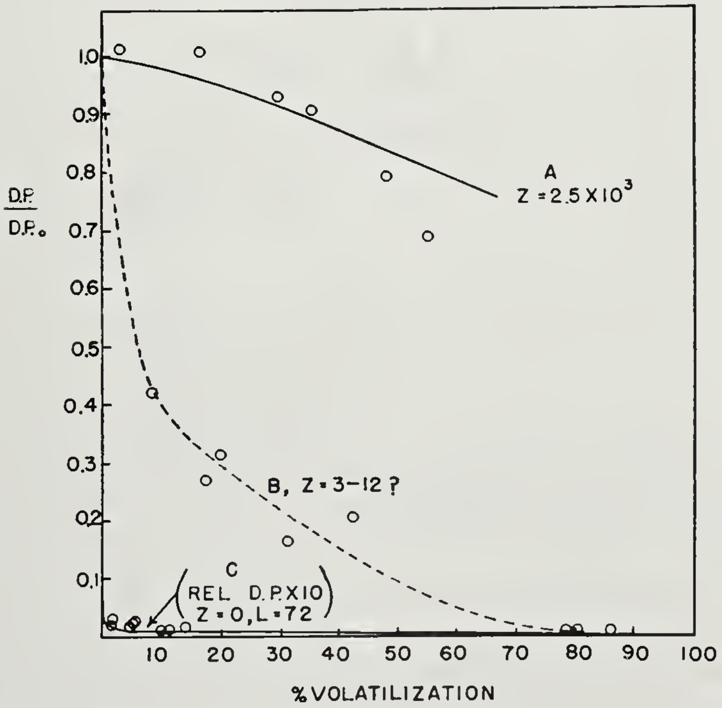


Figure 9. Relative degree of polymerization of polymer residues during depolymerization. A. Polymethyl methacrylate initial MW 177,000. B. Polystyrene initial MW 230,000. C. Polymethylene initial MW 5×10^6.

be fitted because of computational problems, occupies an intermediate position.

Passing on to the rate of volatilization, we see in Figure 10 the experimental rates for the three polymers. For large Z/N we expect the type of curve actually obtained for the methyl methacrylate polymer of high molecular weight. The other curve for methyl methacrylate is usually observed for commercial material containing peroxide. This leads to a high rate of volatilization at low temperatures, and then a cessation of reaction as the initiating substance or group is presumably used up. Polymethylene again represents the other extreme, the rate curve starting low and passing through a maximum (see Figure 11). There the full line represents random theory and the lower dashed line the experimental data. It is concluded that a slightly perturbed random process is operating. Referring back to Figure 10 we see that polystyrene is again intermediate with a broad maximum displaced to the right of the position predicted by random theory.

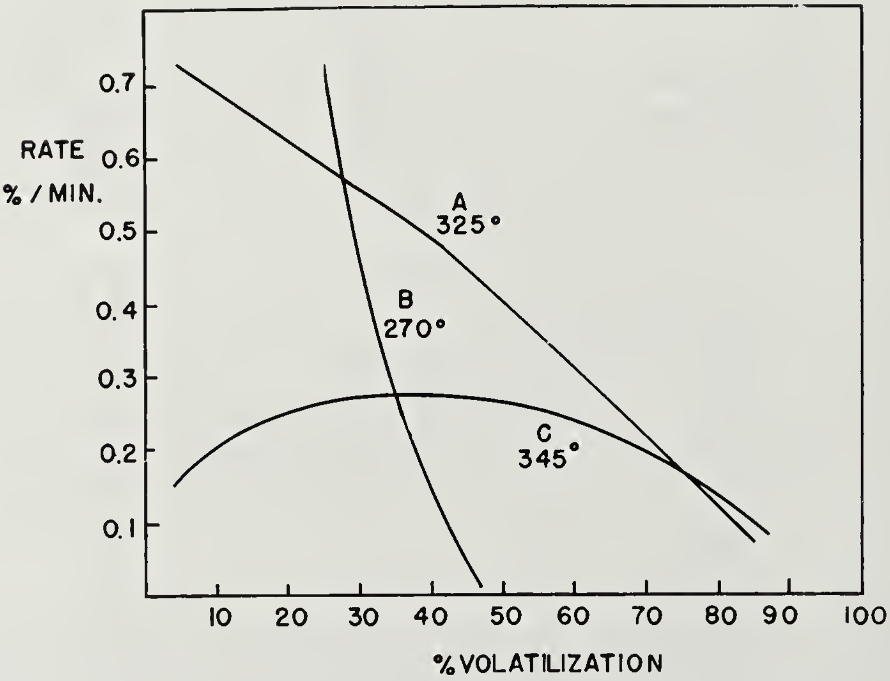


Figure 10. Rates of volatilization *vs.* per cent volatilized for three polymers. A. Polymethyl methacrylate, prepared at 0°C in absence of catalyst. MW $\approx 5 \times 10^6$. B. Polymethyl methacrylate, commercial. MW $\approx$ 150,000. C. Polystyrene thermally polymerized. MW $\approx$ 230,000.

The three principal polymers so far discussed, namely, methyl methacrylate, styrene, and methylene show a consistent pattern with respect to monomer yield, rates of volatilization and decrease in chain length. On the basis of the vanishingly small monomer yield, Table 31, the monotonically decreasing curve of polyethylene, Figure 11, would not have been anticipated. This apparent discrepancy was one of the motivations for our investigation of polymethylene[293]. Now there are two important structural differences between the two polymers. The molecule of polyethylene contains branches, mostly of short length. Secondly, the resulting tertiary C—H bonds are more readily broken than the secondary ones. This is clearly shown by the investigations of Oakes and Richards[308] who found by infrared analysis that a more highly branched sample contains initially fewer vinyl groups on pyrolysis, an indication of the reduced relative probability for secondary H-transfer. Moreover, the fraction of vinyl groups becomes larger during the later stages of the reaction. The ratio of the specific rate constants for tertiary and secondary bonds may be approximately 10, judging from early work on hydrocarbons of low molecular weight. One might think then that branching is the cause for the absence of a maximum.

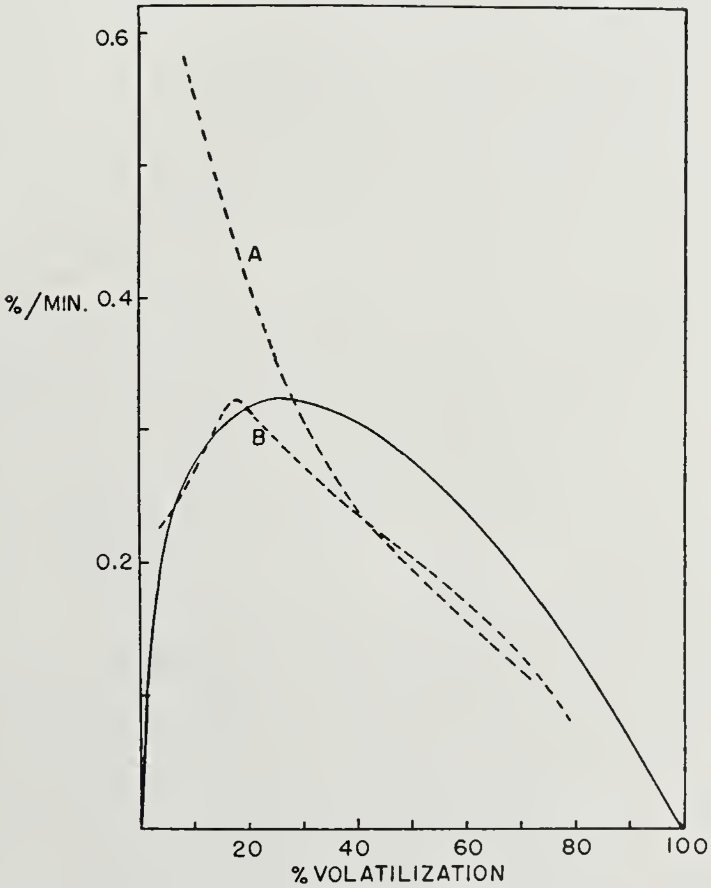


Figure 11. Rates of volatilization *vs.* per cent volatilized. – – – Experimental; —— Theoretical. A. Commercial polyethylene MW ≈ 20,000. B. Polymer prepared from diazomethane MW ≈ 5 × 10^6.

The statistics of randomly degrading branched chains suitably modified for the differences in bond strengths has been recently treated[309]. For the branch frequencies and lengths characteristic of polyethylenes, an increase in the rate, but not even a shift of the maximum results. The persistence of the phenomenon of maximum rate is not unexpected, since the number of chain ends must still increase at the beginning. This leaves open the possibility that the presence of branches modifies the reaction mechanism postulated, that is, the preponderance of intermolecular transfer, in favor of a partially intramolecular reaction (see the chemical scheme above). It is a question, however, whether this is sufficient to explain the observations. In this connection it should be mentioned that all the aliphatic polymers other than polymethylene listed in Table 31 have rate curves with no maxima[297]. In view of the low monomer yields this points to a high degree of intramolecular transfer. Further studies on the molecular weight variation during pyrolysis of these polymers are desirable in order to clarify this point.

A novel method of detecting transfer involving hydrogen atoms is to replace the suspected atom by deuterium. Deuterium is known to resist the attack of radicals and to decrease the transfer probability by an appreciable factor[310]. Thus we note in Table 32 a higher monomer yield of α-deuterostyrene than of ordinary styrene in line with this concept. Experiments[311] have also shown that the molecular weight decrease in α-deuterostyrene is retarded as would be expected. This result affords support to the postulate that intermolecular transfer is responsible for the molecular weight decrease. However, it gives no indication of the relative probabilities of inter versus intramolecular transfer.

Comparison of Rates and Activation Energies. In Table 33 are listed available data on over-all activation energies[295, 312–314] and estimated rates of volatilization at 350°C. For some polymers these depend on the history of the sample and on molecular weight. For methyl methacrylate the experimental range observed is shown, otherwise the data are for essentially one representative sample. Sufficient work has been carried out with methyl methacrylate to indicate the extensive nature of the studies which would be required to establish precisely the mechanism and interpret the activation energies in terms of the energies of the elementary steps. In the first place, due to the viscosity of the bulk polymer which is being depolymerized, the termination steps are likely to have appreciable activation energies, i.e., these steps are probably diffusion controlled to some extent[307]. This effect will operate to raise the rate and lower the activation energy. Another effect is the variation of activation energy with molecular weight of polymer. It has been shown[305] that for fractions of polymethyl methacrylate polymerized with the hydrogen peroxide redox initiation system, the activation energy changes from a value of 45 to 32 as the molecular weight increases. The transition occurs at a MW of $\approx 10^5$. This is presumably due to a change in mechanism of termination. With low

MW polymer, where one zip, on the average, suffices to consume the molecule, the radicals are eliminated essentially by evaporation. With high MW polymer mutual termination is likely. Thus a variation of the mechanism occurs in passing between the two extremes of large and small Z/N. This transition has been discussed by Simha[306] in connection with the photo-rate of degradation and determination of absolute rate constants in polymethyl methacrylate by Cowley and Melville[307]. Equation (10b) yields for the limiting over-all rate at $t \to 0$, for $1/\epsilon = Z + 1 \gg 1$

TABLE 33. ESTIMATED RATES OF VOLATILIZATION AT 350°C AND ACTIVATION ENERGIES[291]

Polymer	Est. Rates of Volatilization at 350°C wt %/min	Activation Energy kcal
Tetrafluoroethylene	0.000002	80
p-Xylene	.002	76
Methylene	.004	70
Benzyl	.006	53
Ethylene	.008	70
Trifluorochloroethylene	.044	66
Propylene	.069	61
Styrene	.235	58
α-Deuterostyrene	.268	58
Vinylcyclohexane	.450	52
m-Methylstyrene	.900	59
α,β,β-Trifluorostyrene	2.4	67
Isobutylene	2.4	52
Methyl acrylate	10	37
Methyl methacrylate	5.2–200	55–32
α-Methylstyrene	228.0	58

$$\lim_{t\to 0} dC/dt = 2k_1/X\left[\left(1-\frac{\sigma}{\epsilon}\right)(1-e^{-X})+\frac{\sigma N}{2}\right] \qquad (11)$$

substituting $X = \epsilon N/2$. For $X \to 0$ and $\sigma \to 0$, this reduces to the expression appropriate for methyl methacrylate of low DP (order of 5×10^2), namely

$$2k_1[1 - X/2]$$

For $X \gg 1$, this becomes

$$(I/k_4)^{1/2}\left[k_2\Big/\left(\frac{N}{2}Q_N(0)\right)\right]$$

analogous to the familiar expression in polymerization, Eq. (2) with the term $N/2Q_N(0)$ accounting for the initial weight of polymer. Corresponding variations in the overall activation energy between the limits E_1 and $(E_1 - E_4)/2 + E_2$ as a function of X occur[306]. I is the rate of initiation proportional to k_1/M_n, where M_n is the number average molecular weight, since termination occurs at the chain ends only. Provided $E_1 > 2E_2 - E_4$, the energy is smaller for high molecular weights. Now $E_2 \approx 19$ kcal/mole and the above inequality is not unreasonable, particularly if E_4 were to contain a diffusion contribution. It should be noted that the over-all initial rate, for a randomly initiating polymer and $X \gg 1$, should be independent of molecular weight. In polystyrene the extrapolation to $t \rightarrow 0$ is uncertain. However, over the whole observed range of conversion for the polymer fractions, the rate dC/dt appears to be independent of the DP[312].

Estimates of combinations of rate constants and of some absolute values for polystyrene and polymethyl methacrylate have been made. The original literature[290, 315] may be consulted for these results.

One may then tentatively assign the observed 45 kcal activation energy to the initiation process. On the other hand, for a high molecular weight polymer $M = 5 \times 10^6$, prepared from pure monomer at 0°C, an activation energy of 55 has been observed[312]. This appears to conflict with the above mentioned data. A possible interpretation is that with this high DP so few ends are present compared to chain bonds that initiation is actually at random. If this were so, one would have to conclude that the activation energy for such an initiation is considerably greater than 55 kcal.

However, it has now been found that most polymethyl methacrylate polymers are roughly composed in equal parts of unstable end initiating and more stable random initiating material[312a]. A thorough study of poly-α-methyl styrene has shown the characteristics of random initiation[312b] and an activation energy of 65 kcals for initiation is deduced. On the other hand, recent work leads to the conclusion that polystyrene is initiated at the chain ends[312c]. Electronic computaters[312d] have been used to evaluate the predictions of the theory for random initiation and the data for poly-α-methyl styrene show good agreement with the results computed. Such an analysis, based on high speed computations, is primarily limited by the initial size or size distribution of the polymer, which determines the number of equations and thus the memory required of the computer. "Corresponding states" considerations allow to some extent the application of such results to a wider range of kinetic variables. In this manner one predicts independently the rate and the molecular weight decrease as function of conversion. In a useful alternative, the two sets of data are related to each other, permitting a derivation of one from a knowledge of the other. In particular, it would be desirable for practical purposes, to predict the decrease in molecular weight. The pertinent relations have been derived by Gordon[312e] and in greater generality by Simha[312f] from Eq. (10).

For polymethylene an over-all activation of 68 kcal is obtained[293]. The heat of polymerization is about 25 kcal for polyethylene, therefore the activation energy for depropagation E_2 will probably be greater than 30 kcal. The activation energy for transfer, E_3, which is presumably occurring to the exclusion of depropagation will be somewhat lower. Assuming the relationship, $68 = E_0 = E_1/2 + E_3 - E_4/2$, we find that unreasonable values of E_3 and E_4 would be required to make E_1 less than 80 kcal. Consequently, it seems probable that the initiation act involves considerable C—C bond scissions.

Inhibition. Methyl methacrylate polymers which decompose at relatively low temperatures and are sensitive to traces of peroxides have been inhibited[316] by the presence of the leuco form of 1,4-diamino anthraquinone, although only by a factor of ½ to ⅓. A very low rate has been found for a methyl methacrylate polymer prepared in the presence of tetraphenyl succinodinitrile[316]. This polymer has presumably a diphenyl cyanomethyl group at each end. Thus initiation at the ends which the kinetics data indicate in this polymer is confirmed.

A study[317] of tetrafluoroethylene polymers prepared in the presence of certain substances and with various added material showed no changes in the rate of volatilization. This polymer decomposes only at very high temperatures, >400°C and inhibition may thus be more difficult. However, when the polymer was pyrolyzed under various gases[318], a variety of results was obtained. The presence of O_2, H_2O, H_2S, and SO_2 increases the rate whereas under Cl_2, H_2, toluene, CCl_4, ClF_3, and IF_5 induction periods are obtained. Thereafter the rates rise rapidly and become faster than under nitrogen or in a vacuum. In these latter inhibited reactions the overall process was apparently converted to a nearly random degradation. It seems the latter gases not only react with the radical intermediates, but also attack stable chains, since the rate soon rises. It should be noted (see Table 30), that once hydrogens replace fluorines in polytetrafluoroethylene, the monomer yield is low. Also the thermal stability is reduced to about that of polyethylene or lower and the rate curves have the maxima characteristic of nearly random decomposition. Presumably transfer has become predominant. In these particular polymers another reaction is superimposed on the previous degradation processes, i.e., the formation of hydrogen fluoride.

Side Group Decomposition. So far we have discussed those polymers which decompose through breaks in the backbone or main chain bonds. Another group of polymers react by the breaking of the bonds to pendant groups, and produce small molecules and usually a carbon residue. It was mentioned above that such a reaction occurs with hydrofluoroethylene polymers. Other common systems which decompose in this fashion are vinyl chloride, vinylidene chloride, and vinyl acetate polymers. With polyvinyl chloride or polyvinylidene chloride it has been pointed out[319] that after the initial HCl molecule is eliminated, there remains a double bond in the chain with chlorine atoms allylic to it. Such chlorine atoms are more susceptible to attack by a factor of about 10^2. Hence successive HCl molecules are readily split out from sites adjacent to double bonds. This results in conjugated sequences responsible for discoloration of the polymer[319]. Structural variations such as branches which should lead to tertiary chlorine atoms, may facilitate the initial HCl production[320]. Other imperfections in the molecule produced during polymerization or milling can also act to produce labile chlorine atoms[320].

A similar mechanism has been proposed for the thermal decomposition of polyvinyl acetate[321, 322] which gives mainly acetic acid and a residue.

$$P \xrightarrow{k_1} D_1 + A$$

$$D_n \xrightarrow{k_2} D_{n+1} + A, \qquad n \geqq 1$$

Here a chain molecule, P, is transformed into a chain, D_1, with one double bond and an acetic acid molecule A evolved. Subsequent A's are much more easily removed from the chains, $k_2 > k_1$. Termination occurs when the reaction has proceeded to the end of a chain or to some point of structural imperfection blocking further acetic acid formation.

At the beginning of the reaction:

$$\begin{aligned} \sum D_n &= k_1 P t \\ dA/dt &= k_2 \sum D_n + k_1 P \cong k_1 k_2 P t \\ 2A &= k_1 k_2 P t^2 \end{aligned}$$

Experimentally, straight lines for dA/dt were obtained in the early stages of reaction[321]. Further work showed a maximum in the rate curves which occurred at shorter times the higher the temperature. According to the assumed mechanism this maximum would occur when initiation equals termination. Now, a complete sequence of propagation acts will, on the average, have a life time of N/k_2 sec, each act of acetic acid formation requiring $1/k_2$ sec and there being N units (number average) in a polymer molecule. Consequently, the time it takes for the maxima to occur will be the lifetime of the kinetic chain. From $N/k_2 = t_{\max}$, k_2 is calculated. Moreover the initial over-all rate and activation energy can be combined with the values for k_2 and the absolute rate constants obtained. They are:

$$k_1 = 10^{8.85} e^{-33,200/RT};$$

$$k_2 = 10^{8.5} e^{-20,400/RT}.$$

Effects of Atomic Radiation on Polymers

Polymerization by high energy radiation has been discussed early in this chapter. Effects of such radiation on polymers themselves have recently become extremely important for both practical and fundamental reasons. At least one general review has been published[323]. Several authors[181, 324-326] have discussed the various processes by which neutrons, gamma-rays, beta-rays, etc., undergo primary interaction with matter. Although these primary mechanisms of interaction are fairly specific, depending on the type of particle and its energy, the secondary processes which account for most of the chemical changes do not seem to differ greatly with the type of radiation except as regards to the penetration by particles of the same energy.

For the action of radiation on condensed matter, such as water and organic liquids a spur model is often utilized. Recently Burton[324] and Samuel and Magee[325] have discussed and treated certain systems on this basis. Its essential features are that along the paths or tracks of the rays, interactions occur which create small localized areas of ionization called "spurs." The lifetime of processes connected with this spur model have been discussed by Magee[326]. Qualitatively it seems evident that the lifetimes of ionic species are short compared to those for free radicals. In a polymer below the glass transition temperature one might expect free radicals which are parts of long chains to have a very long lifetime, i.e., days or months. Some chemical evidence indicative of this has been obtained[97] and will be mentioned later.

The view that chemical changes produced by radiation involve free radicals receives considerable support from the polymerization studies discussed earlier. Table 32 lists the free radical yields obtained by the radiolysis of small molecules. By making certain assumptions, based on the composition of the molecule involved, as to the bonds ruptured to form free radicals, and knowing the energy absorbed, one may estimate the per cent energy yield (see last column).

It is evident that at least two factors are important in determining the radiolysis of these compounds: atomic composition and structure. Apparently the presence of electronegative elements, halogens, and oxygen favors decomposition, while unsaturation and particularly conjugated and aromatic groups stabilize the molecule. It seems reasonable to carry over, at least in a qualitative manner, these results on small molecules to polymeric structures.

With regard to the effects of radiation on polymers themselves, there is listed in Table 34 a series of polymers grouped according to their tendency to cross-link into bigger molecules or split into smaller molecules when irradiated. Most of the data come from the work of investigators at the General Electric Company, using high-energy electrons, although similar results are reported for other types of radiation. Poly-α-methyl styrene data are for pile irradiation[327]. As yet little information has been published about the effectiveness of radiation in producing either cross linking or scission. The data in the literature are mostly qualitative and do not allow listing of the polymers in either group according to the degree of their response to radiation. However, it is known that it takes $\approx$20–70 ev to produce cross-links in polyethylene in contrast to about 2000 ev for polystyrene. This resistance of polystyrene is usually ascribed to the presence of the phenyl ring (see Table 32). The polymers that degrade are subgrouped according to their basic structure. Cellulose and all its derivatives noted in the literature degrade to lower molecular weight species. The ring structure may impart some lack of flexibility to the polymer chain and this fact may be of considerable importance in determining its behavior. One striking feature of polymer behavior in this field is that all "α-methyl" type polymers so far studied definitely degrade, indicating that their structure favors chain cleavage. These polymers very likely have less flexibility, also, due to the bulk of the side groups, and in this respect there appears to be some connection with the behavior of the cellulosics.

TABLE 34. EFFECTS OF RADIATION ON HIGH POLYMERS[335]

Polymers that cross link	Polymers that degrade
Polyethylene	Cellulose and derivatives
Polyamides	"α-Methyl" polymers
Natural rubber	Polyisobutylene
Polyacrylic esters	Polymethyl methacrylate
Polyacrylic acid	Poly-α-methyl styrene
Polyacrylamide	Polymethylacrylic acid
Polyesters	Polymethacrylamide
Polystyrene	Halogenated polymers
Polyvinyl alkyl ethers	Polytetrafluoroethylene
Polyvinyl methyl ketone	Polychlorotrifluoroethylene
	(Polyvinyl chloride) [?]
	(Polyvinylidene chloride) [?]

The completely halogenated polymers listed, particularly the fluorinated ones, decompose quite definitely to lower polymer and are quite sensitive to radiation. The exact situation with the vinyl and vinylidene chloride polymer is not clear. Lawton lists them as degrading, but Bopp and Sisman note that after an initial softening they harden and are presumably cross-linking. It is known that they evolve hydrogen chloride, which reaction very likely results mainly in double bond formation, although some loss of hydrogen chloride between chains could result in cross-linking. Further investigation may very well place them in the groups of cross-linking polymers, which from a theoretical point of view one might anticipate.

Results of irradiation depend on whether the irradiated polymer is in contact with oxygen, in which case oxidative degradation[328, 329, 330] may lead to a different result than when the polymer is irradiated in vacuo or under nitrogen. The form of the polymer, i.e., the surface-to-volume ratio, and dose rate are naturally very important when air oxidation is possible.

The presence of a few para-bromo groups in polystyrene has been shown to cause an increase in molecular weight, even when presumably the presence of air caused degradation of pure polystyrene to much lower molecular weight[331]. It is reasonable to assume that hydrogen bromide was formed with the necessary atoms coming from different polymer chains, which then cross-linked.

A comparison[330] of the behavior of polymers under irradiation with that found on thermal decomposition might be expected to help in elucidating the processes occurring. In Table 34 are listed the heats of polymerization and thermal decomposition data on nine polymers. The heats of polymerization[332] reflect the degree of steric hindrance between units in the chain, a low heat implying a large amount of steric hindrance. With the exception of polyisobutylene, it is seen that a low monomer yield is associated with cross-linking. It would seem that α-hydrogens favor cross linking and α-methyls favor scission when polymers are irradiated, whereas it has been fairly well demonstrated in thermal decomposition that the former favor transfer reactions and the latter depropagation. Polyisobutylene is an exception with respect to monomer yield but is similar to the other two "α-methyl" polymers as to thermal stability and shape of the thermal decomposition rate curve.

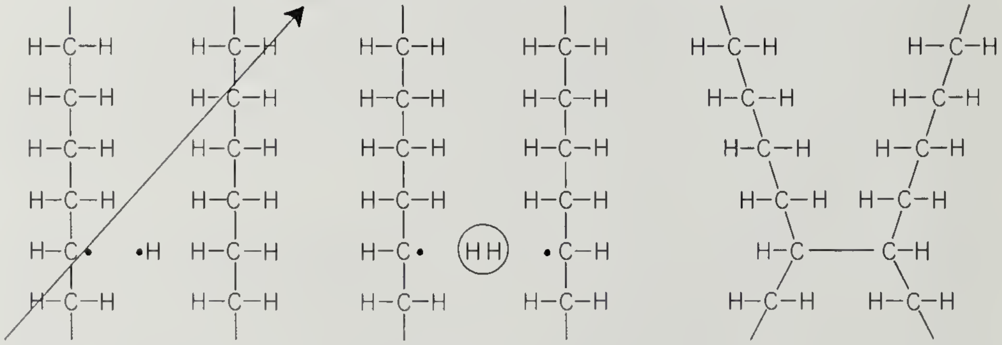
It has recently been suggested that an important factor in the behavior of polymers under irradiation is the stability of the radicals formed in each system[333]. For instance, "α-methyl" polymers that degrade form tertiary type radicals when chain scission occurs, while polymers that cross link form *tert.*-type radicals by loss of a tertiary hydrogen without chain scission. An alternate possibility is that all possible types of radicals are formed but in the former case their structures favor disproportionation while in the latter case they favor combination.

Polyethylene has probably received the most attention in studies on the effects of irradiation[329, 334-337]. Interesting work attempting to elucidate the mechanism of cross-linking, in this case utilizing β-rays, is that of the General Electric Company group[335]. Several materials were irradiated: polyethylene, a $C_{28}n$-hydrocarbon, and a high molecular weight ($\approx 1 \times 10^6$) polymethylene. Polymethylene is linear, whereas polyethylene is highly branched. Actually, in one gram of the polyethylene there would be, roughly within a factor of 2, as many molecule ends as in one gram of the C_{28} *n*-hydrocarbon.

Analyses of the volatiles from the radiation of polyethylene have been made[335]. The major product is hydrogen, $\approx$80 per cent; the remainder hydrocarbons, C_2's, C_3's, and C_4's predominating. The branches in polyethylene are believed to be about 5 carbon atoms in length[338]. When irradiated, the C_{28} hydrocarbon gives similar results, $\approx$80 per cent H_2, but somewhat less C_2, C_3, and C_4 compounds, while the polymethylene gives $\approx$99 per cent hydrogen[339]. These results indicate a fairly random interaction of the radiation with the polymer and cleavage of both C—H and C—C bonds with, in the case of polyethylene, a small preference for the branch points. Stoichiometrically, the evolution of hydrogen implies unsaturation or cross linking, and both types of structural change are observed. Very likely chain cleavage occurs to some extent, as evidenced by the appearance of volatile hydrocarbons from two of the materials studied. On a random cleavage basis, the high molecular weight of the linear polymethylene would preclude the appearance of appreciable volatile hydrocarbons during irradiation. Comparison of the pyrolysis[293] and irradiation data[335] on volatile products does not show any striking differences as to the hydrocarbons produced. The chief difference is the large quantity of hydrogen produced in the latter case.

It is difficult to conceive of any selectivity in product formation due to the primary interactions of the radiation, and hence any such effect should probably be attributed to secondary processes. Actually, the roughly equal yields of C_2's, C_3's, and C_4's observed in the case of the irradiated polyethylene, which is believed to have numerous C_5 branches, are not incompatible with a random mechanism.

The following simplified scheme for the cross-linking reaction would appear to satisfy the known facts. Three stages of the process are depicted.



First, the radiation, in passing through, causes ionization which quickly subsides, leaving atoms and radicals. There is, of course, statistically twice as much chance of breaking a C—H bond as a C—C bond and it must be assumed that a good portion of the C—C bonds cleaved recombine. However, an active hydrogen atom will readily abstract a nearby hydrogen atom, forming H_2 (stage 2) and leave two adjacent free radicals which combine (stage 3) to form a cross-link. If an adjacent hydrogen on the same chain is captured by the first atom, then double-bond formation would result. Presumably this mechanism applies in different degrees to other polymers that cross-link.

With atomic pile radiation[337] it has been shown that the number of cross-links formed per unit energy absorbed in paraffin hydrocarbons is not appreciably affected by molecular weight or the physical state of the material during time of exposure. In this work[337] the absorbed energy required to produce one cross-link was 24 ev. Furthermore, it was estimated that 0.35 C—C bonds were ruptured per cross-link formed. On the basis of the simplified mechanism described above and random breaking of C—C and C—H bonds one would have predicted a value of 0.5. However, we know that the reaction is somewhat more complicated since appreciable amounts of unsaturation are also produced[334, 340]. It is also reasonable to suppose that some broken C—C bonds reform. The former effect would raise the value for the fraction of C—C bonds ruptured while the latter effect would lower it. Consequently, it seems that the observed value (0.35) is easily compatible with random primary interactions. Recent work[329] with γ-radiation and a somewhat different technique for the estimation of cross-links indicates that 53 to 70 ev are required for a cross link in polyethylene. The first value is based on the assumption that 20.8 is the radiochemical yield of ferric ion in ferrous sulfate solutions, whereas the latter is based on 15.6. Somewhat as in styrene it was also observed that oxygen prevented[329] cross-linking. The energy required in the presence of air to produce a cross-link was 133 to 178 ev.

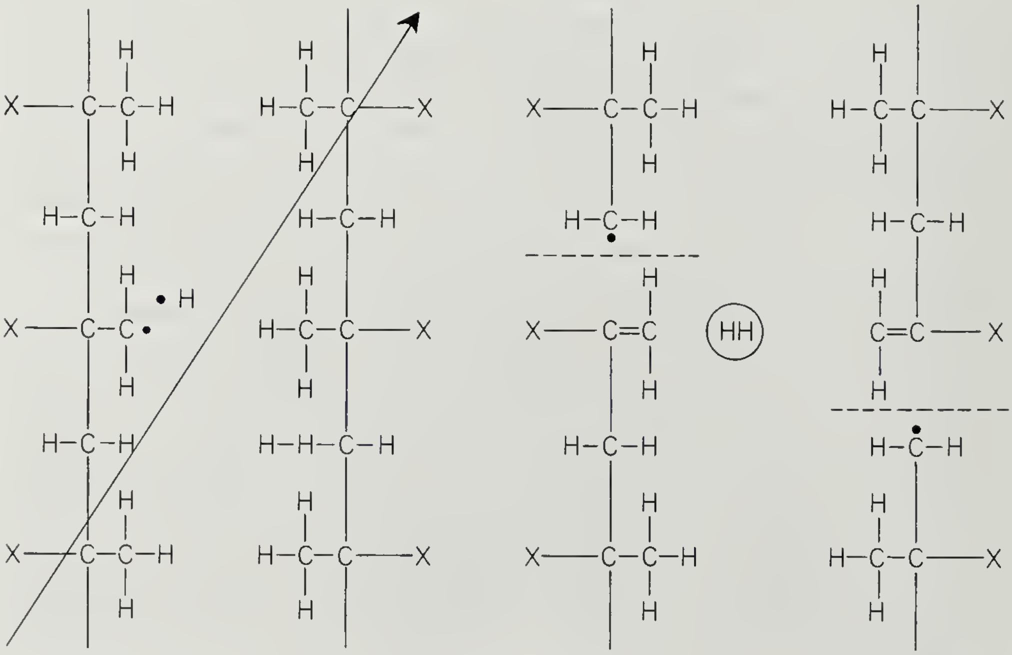
A treatment of the effect on polyethylene produced by radiation has been developed in which it is assumed that a certain constant fraction of ruptures is also occurring[341]. The basis of the approach is that these ruptures produce a random decomposition of the primary molecules. Then customary gel theory allows one to write a relationship between the amount of gel formed in the irradiated polymers and the initial molecular weight distribution. Broad distributions are found, $M_w/M_n \sim 5$ to 20, which are well known to exist in polyethylene. The interesting point is that the results support a mechanism producing simultaneous fractures and cross-links.

In the case of "α-methyl" polymers it is evident from Table 35 that a high degree of strain exists in the chain due to steric hindrance, and that the bonds are broken more easily. Therefore one must assume, as outlined below, an initial production of hydrogen atoms or small radicals from dis-

Table 35. Heats of Polymerization and Thermal Decomposition Data of Polymers[330]

Polymer	Heat of Polymerization (kcal/mole monomer)	Monomer Yield (Wt. %)
Cross link		
Ethylene	22	0.025
Propylene	16.5	2
Methyl acrylate	19	2
Acrylic acid	18.5	—
Styrene	17	40
Degrade		
Methacrylic acid	15.8	—
Isobutylene	13	20
Methyl methacrylate	13	100
α-Methyl styrene	9	100

ruption of side groups which abstract hydrogen atoms. The radicals so formed, whether by abstraction of a hydrogen of the methyl group or of the main chain, decompose to give unsaturated end-groups and cleaved molecules as shown.

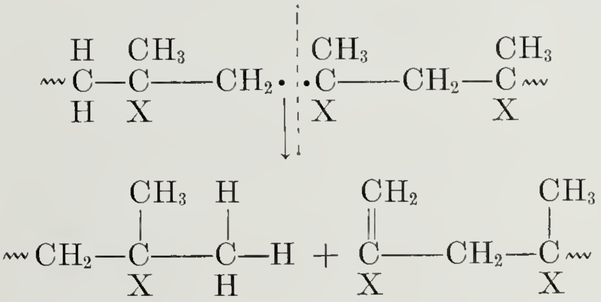


If one makes the reasonable assumption[330] that the scission reaction of a radical along the polymer chain is affected by the same factors as the depropagation reaction of a chain into monomer and smaller radicals, then it follows that

$$E_s = E_p + H_p$$

where E_s is the activation energy for scission, E_p that for propagation, and H_p is the heat of polymerization. Since activation energies for propagation are quite low, 5 to 8 kcal, compared to heats of polymerization, it is evident that scission will be much more probable in polymers with low heats of polymerization, and that the observed differences in such heats reflect the operation of a strong steric influence on the scission reaction.

An alternate and probably simultaneously operating mechanism would be a simple rupture of chain bonds to produce radicals which disproportionate.

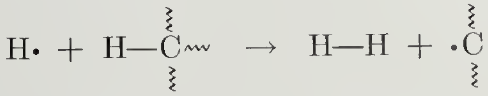


$$\sim\underset{H}{\overset{H}{C}}-\underset{X}{\overset{CH_3}{C}}-CH_2\cdot\ \vdots\ \cdot\underset{X}{\overset{CH_3}{C}}-CH_2-\underset{X}{\overset{CH_3}{C}}\sim$$
$$\downarrow$$
$$\sim CH_2-\underset{X}{\overset{CH_3}{\overset{|}{C}}}-\underset{H}{\overset{H}{\overset{|}{C}}}-H + \underset{X}{\overset{CH_2}{\overset{\|}{C}}}-CH_2-\underset{X}{\overset{CH_3}{\overset{|}{C}}}\sim$$

Here the same steric effect would of course be a large factor against any recombination.

At first glance the situation in polytetrafluoroethylene would seem to be difficult to understand. The material is probably much more sensitive to radiation due to the fluorine atoms. However, neglecting this aspect, bond energies allow one to make an interesting interpretation of the facts. An important step in the cross-linking process for polyethylene involves the abstraction of a hydrogen by a hydrogen atom. The reaction is written below with the analogous one for polytetrafluoroethylene. The pertinent bond energies for these reactions are listed.

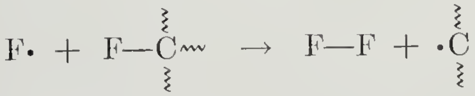
Polyethylene



$$H\cdot + H-\underset{\wr}{\overset{\wr}{C}}\sim \rightarrow H-H + \cdot\underset{\wr}{\overset{\wr}{C}}$$

90 kcal 100 kcal

Polytetrafluoroethylene



$$F\cdot + F-\underset{\wr}{\overset{\wr}{C}}\sim \rightarrow F-F + \cdot\underset{\wr}{\overset{\wr}{C}}$$

120 kcal 37 kcal

It is seen that, in the hydrocarbon case, a 90-kcal C—H bond is broken with the formation of a 100-kcal H—H bond. In the fluorocarbon situation, a 120-kcal bond must be broken and only a 37-kcal F—F bond produced. On this basis it is easily seen why cross-linking does not occur. Also, with chain cleavage and fluorine atoms available, the predominant reaction would be the formation of 120-kcal C—F bonds, producing permanent cleavage and unsaturation as actually found [342]. It follows then that low bond energies between the carbons in the chain and substituent atoms and high bond energies between substitutent atoms are needed for cross-linking. On this basis polyvinyl chloride and vinylidene chloride should cross-link with the formation of hydrogen chloride, although the formation of double bonds may be the major reaction.

Fluorocarbon polymers are in general considered to have low "resistance" to ionizing radiation, principally because of the rapid deterioration in physical properties of polytetrafluoroethylene when irradiated. However, other fluoropolymers, for example polytrifluorochloroethylene, are somewhat less sensitive. Such considerations suggest that the radiosensitivity of polytetrafluoroethylene is not the consequence of high numbers of chemical acts, scissions, due to irradiation, but the result of a greater sensitivity of physical properties to molecular size. As far as physical properties go, the direction of irradiation effects, i.e., to higher or lower molecular size, may be more important than the actual number of scissions or cross-links occurring with a given dose.

It seems fairly certain that radical or atomic species determine to a great extent the behavior of polymeric materials when they are exposed to high-energy radiation. The results in general follow a statistical pattern and would seem to be explainable on the assumption that all possible radical species are formed and that such formation is followed by processes fundamental to and characteristic of the individual species.

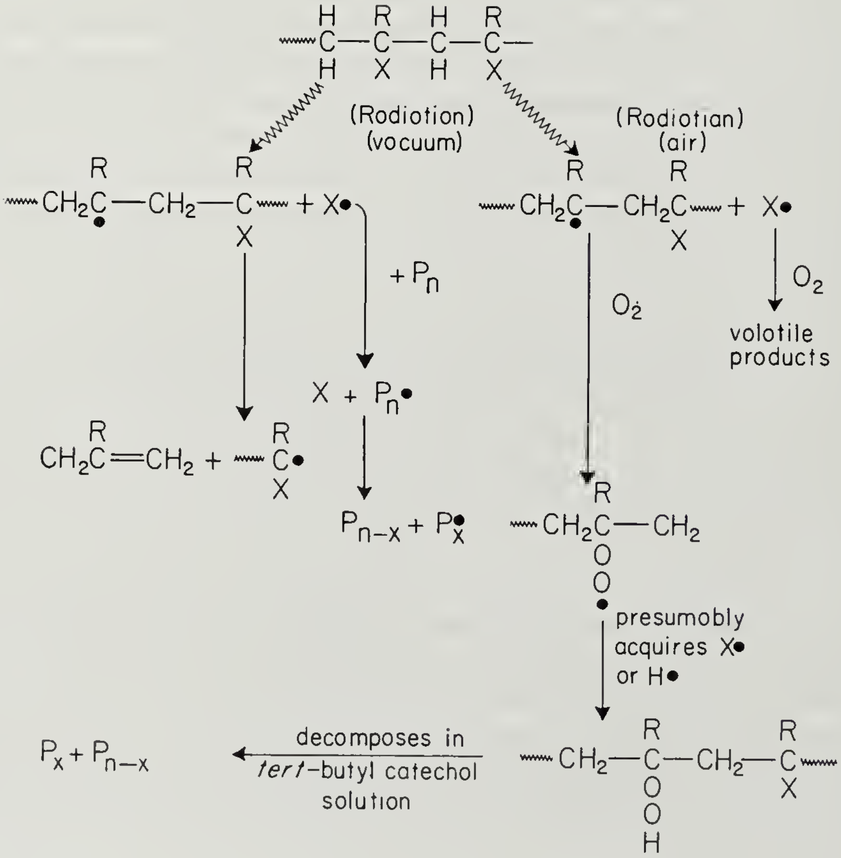
An important question in the study of the radiation effects in polymers concerns the lifetime of the free radicals formed. Recently it has been demonstrated that free radicals or atoms when produced in frozen hydrocarbons or monomers at about 90°K, can be immobilized and stored for extended periods of time, their existence in significant quantities being determined either spectrometrically[343] or by polymer formation upon warming[186]. It would appear probable that solid polymers at room temperature, especially those with glass transitions considerably above this temperature, after exposure to high-energy radiation are also likely to contain active species capable of producing chemically measurable effects. Experiments designed to test this hypothesis have recently been carried out[97] using polymerization to detect the presence of activity in irradiated polymethyl methacrylate. The polymer was heated at 100°C for 24 hr in a vacuum to remove any peroxidic activity[189]. Then it was sealed off and irradiated in an evacuated viscometer designed in such a manner that after irradiation the viscometer could be attached again to a vacuum system and a given amount of methyl methacrylate monomer condensed on the polymer. The container with the frozen monomer and polymer was then placed in a constant temperature bath at 30°C and the viscosity of the polymer-monomer solution noted as soon as the solution became uniform. The viscosity was found to be always higher initially by about a factor of two when irradiated polymer was used. On measuring the rates dilatometrically at 30°C, it was also found that with irradiated polymers shorter induction periods were obtained. On the basis of these experiments it is estimated that 10^{-5} mole/liter of free radical existed in the irradiated polymers, after a dose $\approx 10^7$ *r*. Provided these effects are not due to traces of absorbed or occluded oxygen in the polymer, forming peroxidic groups active at 30°C during irradiation, this result indicates the presence of long-lived free radicals in the polymer, since the polymerization experiment occurred several days after irradiation.

An interesting property of irradiated polymethyl methacrylate is the foaming that occurs on subsequent heating to about 120°C[344]. This is interpreted[344, 345] as the expansion of the gaseous products of radiolysis upon heating, enhanced by the lowered bulk viscosity of the degraded material. Analysis of the gases indicates that they arise mainly from disintegration of the ester groups. If the irradiated polymer is not heated no monomer is detected. With heating a considerable percentage of monomer appears, much more than is obtainable from unirradiated polymer[97]. This result suggests again that some free radicals are immobilized in the irradiated polymer. Assuming that these radicals unravel to their ends upon heating, the number of radicals would be obtained by dividing the monomer mole yield by the degree of polymerization. This procedure leads to a value of about 10^{-5} moles of radicals per liter, which agrees with the polymerization result. It would seem that the foaming may be aided by this process.

A possible method of detecting[97, 331] free radicals is to compare conventional intrinsic viscosities with those measured in an inhibitor containing solvent. On the assumption that upon solution the free radicals would ordinarily couple, lower intrinsic viscosities should result in the presence of inhibitor, due to prevention of coupling. Unfortunately, the concentration of free radicals mentioned above is much too small to be detected in this manner.

When polymethyl methacrylate is irradiated in air a lower intrinsic viscosity is obtained when *tert.*-butyl catechol is added to the solvent[97]. No such effects occur when irradiations are carried out in vacuum. When the inhibitor is added after the irradiated polymer is in solution, the viscosity immediately begins to fall. After a period of time it levels out at a much lower value. For instance, it fell in one case from an η_{sp}/c of 1.6 to 1.28 over a period of ≈ 1500 minutes. These observations indicate that a peroxide group is produced during the irradiation, the decomposition of which involves a chain scission and is induced by the inhibitor. The reaction is analogous to the dimethyl aniline activated peroxide decompositions. Hydroquinone also shows a weak effect. The temperature dependence of the process with *tert.*-butyl catechol yields an activation energy of about 15 kcal.

For methyl methacrylate polymers the energy needed to produce a main chain scission has been reported by several investigators. The values are in ev 61, pile and γ-radiation[345], 62 β-radiation[346], and 58 γ-radiation[97]. With the polymer in a finely divided form, O_2 was observed to more than double this value up to 150 ev. However, after the *tert.*-butyl catechol had reduced the viscosity, one would calculate 116 ev, that is, when the scissions that occurred because of the peroxide groups in the irradiated polymer were added to those produced during its irradiation. Within experimental error the 116 ev figure was twice that of the 58 figure for vacuum irradiated samples. This factor of two may be fortuitous. However, the over-all result does support a mechanism such as presented earlier. A simplified sequence for polymethyl methacrylate degradation that seems to satisfy the evidence is as follows:



The X• represents the ester group in methyl methacrylate which in reality is ruptured in many different ways by the radiation. The P's refer to polymer molecules with the subscripts indicating the number of monomer units in the chains. Some of the initial bond ruptures may involve ions. However, the fact that oxygen can interfere with both cross-linking and degradation, depending on the type of polymer and the extent to which it does, suggests that both effects do not occur to a large degree as ionic primary processes. Secondary free radical processes evidently play a major role as depicted. For polymers that cross-link the vacuum reactions in the scheme need only be revised to depict combination of the pertinent radicals instead of scission. As mentioned earlier, steric repulsion reflected in the heats of polymerization may be a pertinent factor here. Additional support for these mechanisms comes from the observation[345] that inhibitor type chemicals in 10 per cent concentrations also protect methyl methyl methacrylate polymer against degradation. The protection ranges from 57 to 72 per cent. The aromatic character[347] of these protectors may also furnish another mode of protection than mere capture of radicals, i.e., energy transfer.

The results of studies on deuterated polyethylene and five partially deuterated polystyrenes have been interpreted to indicate that the irradiation produced processes in these polymers involve free radicals and hydrogen atoms[347a]. In polyethylene the indication is that once formed, hydrogen atoms either abstract other hydrogen atoms or recombine. In polystyrene they also add to the phenyl group. The result is that more cross-links are formed than hydrogen molecules evolved. The opposite is the case with polyethylene since no unsaturation exists in the material. Polydienes behave similar to polystyrene in this respect. The results with deuterated samples also show that in polystyrene the hydrogen evolved comes to some extent from all positions in the monomer unit. The relative probabilities of evolving an α, β, or ring hydrogen are 1.0, 0.9, and 0.4, respectively. Presumably cross-linking also does not occur totally at any specific position. A theoretical treatment of the possible free radical mechanism for cross-linking and degradation in polymers and the resulting kinetics has been given[347b].

Degradation in Solution

The degradation of polymers in solution has been studied by several investigators[331, 348-351]. In aqueous[348-350] as well as organic systems[331, 351] degradation as measured by viscosity changes is, so far as has been observed, only pronounced in the presence of oxygen. To achieve a given effect, a 100-fold greater dosage is needed in vacuum studies. When oxygen is present a post-effect occurs, i.e., on irradiation the fall in viscosity continues after the exposure is discontinued. This observation suggests that a relatively long life intermediate, such as a hydroperoxide group, is involved in the scission reaction.

For polystyrene this degradation is most rapid in carbon tetrachloride[331] or chloroform[351] solutions. Mercaptans retard the degradation while diphenyl picryl hydrazyl has little effect during irradiation but does reduce the post-effect.

Certain substances added after irradiation accelerate the post-effect[351], such as aniline, octyl mercaptan, mercapto-ethylamine, and naphthol. Other substances[351], for example n-tolyl thiourea retard the post-effect. It seems evident from these results that hydroperoxide groups are formed, the decomposition of which leads to chain scission. These results may have some bearing on radiation sickness[352]. It is known that β-mercapto-ethylamine exerts a protective action against radiation sickness.

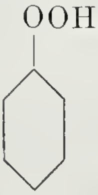
Oxidation of Polymers

Almost all known polymers of the organic type oxidize under service conditions at rates sufficiently rapid such that concomitant deleterious effects render them relatively useless within short periods of time. This process is usually speeded up by high temperature, ultraviolet light, or atomic radiation, and free radical producing substances.

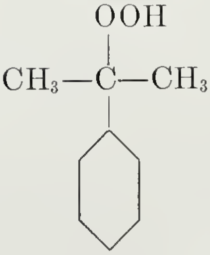
For the purposes of this discussion, polymers will be divided into two groups. Those containing double bonds in chains, i.e., polydienes such as natural rubber and related synthetic materials and those which are essentially saturated except for aromatic groups. In the latter category would be polyethylene, polyisobutylene, and polystyrene, which oxidize at a much slower rate than the materials in the former group. The former systems have been probably the most studied, and are as a result rather well understood. Many small olefins have also been investigated, often as model compounds, for the more complicated polymers. Several reviews[353-355] of olefin oxidation have been published.

In the oxidation of many olefinic compounds large yields of hydroperoxides are obtained, provided, of course, that the reaction conditions are moderate enough to leave these somewhat sensitive materials undecomposed.

Organic peroxides or hydroperoxides are according to our present knowledge the primary products obtained when oxygen reacts with various unsaturated and saturated compounds. α-Hydroperoxides[356] are often isolated in the oxidation of monoolefins, or aromatic derivatives containing reactive α-hydrogens. Typical products obtained from, for example, cyclohexene and cumene are:



and



In general such hydroperoxides of unsaturated or aromatic compounds are more stable than those produced from saturated compounds. Oxygen can also copolymerize with olefins to produce polymeric peroxides[357]. Rarely, however, do the above reactions produce cleanly the peroxidic compound alone. Associated products are normally ketones, aldehydes, acids, water, and carbon dioxide. Such compounds are also the usual decomposition products of peroxides. The chemistry and decomposition of peroxides have been reviewed in a recent book[76].

Chain Mechanism. The typical chain mechanism which is commonly employed[354] for the oxidation of olefins, and hence applicable to polydienes, is as follows:

$$\begin{array}{llllr}
\text{Initiation} & & & & \\
\left.\begin{array}{l}\text{Thermal}\\ \text{Photo}\\ \text{Labile substances}\\ \text{Atomic radiation}\end{array}\right\} & & \longrightarrow & \text{Radicals} & I \\
\text{Propagation} & R\cdot + O_2 & \longrightarrow & RO_2\cdot & k_2 \\
 & RO_2\cdot + RH & \longrightarrow & RO_2H + R\cdot & k_3 \\
\text{Termination} & \begin{array}{l}2R\cdot\\ R\cdot + RO_2\cdot\\ 2RO_2\cdot\end{array} & \left.\begin{array}{l}\longrightarrow\\ \longrightarrow\\ \longrightarrow\end{array}\right\} & \begin{array}{l}\text{Stable}\\ \text{Inactive}\\ \text{Products}\end{array} & \begin{array}{r}k_4\\ k_5\\ k_6\end{array}
\end{array}$$

Initiation may occur via a variety of reactions. Pure thermal initiation is extremely slow but may be important since the product of the reaction is a peroxide, the decomposition of which in turn initiates the chain reaction. The observed reaction is autocatalytic. If the conditions are such that the peroxide decomposes rapidly the mechanism is essentially that of a branching chain reaction. That is, step three would produce three free radicals for each one consumed. Quantum yields greater than one and dependence of over-all rates on the square root of the initiation rate have been established[358]. Inhibitory effects of so-called antioxidants, i.e., aromatic amines, hydroquinones and catechols, are also pronounced[112].

The above mechanism leads to the following expression for the rate of oxygen consumption for long kinetic chain lengths[359]:

$$\frac{1}{\left(\frac{-dO_2}{dt}\right)^2} = \frac{1}{I}\left[\frac{k_4}{k_2^2[O_2]^2} + \frac{2k_5}{k_2k_3[RH][O_2]} + \frac{k_6}{k_3^2[RH]^2}\right] \tag{12}$$

If the reaction is carried out at high oxygen pressure then:

$$\left(\frac{dO_2}{dt}\right)_\infty = \left(\frac{I}{k_6}\right)^{1/2} k_3[RH] \tag{13}$$

Combination of the two expressions gives the following relationship:

$$r = \frac{\left(\frac{dO_2}{dt}\right)_\infty^2}{\left(\frac{dO_2}{dt}\right)^2} = 1 + \frac{2\phi k_4^{1/2}k_3[RH]}{k_6^{1/2}k_2[O_2]} + \frac{k_4k_3^2[RH]^2}{k_6k_2^2[O_2]^2} \tag{14}$$

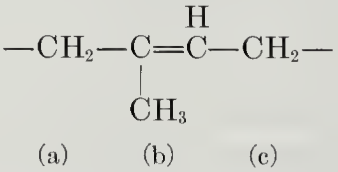
where

$$\phi = \frac{k_5}{k_4^{1/2}k_6^{1/2}}.$$

Assuming $\phi = 1$, a somewhat simpler expression for the over-all rate is obtained:

$$\frac{-dO_2}{dt} = I^{1/2}k_6^{1/2}k_2[RH]\left[\frac{k_6^{-1/2}k_2[O_2]}{k_4^{-1/2}k_3[RH] + k_6^{-1/2}k_2[O_2]}\right] \tag{15}$$

Equation (13) is applicable to most olefins when the pressure of oxygen is greater than 100 mm. Bolland[360] has studied the effect of olefin structure in this high pressure region. Using propene as a reference at 45°C, it is found that substitution of aromatic or unsaturated groups on the propene structure in the 1 or 3 position greatly increases the over-all rate and k_3. Certain cases of decreased reactivity are attributed to steric effects. Substitution in the 2 position of propene has little effect. In propene an E_3 of 13 kcal is found. For other olefins E_3 ranges from 13 down to 6 kcal. For the isoprene unit:



$$-CH_2-\underset{\substack{|\\ CH_3}}{C}=\overset{H}{C}-CH_2-$$

the relative activity of the three positions a; b; c; is 1:3:11[354].

The variation with oxygen pressure depends on the relative rates of reactions (13) and (14). Wider ranges of oxygen pressure dependence occur with smaller k_2's. Therefore depending on the reactivity of olefin radicals different ranges are observed. For instance with hexadecene-1 no dependence occurs below 1 mm, while with 2,6-dimethyl-heptadiene-2,5 the dependence extends to pressures >800 mm. Also, since k_3 is the only step with appreciable temperature dependence, i.e., activation energy, higher temperatures in general extend the range of pressure dependence.

If termination by step 5 is favored we will have ϕ values greater than 1. In copolymerization very large ϕ values are obtained. However, in oxidation relatively small ϕ values of 0.3 to 6.5 are reported. Values between 1 and 3 are the most common.

Although with photo initiation or with benzoyl peroxide and azoisobutyronitrile, square root dependence on initiator is observed in the autocatalytic reaction, the rate is found to be proportional to hydroperoxide concentration. This means that a bimolecular reaction between hydroperoxide is the initiation step[361]. However, at low concentration of hydroperoxide existing during the early stages of reaction, square root dependence, hence unimolecular initiation is found. This change in mechanism appears to be connected with molecular association of the hydroperoxide. Infrared studies[361] provided definite evidence of hydroperoxide association which decreased with dilution. This effect is, of course, temperature sensitive, the bimolecular process being favored at lower temperatures.

Although most of the evidence in olefin oxidation points to radical attack on the alpha-methylene hydrogen atoms, some workers[362, 363] do report indications of radical addition to the double bond. Thus the reaction is undoubtedly more complicated than outlined. However such a process would not greatly alter the mechanism described.

The advanced stage of the autocatalytic oxidation of olefins and unsaturated polymers has been treated[364]. A characteristic phenomenon of a maximum rate occurs when the hydroperoxide concentration reaches a certain steady value. At this point the kinetic chain length is unity.

Studies[364] on vulcanized natural rubber showed typical autocatalytic behavior at 50°C, a steady rate resulting only after very long periods of time. At 120°C a steady rate was obtained immediately. At the low temperatures light accelerated the attainment of the steady rate. At 120°C the photoactivation had no effect on the rate. These results indicate the occurrence of a maximum rate dependent only on the temperature.

Another method of studying the oxidation of vulcanizates is by means of stress relaxation experiments. Basically the method consists of putting a sample under stress and measuring the decay of stress as the oxidation reaction proceeds. Clearly, chain scission will decrease the stress. Thus, such a study gives the rate of scission. This has been measured along with rate of oxygen consumption and hence one derives ratios of the molecules of O_2 reacted to the number of scissions. At 50°C during thermal oxidation about 15 molecules of O_2 are absorbed to one scission[364], while in photo-activated oxidation, when the reaction proceeds at the maximum rate, the ratio is unity. At 120° the ratio was unity for both thermal and photo-activated oxidation.

Although it appears that the scission reaction is associated with the hydroperoxide decomposition, the over-all oxidative degradation of rubber is undoubtedly too complicated and incompletely elucidated at present for such definitive statements.

Certain metallic compounds greatly enhance the rate of oxidation. Compounds of iron, cobalt, nickel, copper, and manganese are highly active. The evidence in hand in general points to reduction-oxidation reactions such as discussed earlier in the section on the redox systems for initiating polymerization. From this point of view these compounds then probably function by increasing the rate of hydroperoxide decomposition.

Oxygen plays an important role in the breakdown of rubber on milling. Under normal conditions it is noted that the decrease in viscosity as a function of milling temperature has a minimum at about 100°C. The accelerated breakdown with temperature above 100°C has the general features of oxidative degradation. For instance, inhibitors will retard the decrease in viscosity. However, the breakdown below 100°C increases with decreasing temperature, i.e., has a negative temperature coefficient and inhibitors do not mitigate the deterioration. An early suggestion[365] was that mechanical rupture of primary bonds occurred on cold milling, producing radicals which were stabilized by oxygen. In the absence of oxygen such breakdown is negligible. This is presumably due to recombination of radicals. More recently it has been shown[366] that this picture of degradation on cold milling is essentially correct. For, in the absence of oxygen, inhibitors have the same effect as oxygen in producing breakdown. Benzoquinone and thiophenol had roughly the same effectiveness as oxygen while various other compounds had less effect, phenol for instance, having almost no ability to terminate chains.

Nonolefinic polymers such as polyethylene and polystyrene oxidize relatively slowly on heating, compared to olefinic polymers and this oxidation is reduced drastically by antioxidants[367]. In contrast to olefinic polymers it is difficult to detect peroxide or hydroperoxide in these materials when they are highly oxidized. Ultraviolet light, on the other hand, produces quite rapid oxidation[367] which is autocatalytic. The group responsible for the initiation of radicals and the autocatalytic behavior in this case seems to be the carbonyl group[368, 369]. The mechanisms involved are similar to that outlined above and to the oxidation mechanisms of small paraffinic molecules[370].

The oxidative degradation of polyethylene in ultraviolet light is a chain reaction of very short chain length[368]. This follows from the ineffectiveness of antioxidants for the light reaction. In addition antioxidants being powerful light absorbers, sensitize oxidation[368]. Hence the problem of protecting against light is chiefly solved only by incorporating carbon black or other opaque pigments[367] which prevent light from penetrating the polymeric material. During photo-oxidation polyethylene and polystyrene films become insoluble indicating cross-linking reactions.

Infrared studies invariably show progressively increasing carbonyl content in oxidized polymers and small amounts of hydroxyl groups. A study of volatile products[371] at low extents of reaction, showed for polystyrene a variety of products in small quantities. While most of the products were compatible with those likely to result from the oxidation of polystyrene, some may have originated from trace contaminants. A study at higher extents of reactions would be desirable.

The ultraviolet absorption of polystyrene films increases with oxidation in the region from 280 to 380 millimicrons[372]. This absorption is approximately proportional to carbonyl content as seen from infrared spectra.

The oxidation of polystyrene is enhanced by small amounts of monomer which presumably, due to its unsaturated structure, oxidizes more easily. The resultant carbonyl-containing products sensitize the polymer for photo-oxidation[372]. In ultraviolet studies a post-effect has been observed in the light-induced oxidation reaction[372]. Films stored in the dark at room temperature after exposure developed increased absorption at about 340 millimicrons with time. This post reaction can be resolved into two first order components, with activation energies $\sim$20 and $\sim$24 kcal, one with a fast and one with a slow rate[191, 373]. It has been suggested that the slow reaction is due to a *cis-trans* isomerization, and the fast reaction is the result of a hydroperoxide decomposition.

Experiments with styrenes deuterated in specific positions have been carried out[191, 374]. In general those containing deuterium in the α-position are much less rapidly oxidized than those with protium in that position. In addition, the post-effect is smaller in the α-deuterated polystyrenes. These facts are in general compatible with free radical attack on the *tert.*-hydrogens in the polystyrene chain. However, the hydroperoxides produced must be extremely labile. Other workers[192] found it impossible to produce a hydroperoxide of polystyrene, while polystyrene-containing isopropyl groups on the ring readily reacted to give good yields of hydroperoxide. The accumulated evidence appears then to suggest that a hydroperoxide group on the *tert.*-carbon of the polystyrene chain is very unstable, but that the oxidation does at least in part occur through a reaction at this position.

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CHAPTER 4

POLYMERIZATION OF OLEFINS (To Liquid Polymers)

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INTRODUCTION

Man and nature have produced substances of great utility by polymerization of simple molecules. Natural and synthetic oils, plastics, and fibers are only a few of the polymers with which we are familiar. Catalysis is the key to polymerization which controls the type as well as the quality of the many polymers that can be obtained from the same chemical building block. Almost invariably it is the new and useful *physical* properties of the polymers which provide the incentive for their creation. This chapter deals with the polymerization of gaseous olefins to liquid products which are used primarily as fuels. Here, too, polymerization is carried out to improve the physical properties. Gaseous olefins, difficult to store and transport, are converted to volatile liquid fuels suitable for storage and for use in the internal combustion engine. No improvement is achieved in heat release or in burning properties as measured by octane number.

The scope of the polymerization field is extremely broad. Yet in the case of hydrocarbon polymers, the monomer molecules are chosen almost entirely from the group C_2-C_5 olefins. For the simple polymerization reaction,

$$2C_n H_{2n} \rightarrow C_{2n} H_{4n}$$

the product polymer molecule has unchanged C/H ratio and still possesses one unsaturated bond per molecule. It is the function of the catalyst under the particular reaction conditions to alter the polymer length from 2 to perhaps a million monomer units, to determine the polymer size distribution, and to control the degree of side reactions, which may be great. Also, as has been recently emphasized, it is the function of the catalyst to control the polymer product through stereospecificity of the reaction.

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Interest in polymerization in the petroleum industry came about through the use of cracking processes, first thermal cracking and then catalytic cracking. Such processes normally produce rather large quantities of light hydrocarbons containing unsaturated species of hydrocarbons. In the early days of thermal cracking, most of the light hydrocarbons were consumed as fuel in the refinery. However, as the demand increased for more and more gasoline of improved quality, it became economically attractive to utilize these in polymerization processes to produce higher boiling materials of high octane number. The large quantity of light hydrocarbons produced in the cracking process cannot be blended into gasoline without exceeding the vapor pressure limits set for commercial gasoline. However, by turning to polymerization processes, one can utilize the light hydrocarbons. In effect, the polymerization acts as a vapor pressure control device and the products of cracking can be more fully utilized.

Polymerization of olefins has been known for nearly a century. However, it is only in the last thirty years that it has assumed importance in the petroleum industry. The first commercial polymerization began in 1931 with a 100 barrel per day plant[195a], followed in 1934 with a plant ten times this size[22a]. Both of these were thermal plants employing high pressures and temperatures. It is interesting to note that only one more year elapsed before the commercial introduction of a catalytic process[85a] employing more moderate conditions with improved selectivity to desired products. Since that time the use of catalytic polymerization has increased steadily until, at the beginning of 1956, there were about 150 units in the United States with a total capacity of 142,000 barrels per day. Also, polymerization assumed special importance during World War II when the polymer gasoline was hydrogenated thus forming an important ingredient of aviation gasoline.

Since the introduction of catalytic polymerization, many of the technical developments have centered around process equipment. In contrast, a new development is the so-called "Polyform" process[138a] in which olefinic gases and naphtha are processed together, undergoing thermal polymerization and reforming. This process enjoyed some success until the advent of catalytic reforming.

A logical further step is the catalytic dehydrogenation of gaseous paraffins, followed by catalytic polymerization. Previously this was not economically attractive. However, the demand for high quality gasoline and the utilization of available olefins—previously a by-product—have now provided the basis for the production of olefins by dehydrogenation for processing to gasoline[77a]. Such olefins can be used in alkylation or polymerization. Further commercial development in this direction can be expected.

Catalysts used in the commercial polymerization of low molecular weight gaseous olefins to low boiling liquid hydrocarbons are of the acid type. Sulfuric and phosphoric acids are most widely used. A process employing hot sulfuric acid polymerizes all butenes, whereas the cold sulfuric acid process is highly selective for the polymerization of isobutene in a butene mixture. High octane number gasoline is produced by polymerization of C_3 and C_4 olefins over phosphoric acid of high concentration. The phosphoric acid may either be impregnated on an inert carrier, kieselguhr, or it may form a thin liquid film on an inert surface, such as quartz chips. Silica-alumina catalysts also have been employed, but on a much smaller scale.

In general, evolution of a theoretical understanding of catalytic polymerization has lagged behind the art and commercialization. At present, however, there is a reasonably comprehensive understanding of the mechanism and this will be discussed later.

As stated earlier, this chapter is primarily concerned with the polymerization of ethene, propene, butene and to some extent pentene into the C_8 to C_{12} hydrocarbon range. Polymerization of gaseous olefinic hydrocarbons to large molecular polymers has also assumed major importance in recent years, particularly in the rubber and plastics industries. This, however, is outside the scope of the present discussion, which presents a critique of the thermodynamics of polymerization followed by a discussion of the various aspects of the reaction mechanisms and, finally, a survey of the commercial applications for the production of low molecular weight polymers. An attempt will be made in the following chapter to digest and interpret the background of knowledge about the theory and practice of polymerization.

Thermodynamics of Polymerization

The thermodynamics of polymerization of olefinic hydrocarbons is discussed briefly by Sachanen[166] in his book on petroleum chemistry. General free energy equations as a function of temperature are given for the simple olefins. The thermodynamics of monoolefin hydrocarbons is presented in a comprehensive publication by the U. S. National Bureau of Standards[96a]. Jessup[93] has discussed the heat and free energy of the polymerization of ethylene. The detailed equilibrium aspects of polymerization, however, have not been described to any great extent in the literature. Rather than conduct an exhaustive search of the literature, a modest effort has been made to determine some of the regularities that exist in the free energy changes taking place during polymerization. Thermodynamic data used have been taken from the literature[93]. The study about to be described has been made on the basis of theoretical reactions of gaseous monoolefins polymerizing to give gaseous olefins of higher molecular weight. Admittedly, such a consideration can be far from the actual cases, since many polymerization reactions are carried out at conditions where the gases deviate from ideality and where phase changes occur, i.e., to liquid products. To include all these factors would require a great deal of effort and time. For the purposes of this chapter, therefore, phase changes and deviations from ideality have not been included. Rather, the purpose has been to make a few points regarding the general information that can be obtained about polymerization from thermodynamic considerations. Furthermore, the studies have been made largely with C_3 and C_4 olefins primarily because

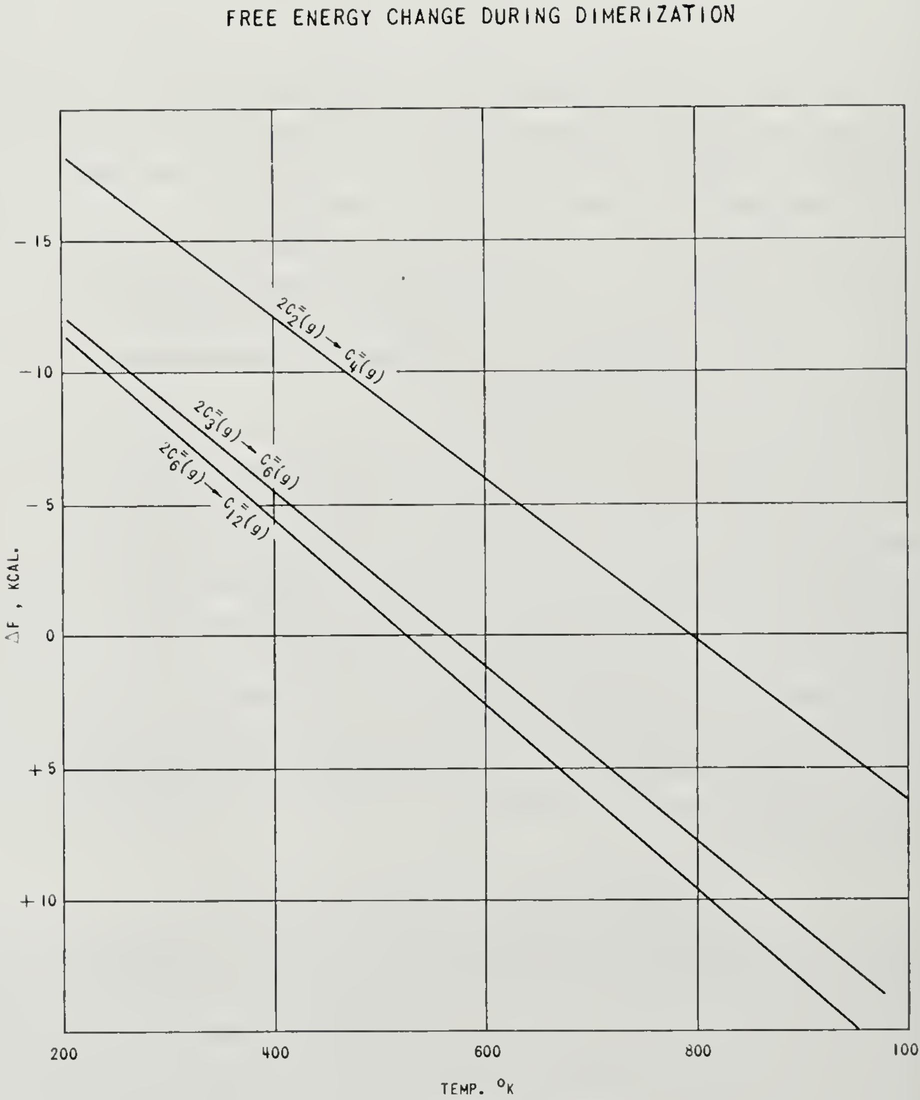


Figure 1. Free energy change during dimerization.

these are the reactions of practical interest which come within the scope of this chapter.

Figure 1 shows the free energy change which occurs during dimerization of C_2 through C_6 monoolefins as a function of temperature. The dimerization of ethylene to butene-1 is much more favorable at a given temperature than dimerization of any other of the light olefins. Beginning with propylene, the free energy-temperature relation soon becomes almost a single line. (The lines for C_4 and C_5 are not shown since they are almost superimposable on the C_6 line). In other words, the free energy of dimerization of terminal bond olefins at a given temperature to form terminal bond olefins becomes almost constant above propylene (see Table 1 and Figure 2, Ref. 96a).

These results are for terminal bond olefins dimerized to the corresponding higher olefins. The dimerization of terminal bond olefins to isomers of the corresponding higher olefins at a given temperature is more favorable than for the terminal olefin since the latter is always the structure of highest energy. Hence the equilibrium conversion of an alpha olefin to a high alpha olefin will always be less than the corresponding conversion of an alpha olefin to an isoolefin. A comparison of this for propylene is given in Table 2 and Figure 2. Dimerization of beta olefins or isoolefins to the corresponding higher olefins will be similar to the alpha olefin-alpha dimer relationships. However, dimerization of beta olefins or isoolefins to alpha olefins will always be the least favorable reaction. The exact relationship cannot be calculated since data for the higher beta and isoolefins are not yet available.

TABLE 1. FREE ENERGY CHANGE OF DIMERIZATION FOR TERMINAL OLEFINS TO TERMINAL OLEFINS

Monomer	$\Delta F°$, Kcal 298.1°K	 600°K	 900°K
C_2	−15.34	−5.99	3.07
C_3	−9.18	1.2	10.9
C_4	−9.5	1.2	11.5
C_5	−8.6	2.5	13.16
C_6	−8.5	2.4	13.1
C_8	−8.5	3.7	13.2
C_{10}	−8.5	3.5	13.1

It is obvious that pressure exerts a marked effect on polymerization equilibrium. Figure 3 shows the relationship of the product of the equilibrium constant and pressure of reaction in atmospheres and the per cent conversion for any dimerization reaction.

The production of polymers higher than dimers from alpha olefins invites an interesting thermodynamic study. The free energy change *vs.*

temperature curves fan out from a constant point (area) of 0 value at a temperature between 500 and 600°K. Figure 4 illustrates this point for the polymerization of propylene to higher terminal olefins. Table 3 shows the regularities in the free energy changes in the polymerization of propylene and butene-1. The free energy change of adding an additional monomer unit to a growing chain appears to be constant after the dimer has been formed. The well-known fact that polymerization can be made to occur at temperatures below about 800°K, depending on the pressure, can be verified from these curves. High pressures are required at high temperatures. Above this temperature level the opposite reaction, namely cracking, begins to occur. At the higher temperature it is obvious that the lower polymers will be the only ones formed if any polymerization occurs. Conversely, at low temperatures the higher polymers will predominate at equilibrium. This can also be seen in the paper by Jessup[93] where the equilibrium concentrations of various ethylene polymers are shown as a function of temperature.

TABLE 2

Conversion for the Reaction: $2C_3$ (g) → Hexene-1 (g)

T (°K)	−ΔF	K	% Conversion			
			1 Atm.	10 Atm.	50 Atm.	100 Atm.
298.1	−9.18	5.5×10^6	99+	99+	99+	99+
400	−5.62	1.17×10^3	98	98	99	99+
500	−2.2	9.2	84	95	98	98
600	1.2	0.36	36	73	88	92
700	4.4	0.04	7	38	68	76
800	7.7	0.01	2	15	37	51
900	10.9	0.004	1	7	25	38

Conversion for the Reaction: $2C_3$ (g) → *trans*-3-methylpentene-2 (g)

T (°K)	ΔF	K	% Conversion			
			1 Atm.	10 Atm.	50 Atm.	100 Atm.
298.1	−13.24	5.25×10^9	← 99+ →			
400	−9.52	1.65×10^5	← 99+ →			
500	−5.90	3.8×10^2	97	← 98+ →		
600	−2.32	6.97	81	94	97	98
700	1.22	0.42	38	76	96	97
800	4.78	0.05	9	42	70	78
900	8.30	0.01	2	15	37	51

If one considers the polymerization of a single species of olefin, some interesting conclusions appear. Consider for instance the olefin propylene and compare the dimerization with trimerization, tetramerization, etc. The free energy change for the formation of the higher polymers theoretically can be directly estimated from the corresponding energy of dimerization. If heat and entropy effects are constant for the addition of each new unit, then for the high molecular weight polymer the free energy change per mole of monomer should approach twice the corresponding change for the formation of dimer. That this is almost true is seen in Table 4. In the formation of each dimer one double bond disappears from two monomer molecules. However, in the formation of an infinite polymer each monomer effectively loses a double bond. The heat of reaction follows the theoretical relationship more closely than the free energy change. This can only mean that the entropy change is not constant in the polymerization reaction up to the hexamer. It is quite likely, however, that the free energy change would approach the theoretical value for polymers somewhat higher than $n = 6$.

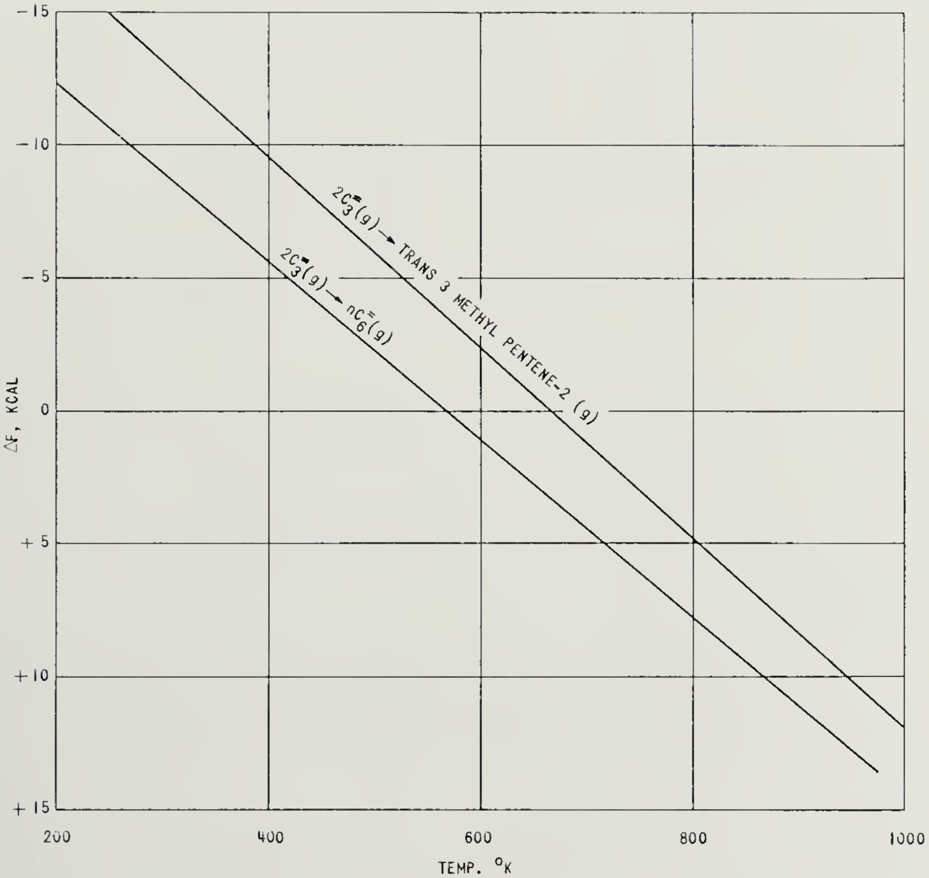


Figure 2. Free energy change during dimerization.

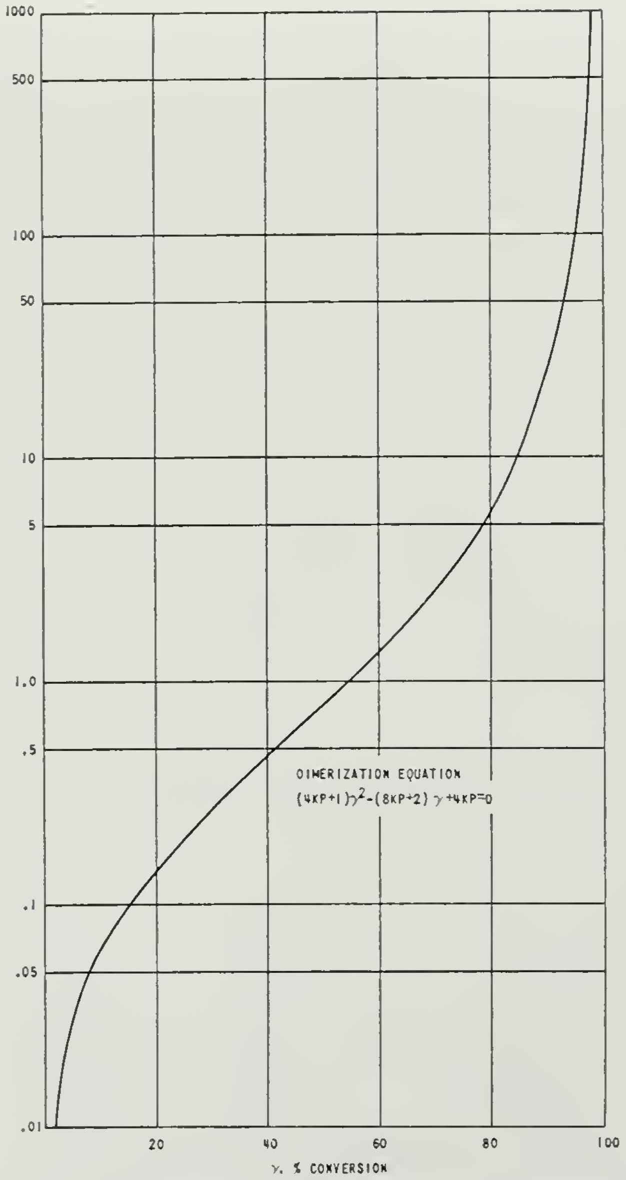


Figure 3. Conversion obtainable in dimerization reactions.

This interesting relationship can be examined for the case of ethylene polymerization, using Jessup's data[93]:

$$\Delta H_{n=1000}/\Delta H_{n=2=1.85};\ \Delta F^{\circ}_{n=1000}/\Delta F^{\circ}_{n=2=1.93};$$

both at 298.16°K. For an estimation of the heat and free energy change of polymerization of any monomer, the theoretical ratio for any size polymer together with the corresponding values for dimerization can be employed.

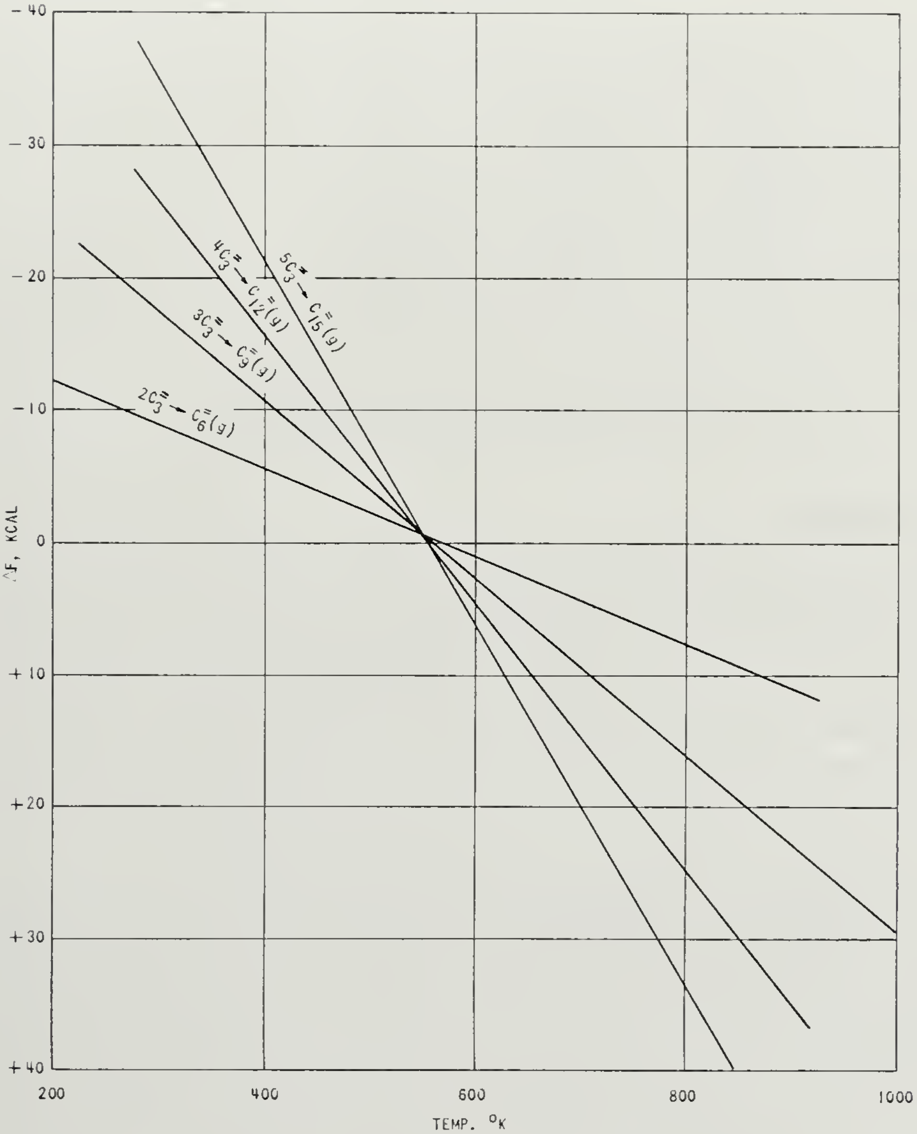


Figure 4. Polymerization of propylene.

Table 3. Standard Free Energy Change in Kcals of Polymerization per Unit Added

Temp.	C_3				C_4		
	Dimer	Trimer	Pentamer	Hexamer	Dimer	Tetramer	Pentamer
298.1	−9.18	−9.01	−8.93	−8.92	−9.5	−9.22	−9.17
600	1.2	1.5	1.65	1.69	1.2	1.63	1.71
900	10.9	11.45	11.7	11.76	11.5	12.1	12.15

TABLE 4

$\Delta F^\circ_{298.1}$, per Mole Monomer Added for the Reaction: $nC_3H_6(g) \rightarrow C_{3n}H_{6n}(g)$

n	$\frac{-\Delta F^\circ}{n}$	Ratio n-mer/dimer	$\frac{-\Delta H}{n}$	Ratio n-mer/dimer	Theoretical Ratio n-mer/dimer
2	4.59	1	9.86	1	
3	6.01	1.31	13.13	1.33	1.33
4	6.72	1.46	14.76	1.5	1.5
5	7.14	1.56	15.74	1.6	1.6
6	7.43	1.62	16.40	1.66	1.66
00	—				2.00

MECHANISM OF CATIONIC HYDROCARBON POLYMERIZATION REACTIONS

Introduction

As so frequently happens, the art of catalytic polymerization of olefins was developed many years before the theoretical basis was understood. By 1937, when the A. C. S. monograph[21] "Polymerization" appeared, catalytic polymerization of olefins had long been known and a number of commercial plants were in operation in the United States for production of gasoline from propylene and butylenes. The process conditions and products had been described in detail[35, 36, 84, 85, 88, 114, 185]. However, while the presently accepted cationic nature of the catalytic reaction had been suggested in 1934[208], it had not gained acceptance readily.

The difficulty in formulating the theory of catalytic polymerization arose from a confusion of information owing to (1) the wide array of seemingly unrelated catalysts which were effective; (2) the complicated nature of products arising from side and consecutive reactions accompanying polymerization; (3) the variations in reactivity of specific olefins to polymerization and side reactions; and (4) the importance of trace impurities critical as co-catalysts or poisons. Furthermore, the desire for useful products of either low or high molecular weight range led to the development of two different polymerization arts employing widely different polymerization conditions. Fortunately, there has evolved a systematic theoretical explanation of polymerization which brings into a consistent pattern the essential observed facts. It correlates and greatly simplifies many seemingly unrelated catalyst and reaction behaviors. No doubt many important details of the polymerization reaction mechanism are not well understood. However, the basic theory, by placing emphasis, perhaps unexpectedly, upon the ionic nature of the active hydrocarbon complex, permits consideration of those factors important to reaction and therefore permits prediction of reactions and new catalyst systems, which are generally correct.

It now seems possible to classify catalytic polymerization as being either free radical or ionic in nature and to further subdivide ionic polymerization into cationic or anionic. Catalysts for free radical polymerization are peroxides and other well-known sources of free radicals. Anionic polymerization catalysts are basic substances such as metallic sodium. Cationic catalysts include acids such as sulfuric acid, solid oxides such as alumina-silica, and Friedel-Crafts catalysts such as aluminum chloride. It was these cationic polymerization catalysts which appeared to be chemically unrelated for so long. These are all able to act as strong acids and it is this fundamental property which gives rise to their catalytic activity for polymerization.

In the following discussion an attempt will be made first to outline the generalized basis for the cationic theory of polymerization. A brief resumé of the history of polymerization mechanism theory follows. Then, the catalytic reaction steps will be discussed in more detail from the point of view of hydrocarbon structure. Finally, evidence for the particular action of the catalyst will be presented.

No attempt will be made to describe free radical or anionic polymerization. Nor will emphasis be placed on production of high molecular weight polymers for which there is a wealth of detailed information on the physical and chemical nature of the product.

Excellent recent reviews of the mechanism of cationic polymerization have been presented by Schmerling and Ipatieff[168], Pepper[144], Plesch[155], Langlois[106], Hamann[61], and Baroni[4]. A detailed review by Heiligmann of all theories appeared in 1949[67]. Concepts of the reactivity of the double bond, including polymerization, have been presented by Price[158]. Earlier, the status of polymerization was reviewed by Thomas[190] and by Burk *et al.*[21]. Emphasis on process features has been presented[34, 120]. Comprehensive reviews emphasizing high polymers have also appeared[30].

Generalized Cationic Polymerization Reactions

In the theory of cationic polymerization, the catalyst is considered to be a strong acid of the Bronsted type; that is, a proton-containing acid. Examples of such strong Bronsted acids which act as catalysts are, in idealized form, $(H^+)(AlCl_4^-)$, $(H^+)[Al(\text{-O-Si})_4]$, $(H^+)(HSO_4^-)$. For the Friedel-Crafts type of catalysts such as aluminum chloride, the Bronsted acid can be considered to be the unstable acid $HAlCl_4$ formed from $AlCl_3$ and HCl, utilizing the known propensity of Al^{3+} to become four coordinated. As the theory developed, $AlCl_3$ has been called the catalyst and HCl the co-catalyst or, by some authors, the promoter.

Examples of catalysts, co-catalysts, and the idealized Bronsted acid formed are:

$AlCl_3$	BF_3	SO_3	SiO_2-Al_2O_3	"Catalyst"
HCl	HF	H_2O	HOH	"Co-catalyst"
$HAlCl_4$	HBF_4	H_2SO_4	$HAl(OSi\equiv)_4$	Idealized Bronsted acid

The sequence of chemical reaction steps for the catalytic polymerization of olefin by aluminum chloride is, in simplest form, as follows:

Initiation

$$\underset{\text{Catalyst}}{AlCl_3} + \underset{\text{Co-catalyst}}{HCl} + \underset{\text{Olefin}}{C_2H_4} \rightarrow$$

Polymerization

$$\underset{\text{Active hydrocarbon-catalyst complex}}{(C_2H_5^+)(AlCl_4^-)} + C_2H_4 \rightarrow$$

Termination

$$(C_4H_9^+)(AlCl_4^-) \rightarrow C_4H_8 + HCl + AlCl_3$$

In certain instances, instead of the termination step shown, a chain transfer can occur by the removal of a hydride ion from another hydrocarbon to the carbonium ion or by transfer of a proton to another hydrocarbon from the carbonium ion.

There is an advantage in formulating the reaction with the electrical charges rather than as an un-ionized ester; it is to emphasize the importance and fundamental influence of the polar nature of the catalyst and of the hydrocarbon portion of the active complex. This reaction scheme has been termed a cation or carbonium ion reaction. Carbonium ion is merely the name given to the species R^+ and does not imply, or mean to imply, that R^+ is a free dissociated ion wandering in the hydrocarbon solution. The term "carbonium ion" is used in the sense of bearing an electric charge, in the same way that sodium ions and chloride ions exist fixed in lattice positions in crystalline rock salt. Considerations of the dielectric constants of the solution and ionization energies make it certain that R^+-$AlCl_4^-$ are not *dissociated* and separated in the usual hydrocarbon solvents in which cationic polymerization occurs. As a matter of fact, then, the reactive species is $R^+AlCl_4^-$, and might better be called an ion pair, polarized complex, or other similar term. Moreover, depiction of the anion in equations is not superfluous since the reaction must occur in the strongly polar environs of the anion which influences the reaction.

Before proceeding to a detailed consideration of polymerization reactions, it is appropriate to point out the types of reactions which occur together with polymerization and which can lead to such a variety of products. In addition to polymerization, carbonium ions can:

1. Expel a proton.
2. Lose a proton by transfer to an olefin.
3. Add a hydride ion by transfer from a hydrocarbon.
4. Depolymerize (crack).
5. Isomerize - skeletal, double bond or racemic.
6. Exchange hydrogen with catalyst protons.
7. Lose a hydride ion to become a "double" carbonium ion (which can react further including cyclization).

It will be readily appreciated that certain of these reactions lead to complex products. For example, following the loss of a hydride from a carbonium ion, (reaction 7) $C_nH_{2n}^{++}$ so produced can lose a proton, becoming $C_nH_{2n-1}^{+}$ which can undergo intramolecular polymerization, i.e., cyclization, following which loss of hydrogen by transfer forms first a cyclic olefin and finally an aromatic molecule. Also, olefins under the influence of acid catalysts can polymerize, then crack to olefins of carbon chain length other than that of the initial reactants. These new olefins can become saturated via hydrogen transfer. For example:

$$C_3H_6 + C_3H_6 \rightarrow C_6H_{12} \rightarrow C_2H_4 + C_4H_8 \xrightarrow{+2H} C_2H_4 + C_4H_{10}$$

It is therefore possible to obtain a product containing cyclic compounds, including aromatics as well as a variety of olefins and paraffins of low and high molecular weights, from simple olefins. Reaction conditions leading to a preponderance of the products of such side reactions have been contrasted to "pure polymerization" and termed "conjunct polymerization"[89].

History of Polymerization Mechanism Theory

It is, of course, not possible to assert that the theory of cationic polymerization, or any other theoretical mechanism, has been "proved". However, the cationic theory is most generally accepted because of its ability to fit the observed facts. To a certain extent, and from a superficial viewpoint, modern cationic theory is a modification of earlier theories of ester formation. Early publications by Ipatieff, Lwow and others[49, 84, 95, 100, 113, 132] on phosphoric acid polymerization of olefins attributed the catalytic process to an intermediate ester formation. The ester molecules were assumed to react with each other to produce a polymer and regenerate phosphoric acid or to liberate activated olefin molecules which react with molecules of ester or other molecules of olefin to produce polymers and regenerate phosphoric acid. During the early 1930's, a number of commercial plants were in operation in the United States for the polymerization of olefins to motor gasoline. This provided an increased interest in the chemical nature of the products. Detailed analyses of these products better defined the requirements of a comprehensive reaction theory. From such studies, Ipatieff and co-workers pointed out the importance of reactions other than "pure" polymerization, and gave the name "conjunct" polymerization to reactions where such side reaction predominates. A most significant finding was made in 1936 when Ipatieff and Grosse[86], working with aluminum chloride polymerization of ethylene, found that aluminum chloride, when pure, will not polymerize ethylene but that the addition of hydrogen chloride or water is necessary for the reaction to proceed. They postulated the addition of hydrogen chloride to the olefin to form an alkyl chloride under the influence of the Friedel-Crafts catalyst, followed by addition of an olefin to the alkyl chloride and, finally, removal of the hydrogen chloride to generate a polymer olefin.

A mechanism involving formation of a polar complex with the Lewis acid was proposed by Hunter and Yohe[83]. The suggestion for a mechanism of polymerization dependent upon an electron-deficient carbon atom was proposed and vigorously supported by Whitmore[208] and also by Prins[160]. The idea of explicit separation of charges was developed by Price and Ciskowski[159].

The need for a co-catalyst with a Friedel-Crafts catalyst was again emphasized in 1946 by Pines and Wackher[150], Oblad and Gorin[135], Evans, Plesch and co-workers[40, 43, 44, 45, 157] who, much more explicitly, pointed out its significance in the carbonium ion mechanism presently accepted. The English school then undertook a very intensive study of the co-catalyst system, emphasizing the theoretical aspects and carrying out detailed studies with highly purified systems. This culminated in the demonstration, through extreme purification, that all Friedel-Crafts catalysts require a co-catalyst for polymerization, even boron trifluoride in the polymerization of liquid isobutene[42].

The study of other hydrocarbon reactions[5] such as alkylation, cracking, and hydrogen transfer with Friedel-Crafts catalyst was of utmost significance to the theory of the cationic mechanism and its application in catalytic polymerization. The inquiry into complex formation between Friedel-Crafts catalysts and hydrogen chloride (Brezhneva *et al.*[15], Brown[20], Fontana[50], and Blau[13]) has also contributed to the development of cationic theory. Likewise, the fundamental study of the acid properties of oxide cationic catalysts, such as silica-alumina, which catalyze polymerization (Milliken, Mills and Oblad[125]; Tamele[188]; Weil-Malherbe and Weiss[205]; Bitepazh[12]; Thomas[191]; Walling[197]; and Kazanskii and Rozengart[96]) was most important in demonstrating their fundamental acidity and therefore their ability to act in polymerization by the cationic mechanism.

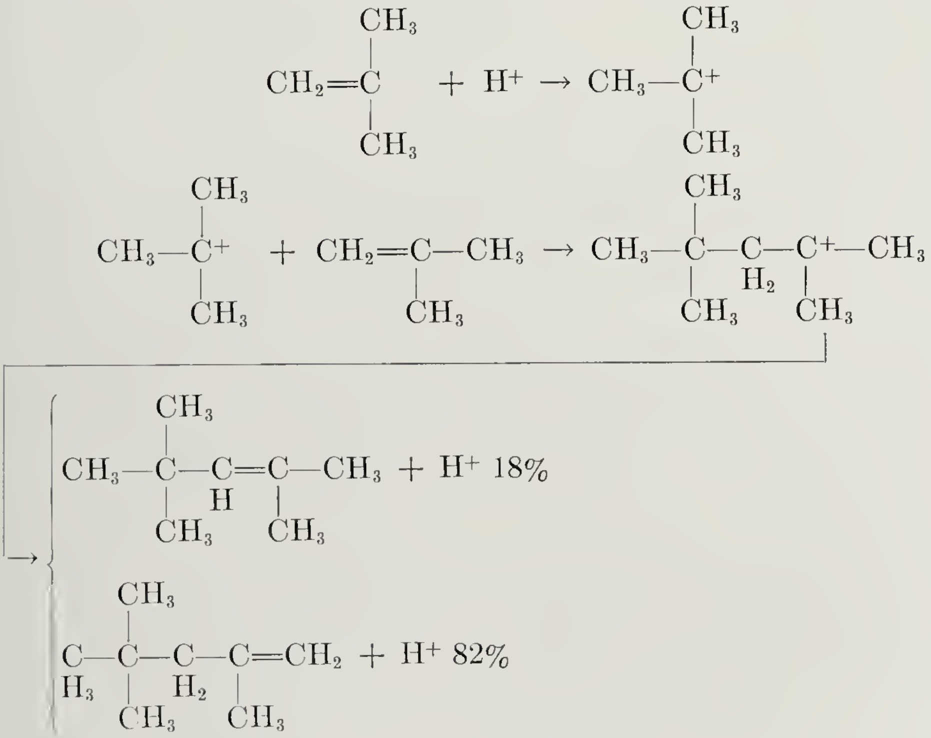
Furthermore, much of the work specifically directed to high polymers has contributed to reactions of particular interest in the field of macromolecules, such as the chain transfer and termination steps.

Hydrocarbon Reactions in Polymerization

"Pure Polymerization." The structural character of hydrocarbon polymers has proved most important from the point of view of utility of the product and reaction mechanism. Those polymers of relatively low molecular weight which result from so-called "true" polymerization will be considered first, followed by a discussion of the much more complex products which occur as the results of consecutive and side reactions, which have been termed "conjunct" polymerization.

The detailed products of true polymerization of C_3-C_7 olefins have been systematically discussed by Schmerling and Ipatieff[168]. As illustrated there, the structures are those expected from a carbonium ion mechanism with (1) formation of electron deficient carbon according to Markownikoff's rule, (2) isomerization of carbonium ions to stable form, and (3) allowance for absence of products where prevented by steric hindrance.

Isobutene. The polymerization of isobutylene will serve as an example:



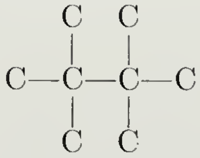
$$CH_2{=}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} + H^+ \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}}$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} + CH_2{=}\underset{\underset{CH_3}{|}}{C}-CH_3 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{H_2}{C}-\underset{\underset{CH_3}{|}}{C^+}-CH_3$$

$$\rightarrow \left\{ \begin{array}{l} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{H}{C}{=}\underset{\underset{CH_3}{|}}{C}-CH_3 + H^+ \ 18\% \\ \underset{H_3}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{H_2}{C}-\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H^+ \ 82\% \end{array} \right.$$

The two octenes are produced in the ratio of about 4:1[118, 209], 2,4,4-trimethylpentene-1 being favored because of greater ease of expulsion of a proton from the primary carbon atom compared to a secondary carbon atom.

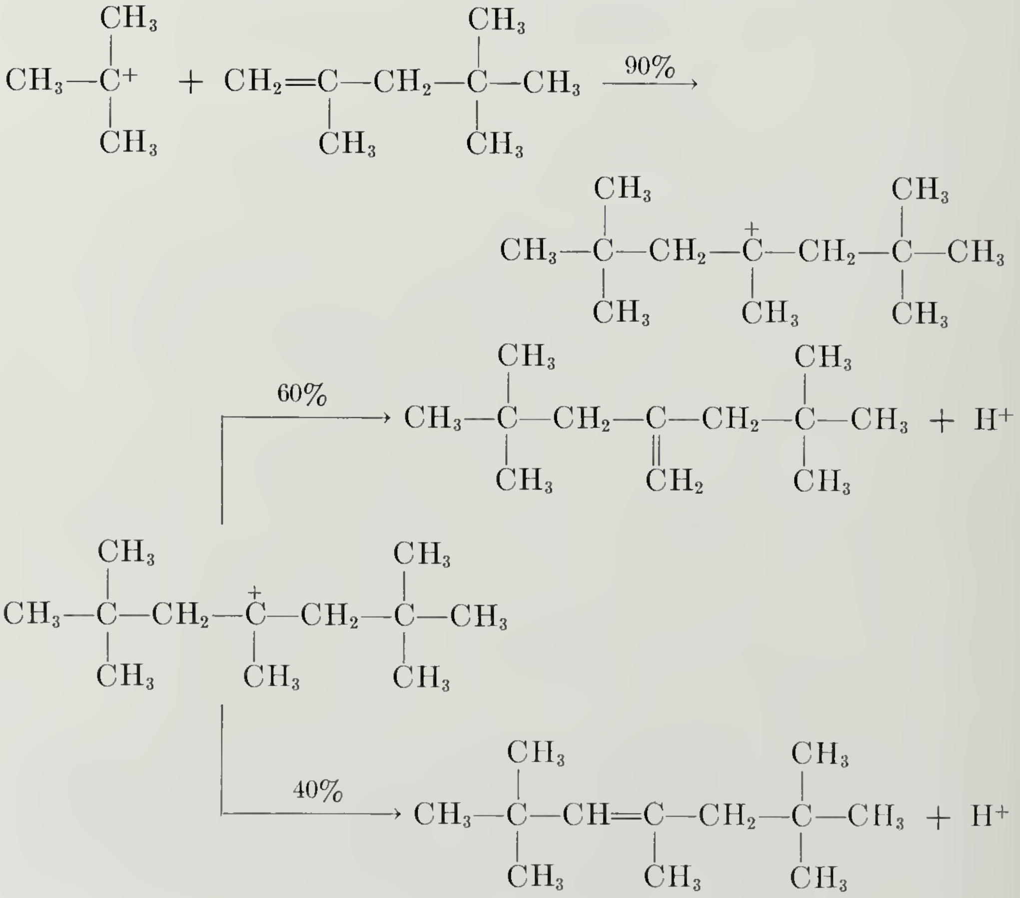
Addition of the proton to the olefin by attachment to the primary carbon atom is in accord with the Markownikoff rule. The structure



$$C-\underset{C}{\overset{C}{C}}-\underset{C}{\overset{C}{C}}-C$$

is believed too difficult to achieve because of steric hindrance. It would also be necessary to have a primary carbonium ion less stable than the tertiary ion shown.

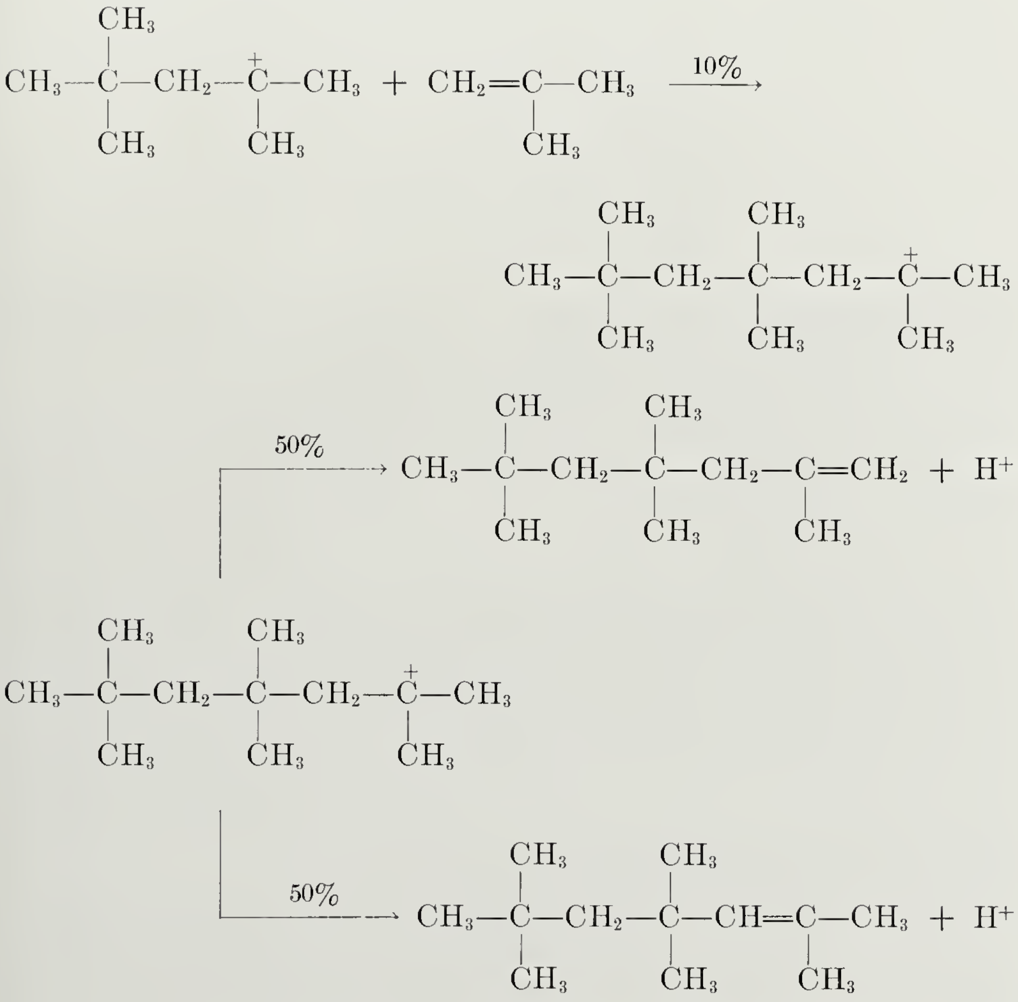
The octyl carbonium ion can, instead of expelling a proton, add a third isobutene molecule[129]. The isobutene trimers have been shown[1, 117, 210] to consist of 55 per cent of 4-methylene-2,2,6,6-tetramethylheptene, 35 per cent of 2,2,4,6,6-pentamethyl-3-heptene, and about 5 per cent each of 2,4,4,6,6-pentamethyl-1 and -2-heptene. The formation of the first two involves the addition of a *tert*-butyl carbonium ion to 2,4,4-trimethylpentene-1. Formation of the last two involves the addition of the isooctyl carbonium ion depicted above to a second molecule of isobutylene. These two additions, shown below, occur in the ratio of about 9:1.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + CH_2{=}\underset{CH_3}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{90\%} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{60\%} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + H^+$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{40\%} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH{=}\underset{CH_3}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + H^+$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_3 + CH_2{=}\underset{CH_3}{C}-CH_3 \xrightarrow{10\%}$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_3$$

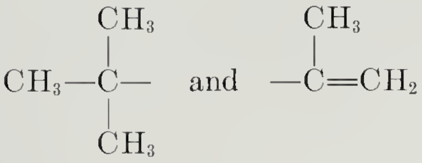
$$\xrightarrow{50\%} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{C}{=}CH_2 + H^+$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_3$$

$$\xrightarrow{50\%} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH{=}\underset{CH_3}{C}-CH_3 + H^+$$

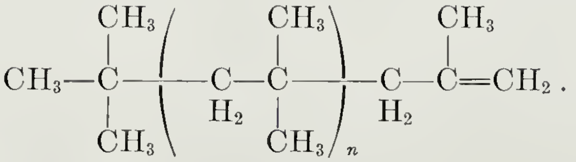
The tetramers of isobutylene have been prepared (Grosse[59]) and partially identified, with findings consistent with those expected from the carbonium ion mechanism. The preparation and structure of high molecular weight polybutenes utilizing Friedel-Crafts catalysts at low temperature have also been described. A linear polymer with side chains was found (Thomas *et al.*[192]).

More recently, Dainton and Sutherland[29] have applied infrared analyses to elucidate the mechanism of boron trifluoride catalyzed vapor phase polymerization of isobutene at room temperature. They have identified by infrared the groups



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}- \quad \text{and} \quad -\overset{CH_3}{C}{=}CH_2$$

which are consistent with the proposed polymer structure



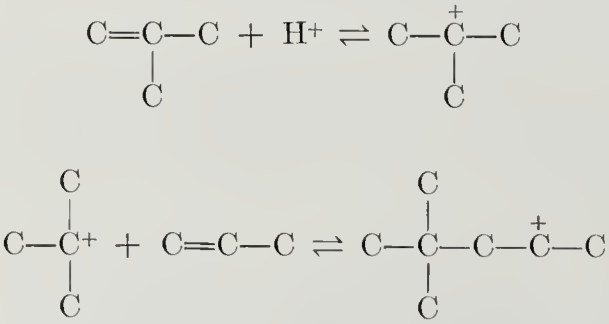
$$CH_3-C(CH_3)_2-\left(CH_2-C(CH_3)_2\right)_n-CH_2-C(CH_3)=CH_2 .$$

Although deuterium oxide was used as co-catalyst, the weak infrared lines for C—D did not permit a conclusion as to position of the D.

Isobutene Plus Propene. The phosphoric acid catalyzed copolymerization of isobutylene and propene yields a copolymer consisting of a mixture of 2,2- and 2,3-dimethyl-x-pentene as shown by the fact that hydrogenation yields 2,2- and 2,3-dimethylpentane. The polymer obtained in the presence of "solid" phosphoric acid at 135° and 38 atmospheres from an approximately equimolecular mixture of the two alkenes contained 40 to 45 per cent heptenes, which yielded a heptane fraction consisting largely of 2,3-dimethylpentane together with a lesser amount of 2,2- and a trace of 2,4-dimethylpentane (Ipatieff and Schaad[90]). At 180° and 40 atmospheres pressure other investigators obtained a 65 per cent yield of polymer hydrogenation which yielded a liquid containing 54 per cent of heptane fraction consisting of approximately 20 per cent of 2,2-dimethylpentane, and 80 per cent of 2,3-dimethylpentane (Hoog *et al.*[77]).

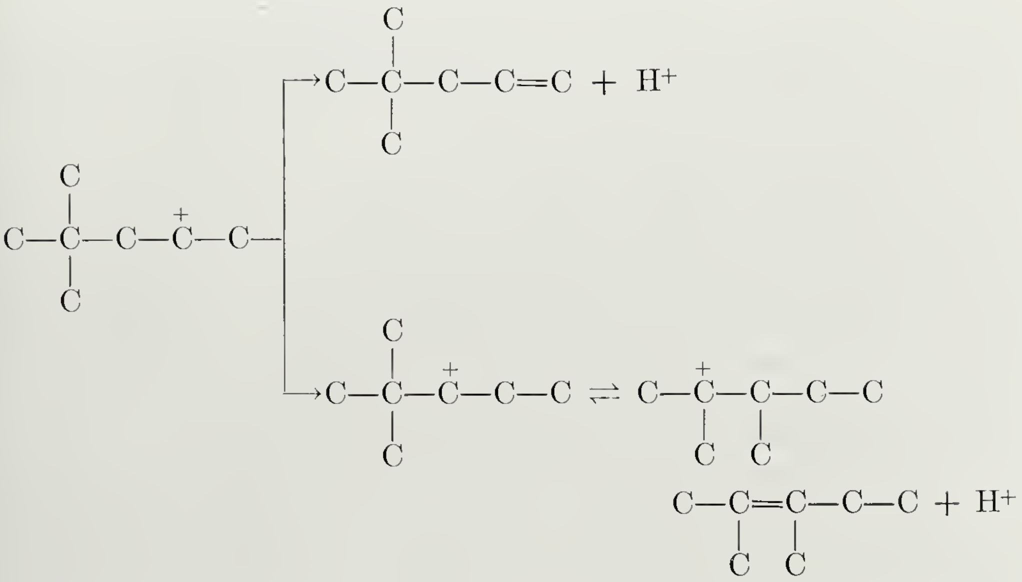
Similarly, hydrogenation of the copolymer of isobutylene and propene formed in the presence of dihydroxyfluoboric acid at 15 to 20° yielded a liquid product, 67 per cent of which was heptane (Brooks[18]). At least 95 per cent of the heptane was 2,3-dimethylpentane. In the absence of isobutylene, propene does not undergo polymerization when treated with hydroxyfluoboric acid at 0 to 40°.

The formation of the heptenes may be indicated by:



$$C{=}C(C){-}C + H^+ \rightleftharpoons C{-}\overset{+}{C}(C){-}C$$

$$C{-}C^+(C)(C) + C{=}C{-}C \rightleftharpoons C{-}C(C)(C){-}C{-}\overset{+}{C}{-}C$$

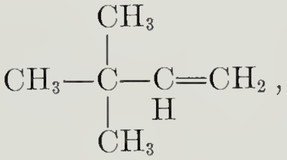


Other polymer structures are also detailed by Schmerling and Ipatieff[168]. In addition, many literature references (e.g., Ipatieff, Schaad and Shanley[92]) as well as the discussion on applications in this chapter, deal with product structure in more detail. In 1931, Sullivan, Voorhees, Neeley and Shankland[185] reviewed the literature on the relationship between chemical constitution and physical properties.

Walling *et al.*[198] have discussed structure of monomer and reactivity. They proposed that by examination of the composition of copolymers of styrene and methyl methacrylate it is possible to distinguish between carbonium ion and carbanion catalysis.

"Conjunct" Polymerization. The diversity of products in "polymerization" was pointed out in 1936 by Ipatieff and Pines[89] who found that paraffins, olefins, cycloparaffins, cycloolefins, and aromatics were formed when propylene was polymerized at 330 to 370°C using 90 per cent H_3PO_4.

The polymerization of olefins with Friedel-Crafts catalysts was investigated by Meier[124] in 1950. Starting with



$$CH_3-C(CH_3)_2-CH=CH_2,$$

he found that "polymerization causes rearrangement of at least half of the neopentyl groups." All polymers from gaseous polymerization of propylene, butene-1, *cis*- and *trans*-butene-2 and isobutene at 0 to 60°C with gaseous boron trifluoride show evidence of rearrangement and extensive disproportionation except in the case of isobutene. Using butene-2 in liquid phase polymerization with aluminum chloride, C_9's and C_{10}'s were as common as C_8's. Most of the C_8's were saturated. On the other hand, many diolefins occurred in the C_{20} range.

Aluminum halide action on paraffins also produces a variety of product types of different molecular weight. For example, working with 2,2,4-trimethylpentane, Condon[27] found that the product was 18 per cent iC_4's, 6 per cent iC_5's, 12 per cent C_6's and C_7's, 26 per cent iC_8's and 38 per cent heavier product including catalyst sludge. Under mild conditions aluminum halide breaks down the paraffin, producing fragments with at least four carbon atoms. The C_5's were formed from molecules having a carbon chain greater than C_8 because almost no C_3's were found.

The transfer and exchange of hydrogen during cationic polymerization are of utmost significance to the catalytic reactions which occur. The transfer of hydrogen occurs under several distinct circumstances, both protons and hydride ions being involved. Hydrogen transfer under acid reactions was recognized by Schmerling and others (e.g., Ciapetta[25]). Also, a hydrogen transfer reaction of butylenes and butyl alcohol was measured under the influence of sulfuric acid[22]. It was suggested that this apparent dismutation and rearrangement are based not on simple reactions of original materials but involve polymeric materials. Until the polymer is formed, no isobutane is evolved.

Farkas and Farkas[49] established that exchange of hydrogen occurs where olefins are polymerized in the presence of deuterophosphoric acid. After polymerization, both the polymer and unpolymerized olefin contain substantial amounts of deuterium.

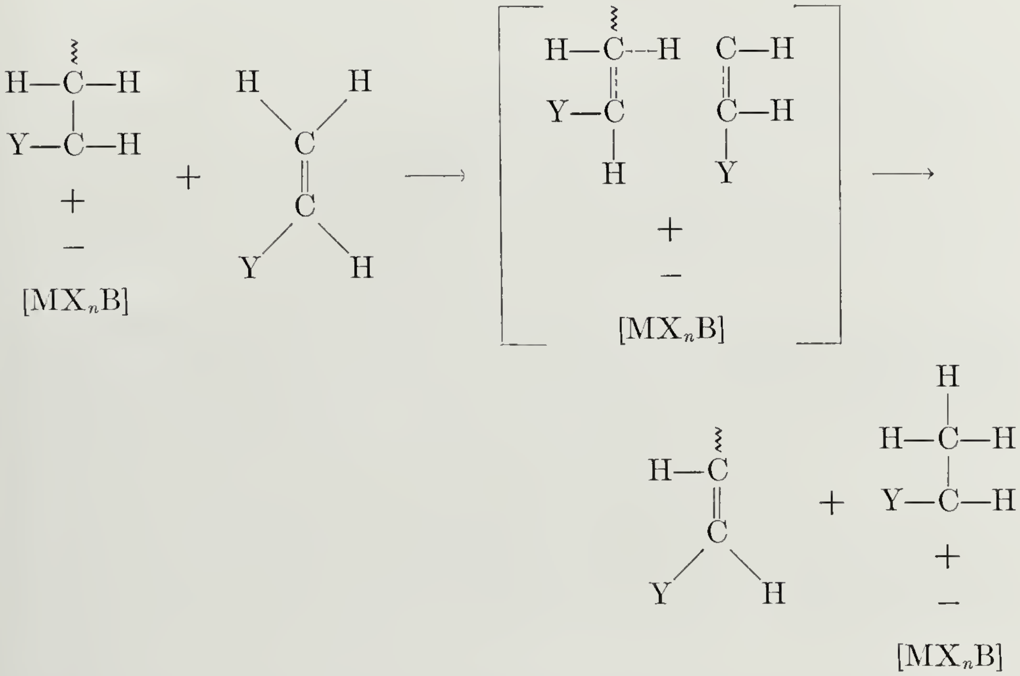
The reversible addition and loss of a proton have experimental backing from the work of Stewart and Harman[181]. They found that a rapid exchange occurred between tritium sulfuric acid and butene-2.

Ohtsuka[138] studied the polymerization of olefinic gases over phosphoric acid. The mechanism proposed was that of proton exchange between the acid and hydrocarbon.

In addition to reactions which demonstrate the transfer and exchange of hydrogen, other reactions occur, such as isomerization, which involve reversible proton addition to form carbonium ions. Rearrangement of hydrogen in olefinic hydrocarbons over aluminosilicate catalysts was measured by Petrov and Frost[148].

The products of polymerization of propylene and 1-butene were carefully examined by Fontana *et al*[51]. To account for the observed products, they visualize a carbonium ion mechanism which features both slow polymer growth and hydride ion transfer.

Likewise, Eley and Richards[39] recognized the transfer of a proton from a polymer carbonium ion to a monomer molecule. For higher molecular weight polymers, such a transfer leaves a "dead" or inactive polymer with a terminal double bond.

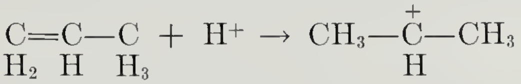


MX$_n$B represents the catalyst anion.

The complex reactions which can occur with hydrocarbons under the influence of acid catalysts have been examined by Schneider and Kennedy[169] who have accounted for a wide variety of products by a series of carbonium ion reactions.

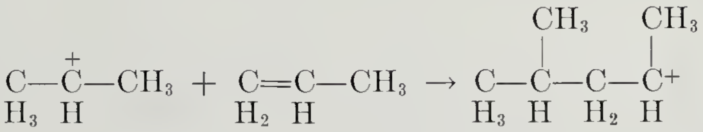
It is evident that the reactions which occur when olefins are acted upon by acid catalysts under many conditions are far from simple. However the products can be accounted for by taking into account all the separate reactions catalyzed by acids. For olefin polymerization the significant reactions are:

1. *Initiation by proton addition*



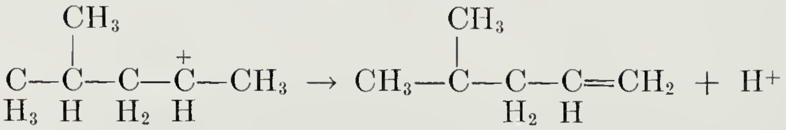
$$\underset{H_2}{C}=\underset{H}{C}-\underset{H_3}{C} + H^+ \rightarrow CH_3-\underset{H}{\overset{+}{C}}-CH_3$$

2. *Propagation by olefin addition*



$$\underset{H_3}{C}-\underset{H}{\overset{+}{C}}-CH_3 + \underset{H_2}{C}=\underset{H}{C}-CH_3 \rightarrow \underset{H_3}{C}-\underset{H}{\overset{CH_3}{C}}-\underset{H_2}{C}-\underset{H}{\overset{CH_3}{C^+}}$$

3. *Chain termination by proton expulsion (Reversal of 1)*



$$\underset{H_3}{C}-\underset{H}{\overset{CH_3}{C}}-\underset{H_2}{C}-\underset{H}{\overset{+}{C}}-CH_3 \rightarrow CH_3-\overset{CH_3}{C}-\underset{H_2}{C}-\underset{H}{C}=CH_2 + H^+$$

4. *Chain termination by proton transfer*

$$C_8H_{17}^+ + C_4H_8 \rightarrow C_8H_{16} + C_4H_9^+$$

5. *Chain termination by addition of a hydride ion*

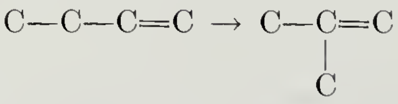
$$C_8H_{17}^+ + RH \rightarrow C_8H_{18} + R^+$$

This reaction has been shown to occur by addition of a hydride ion to a tertiary carbon of the carbonium ion.

6. *Depolymerization* to same or other chain length than that of original olefin

$$2C_5H_{10} \xrightarrow{H^+} C_{10}H_{21}^+ \rightarrow C_6H_{12} + C_4H_8 + H^+$$

7. *Isomerization*



$$C-C-C=C \rightarrow C-\underset{C}{\underset{|}{C}}=C$$

Isomerization leading to double bond shift and racemization of optically active compounds also occurs.

8. *Hydrogen exchange*

$$C_4H_9^+ + D^+ \xrightarrow[\text{(catalyst)}]{} C_4D_9^+ + \underset{\text{(catalyst)}}{H^+}$$

9. *Cyclization*, equivalent to self-alkylation or self-polymerization

$$C_8H_{15}^+ \xrightarrow[\text{(acyclic olefin carbonium ion)}]{} \underset{\text{(cyclic non-olefin)}}{C_8H_{15}^+} \quad \text{(Self-polymerization)}$$

10. *Loss of hydride ion.* It is possible that large carbonium ions can lose a hydride ion to become a reaction "double" carbonium ion.

$$C_8H_{17}^+ \rightarrow H^- + C_8H_{16}^{++}$$

Then: $C_8H_{16}^{++} \rightarrow C_8H_{15}^+ + H^+$ (by loss of a proton and reaction 9).

Catalysts

Cationic polymerization catalysts are listed below. These have been subdivided into: (a) mineral acids, (b) Friedel-Crafts catalysts, (c) clays and related oxide systems, and (d) others.

Cationic Polymerization Catalysts

(a) Mineral acids

H_2SO_4, H_3PO_4, HF, ($Cu\ P_2O_7$)

(b) Friedel-Crafts

Halides of Al, B, Sn, Ti, Zr, Sb.

(c) Clays and related oxide systems

SiO_2-Al_2O_3, SiO_2-ZrO_2, SiO_2-MgO, etc.

(d) Others

I_2, Ag ClO_4, CPh_3Cl

Co-Catalysts. As mentioned previously, the property common to those catalysts listed above is their ability to act as an acid. Furthermore, in all instances, except for those listed under (d) which are not well understood, it is necessary for a cationic polymerization catalyst to possess a proton; that is, to be of the Bronsted rather than the Lewis type of acid. This possibility obviously exists with the mineral acids. However, such a requirement was not obvious with Friedel-Crafts catalyst, in large part because traces of water and/or hydrogen halide are always present as impurities unless specific and sometimes exhaustive precautions are taken to eliminate them.

The inactivity of a pure Friedel-Crafts catalyst for polymerization was first reported by Ipatieff and Grosse[86] in 1936. They reported their experimental discovery that aluminum chloride, when really pure, does not react with pure ethylene even under pressures up to 50 atmospheres at 10 to 50°C and that the presence of traces of hydrogen chloride or moisture are necessary for the reaction. At about this time other investigators[60] were seeking to define the effect of compounds of aluminum such as aluminum methylchloride on ethylene polymerization.

The necessity for an added substance for Friedel-Crafts catalytic activity was not taken up in the literature until ten years later, although it was evidently being investigated in certain industrial laboratories. Using vacuum technique methods to avoid uncontrolled impurities, Pines and Wackher[150] in 1946 reported on their studies with the aluminum chloride and bromide system for alkane isomerization as a function of added oxygen. They found that in the absence of oxygen the reaction does not proceed but that the addition of 0.007 mole per cent oxygen, in the form of air, was sufficient to convert 40 per cent of the *n*-pentanes to butanes and isopentanes when employing aluminum chloride as a catalyst. Two possible mechanisms were suggested:

1.
$$AlX_3 + \tfrac{1}{2}O_2 \rightarrow AlOX + X_2$$
$$X_2 + C_4H_{10} \rightarrow C_4H_9X + HX$$

following which the alkyl halide acts as a chain initiator for the reaction which proceeds through a carbonium ion mechanism.

2. $$C_4H_{10} + O_2 \xrightarrow{AlX_3} 2C_4H_9OH$$

following which the butanol may react by: $C_4H_9OH + AlX_3 \rightarrow C_4H_9OAlX_2 + HX$ and the butanol may also react with the hydrogen halide $C_4H_9OH + HX \rightarrow C_4H_9X + H_2O$ with the alkyl halide acting as a chain initiator.

Oblad and Gorin[135] in 1946 investigated the effect of oxygen and also of other "promoters" on aluminum bromide catalysis, measuring the isomerization of *n*-butane. Erratic behavior of reaction in early experiments led them to the postulate that some impurity material acting as a promoter was being consumed in the reaction. This substance was found to be oxygen and its effect was investigated in detail. The rate of reaction was found to be first order with respect to hydrocarbon and, at a given temperature, to depend on aluminum bromide concentration, oxygen concentration, and amount of surface. It was suggested that a surface is necessary to assure a polar medium in which the reactions involved can take place. "Promoters" other than oxygen were measured including water, bromine, hydrogen, carbon dioxide, hydrogen chloride, hydrogen bromide, and ethyl bromide, and the mechanism discussed in terms of possible formation of hydrogen bromide and alkyl bromides by the oxygen with subsequent reaction to form $[(CH_3)_3\ C^+]$ and $(AlBr_4^-)$.

The publications of Evans, Polanyi, and co-workers first appeared in 1946, and they followed with an intensive study of the role of co-catalysts. Evans, Holden, Plesch, Polanyi, Skinner and Weinberger[40] reported briefly in 1946 that a third substance was necessary for polymerization with Friedel-Crafts catalysts in addition to boron trifluoride and the olefin, and suggested that the necessary substance was water. That same year Evans, Meadows and Polanyi[43] found that purification of isobutene decreased the reaction rate in gas-phase boron trifluoride polymerization, and that addition of water speeded up the reaction. Evans and Polanyi[45] discussed the important theoretical significance on the necessity of a co-catalyst. They wrote the mechanism for polymerization incorporating the co-catalyst in the form shown on page 352. Norrish and Russell[133] disclosed an experimental method of coating an apparatus with $C_{16}H_{33}N^+Me_3Br^-$ so as to make it hydrophobic and eliminate water introduced from glass walls. They then reported[134] kinetic measurements on the role of water in polymerization. Plesch, Polanyi and Skinner[157] discovered that moist air affects the reactivity of titanium tetrachloride for polymerization, and pointed out that this necessitates re-evaluation of previous conclusions on relative reactivities of a series of Friedel-Crafts catalysts without regard for moisture. Plesch[154] investigated the low temperature polymerization of isobutene by titanium tetrachloride and found that trichloroacetic acid is an efficient co-catalyst. He found, however, that monochloro- and dichloroacetic acid possessed practically no co-catalytic activity. Evans, Meadows and Polanyi[44] reported that in the polymerization of isobutene using boron trifluoride, acetic acid can act as a co-catalyst, as can water or *tert*-butyl alcohol.

Pepper[145] studied the effect of solvent on the polymerization of olefins by stannic chloride. He studied the effect of water on the polymerization and measured conductivity of stannic chloride solutions.

One after another Friedel-Crafts system was shown, through purification of reactants, to require a co-catalyst for olefin polymerization. However, polymerization of isobutene in the presence of boron trifluoride appeared to proceed in the liquid phase without the need of a co-catalyst. Finally, Evans and Meadows[41, 42] succeeded in purifying the reactants sufficiently rigorously to find that no polymerization occurred at −80°C for several hours without adding a co-catalyst.

Further work indicated that certain solvents[171] such as ethyl, isopropyl, or *tert*-butyl chloride can act as a co-catalyst. In related work Plesch[153] found it impossible to polymerize styrene with titanium tetrachloride without a co-catalyst, which could be water or trichloroacetic acid.

The most recent discussions[151] have suggested that in some instances hydrogen chloride alone can act as a catalyst. Thus, it appears fundamental to supply a proton; the ionic splitting of hydrogen chloride to supply such a proton is aided by complexing the chloride ion, such as by formation of $AlCl_4^-$. Then, with highly basic olefins it is expected that less need exists for a complexing agent to assist in the removal of the chloride ion.

In an investigation of the polymerization of styrene with titanic chloride, Plesch[153] found by measuring end groups with infrared that certain solvents can act as co-catalysts. The influence of the dielectric constant of the medium on the catalytic polymerization of styrene was studied[54] using stannic chloride plus hydrogen chloride. The rate of reaction was found to increase with increasing dielectric constant of the solvent.

In an investigation of the catalytic polymerization, with emphasis on the mechanism of initiation, Gantmakher, Medvedev and Lipaforate[55] found that a protonic acid is necessary as a co-catalyst only in a medium of low dielectric constant.

Topchiev and Paushkin[193] studied boron fluoride in combination with other compounds such as phosphoric acid. They concluded, among other things, that the acidity and activity of the catalyst for polymerization and alkylation were determined by the property of compounds of the type $H^+ (XOBF_3)^-$. Other complex catalysts have also been studied for polymerization, including dihydroxyfluoboric acid[18].

Catalysts of the group I_2, $AgClO_4$, CPh_3Cl[9] can be considered to act by formation of positive and negative ions, e.g., $2I_2 \rightarrow I^+ + I_3^-$. The polymerization reaction then can proceed by a cationic mechanism.

It has also been established that clay substances and related hydrous oxides possess an acidity essential to their activity and that a co-catalyst is necessary for cationic catalytic activity. Floridin and similar materials have been recognized as powerful catalysts for the polymerization of olefins[57, 108, 109, 110, 200, 201]. A commercial process for the production of gasoline utilized a catalyst of the silica-alumina type[80]. In his report on the polymerization of ethylene, Gayer[57] notes that both Floridin and synthetically prepared alumina-silica exhibited an acid reaction when tested with an indicator. Furthermore, he found that even traces of alkali poisoned these catalysts for polymerization. Kazanskii and Rozengart[95] studied the polymerization of isobutene over hydrosilicate catalysts. They concluded that hydrosilicates of metals, constituting the carriers of the acid properties of the catalysts, serve as the active ingredients in polymerization catalysts prepared by the method of Gayer. Basic ions inactivate the catalysts and it was pointed out that the ability of hydroaluminosilicates to polymerize olefins is due to their acidic nature. The products of polymerization were compared with and found to be very similar to those obtained with phosphoric acid catalyst. They pointed out that polymerization proceeds through the mechanism theory of ester formation or through intermediate formation of a special type ion formed by addition of a hydrogen ion at the double bond as proposed by Whitmore.

Oxides of the silica-alumina type have been established to be acids by detailed experimental measurement of various means (Milliken, Mills, Oblad[125]; Tamele[188]; Bitepazh[12]; Weil-Malherbe[205]; Walling[197]; Stright and Danforth[183]; and Thomas[191]). Moreover, catalytic activity for a variety of related reactions, including polymerization, has been shown to be dependent on this acidity. For such hydrous oxide catalysts, water should be considered to be the usual co-catalyst. Since such high area materials are difficult to dehydrate, special drying means are necessary in order to observe the necessity for water in reacting this group of catalysts. By extensive drying of a silica-alumina catalyst, Hansford[64] was able to show the influence of water in cracking. Also, Hindin, Mills and Oblad[73] as well as Hansford *et al.*[65] showed that water is a co-catalyst needed for high cationic activity, as measured by H—D exchange between the catalyst and hydrocarbons. Large amounts of water act as a poison through competition between bases for the proton which exists, so that oxonium ion is formed instead of carbonium ion. Gayer[57] found that the addition of hydrogen chloride to silica-alumina exerted a great promoting effect in the polymerization of olefins. Small amounts of water improved the polymerization activity of Floridin slightly. The acidic nature of alumina and its catalytic activity on olefin isomerization were found to be greatly enhanced by an added fluoride ion[137].

Nature of HAXn. Although reactions involving ions such as ($C_4H_9^+$) ($AlCl_4^-$) as the active intermediate have been accepted, and although it is evident that reactions such as:

(1) $$HCl + AlCl_3 \rightarrow HAlCl_4$$

(2) $$HOH + Al(OSi\equiv)_3 \rightarrow HAl(OSi\equiv)_3\,(OH)$$

provide for the acid HAXn which can react with an olefin to produce R^+ AXn^-, the existence of HAXn has been a controversial issue. Certain investigators have felt that the reaction $C_2H_4 + HCl + AlCl_3 \rightarrow C_2H_5^+$ $AlCl_4^-$ can occur only under the influence of a base, such as an olefin, without actual intermediate formation of $HAlCl_4$.

For the oxides system, as represented by Reaction (2), Milliken, Mills and Oblad[125] have discussed the possible existence of the Bronsted acid and conclude that it is a "potential" acid and does not pre-exist. Oblad, Hindin and Mills[136] have provided data on exchange of O^{18} between water and the catalyst which is in accord with the dynamic nature of the system—with a rapid reversible change in coordination of the aluminum ion as in Reaction (2). Tamele has considered the reversible addition of water to the Lewis base in silica-alumina but has not considered a base as being necessary for the formation of the strong acid. The acidity of the oxide system has been considered from a structural point of view by Thomas[191].

Investigating the possible existence of $HAlCl_4$, Brown, Pearsall and Eddy[20] in 1950 looked experimentally for the interaction between hydrogen chloride and aluminum chloride or gallium trichloride from 300 to −120°C. No reaction was found unless a hydrocarbon such as toluene is present, which they attribute to the formation of a complex of toluene, hydrogen chloride and aluminum chloride, but not between hydrogen chloride and aluminum chloride. These measurements were of the vapor phase and molecular weight type. Also, Fontana and Herold[50] attempted to detect complex formation between hydrogen bromide and aluminum bromide. Within the limits of error, they could find no evidence for complex formation and concluded that $HAlBr_4$ does not pre-exist. It should be pointed out that these measurements do not exclude the possibility that minute amounts of $HAlX_4$ exist, but such small amounts would be very much less than the amount of hydrocarbon-containing complexes, e.g., toluene-hydrogen chloride-aluminum chloride, which are observed.

Measurement of the exchange reaction of halogen between aluminum halides and hydrogen chloride as well as organic halides has proved to be a powerful tool for the investigation of interaction and complex formation. In 1936, Brezhneva, Roginskii and Shilinskii[15] proposed a method for inserting radioactive halogens into organic molecules. They brought organic bromides in contact with aluminum bromide possessing radioactive bromine atoms[16, 17]. The exchange of bromine atoms permitted them to prepare radioactive bromine compounds such as ethyl, isoamyl, phenyl, α-naphthyl, benzyl bromides and ethylene bromoform, trimethylene bromide and *p*-dibromobenzene. They studied the kinetics in 1937. They also reported (1937) that mixtures of compounds such as ethyl bromide and $C_2H_4Br_2$ showed rapid mutual exchange of bromine atoms when aluminum bromide was added.

Fairbrother[47] in 1937 studied the reaction $AlCl_3 + C_6H_6 + CH_3COCl$ (also *tert*-butyl chloride) and found that the evolved hydrogen chloride had a radioactive level equal to that of the aluminum chloride, indicating complete interchange. He concluded that the first step in synthesis of hydrocarbons catalyzed by aluminum chloride is the ionization to the $AlCl_4^-$ ion and positive carbonium ion.

In 1941 Fairbrother[48] found that aluminum bromide containing radioactive bromine, at room temperature comes quickly to halide equilibrium, with organic bromides, except bromobenzene. Tin bromide and antimony tribromide were found to be less powerful. He correlated the ease of exchange with the energy of formation of a metal complex ion and the ionization potential of the organic radical.

It is, of course, possible to investigate halogen exchange without radioactive tracers. In 1944 Korshak and Kolesnikov[101] employed aluminum bromide with $C_2H_5CO_2Cl$ and found that the evolved gases were 82 per cent hydrogen bromide and 18 per cent hydrogen chloride. Also, Delwaulle[32] studied the halide interchange between halides of germanium, tin, titanium, and silicon over a period of years. They found, for instance, that $GeCl_4$ and $GeBr_4$ exchange halogen at 20 to 60°C and that this exchange is catalyzed by traces of hydrogen chloride or hydrogen bromide.

Wallace and Willard[196] in 1950 investigated the exchange between aluminum chloride and carbon tetrachloride. Solid aluminum chloride exchanges chlorine rapidly with carbon tetrachloride liquid even at -21 to -63°C. The reaction appears to require a surface. Gaseous $AlCl_3 + CCl_4$ showed no exchange at 140°C for 2 hours. Blau, Carnall and Willard[13] studied the exchange reaction between hydrogen chloride and aluminum chloride. In contrast to Richardson and Benson[164], they did find halide exchange at room temperature and at -80°C. This result indicates formation of $HACl_4$ in very small amounts.

Plesch[152] has considered whether the reaction proceeds via: (a) $HCl + AlCl_3 \rightarrow HAlCl_4$; $C_nH_{2n} + HAlCl_4 \rightarrow (C_nH_{2n} + 1) + (AlCl_4^-)$ or (b) $AlCl_3 + C_nH_{2n} \rightarrow C_nH_{2n} \cdot AlCl_3 + HCl \rightarrow (C_nH_{2n}^+ + 1)(AlCl_4^-)$. It seems best at present to write $HCl + AlCl_3 +$ olefin $\rightarrow R^+ AlCl_4^-$ without being certain whether (a) or (b) obtains. The differentiation is not important for many considerations.

The existence of complexes between Friedel-Crafts catalysts and hydrocarbons has also been studied by examining the absorption spectra of triphenyl methyl chloride in the presence of stannic chloride (Hantzsch[66]) and in the presence of $HgCl_2$ (Bentley and Evans[8]). In the latter instance the results were regarded as demonstrating the presence of carbonium ions. In other research the presence of ion pairs was considered. Eley[38] measured the solubility of aluminum halides in benzene. McCaulay, Shoemaker and Lien[116] established the acid-base nature of the hydrogen fluoride-boron trifluoride extraction of the xylene isomers. Evidence for ion pair formation has also been provided by others[7].

Catalytic consideration should consider the spatial arrangement. The relatively large size of anion and small cation should be considered in any atomistic mechanism picture. Emphasizing such geometric considerations, Turkevich and Smith[194] proposed a catalytic mechanism in which hydrogen is interchanged or switched between carbon atoms located 1 and 3 in a hydrocarbon and adjacent oxygen ions of oxyacids.

One of the features to be emphasized in acid catalysis is the very strong nature of effective acid catalysts. The basis is the ability to transfer a proton to a base. Numerous attempts have been made to relate quantitatively activity of acid catalysts to a fundamental function such as Hammett Ho function with a fair but not excellent correlation. On a qualitative basis, the principle set forth by Pauling[142] serves to point out the acid strengths. For relative bond strength S = Valence/coordination number, the bond strength in H_2SO_4 between sulfur and oxygen is $1\frac{1}{2}$ which leaves an oxygen-hydrogen binding of $\frac{1}{2}$. The bond strength in $HAlCl_4$ between aluminum and chlorine is $\frac{3}{4}$, and therefore between chlorine and H is $\frac{1}{4}$. This loose binding of the proton corresponds to a strong acidity. It is evident on this basis, at least qualitatively, that $HAlCl_4$, $HAl(OSi^{\equiv})_4$, etc., are very strong acids; that is, they possess a small affinity for H^+.

Likewise, a detailed consideration of the critical effect of acid concentration (or rather concentration of water) in phosphoric and sulfuric acid, and the effect of nitrogen bases in inactivating such acids, as well as oxide and Friedel-Crafts catalysts, points out the necessity for a high acid strength. The reactivity of sulfuric acid and phosphoric acid is known to be highest at about 98 and 107 per cent, respectively, with a sharp increase in activity as acid concentrations increase to these values. Hammett[62] and also Oblad, Hindin and Mills[136] have pointed out with numerical examples that *small* amounts of water can very markedly decrease the effective strong acid concentration. Similarly, small amounts of nitrogen compounds can inactivate acid catalysts used in polymerization. As discussed there, while a large number of acid molecules are present, all equally capable of catalytic activity, only a few are active at any given time. This behavior has a significance to solid acid catalysts. There, where interaction of adjacent sites occurs, inactivation by a small amount of poison is not proof that only a few sites exist which are capable of activity. The solid surface may be similar catalytically to a liquid acid. On the other hand, certainly in other instances real heterogeneity of acidic sites exists in solid acid catalysts.

Application of Polymerization

The field of applied polymerization of unsaturated compounds is tremendously large and embraces the polymerization of acetylenes, diolefins and aliphatic as well as cyclic olefins, and of non-hydrocarbons. Light oils and gasolines, lubricating oils and viscosity index improvers, rubbers and elastomers, plastics, plasticizers, drying oils, paint bases, and synthetic fibers are just a few of the innumerable products that can be produced by polymerization processes. These polymers can be best grouped into low molecular polymers up to an average molecular weight of about 250, polymers of intermediate molecular weight, and polymers of large molecular size varying from an average molecular weight of about 1000 up to several hundred thousand. Within the scope of this chapter only the first two types of polymers will be considered. These find predominant application in the petroleum industry and the processes discussed in the following pages are therefore largely based on processing refinery olefins and making such products as high octane number gasolines and lubricating oils. Methods for the production of low molecular weight polymers and the nature of these polymers will be described first, followed by a discussion of polymers of intermediate molecular weight.

Low Molecular Weight Polymers

The polymerization of gaseous olefins into dimers, trimers, and higher polymers has been studied intensively during the twentieth century, particularly since the late 1920's. While originally most of the work was concerned with thermal polymerization, recent publications deal almost exclusively with catalytic methods.

Catalysts used in polymerization are predominantly acid catalysts. The most common ones are sulfuric and phosphoric acids and phosphates[14]. Friedel-Crafts type catalysts such as aluminum chloride, zinc chloride, titanium chloride, boron trifluoride and hydrogen fluoride, activated clays and synthetic silica-aluminas are also occasionally used.

Many modifications have been proposed and offer advantages in specific cases and for specific conditions. Metal and metal-containing catalysts with and without an additional acid function are occasionally used, particularly in the polymerization of acetylenes, diolefins and ethylene. Table 5 gives a partial list of light olefin polymerization catalysts with

TABLE 5. CATALYSTS FOR THE POLYMERIZATION OF LIGHT OLEFINS

Mineral	Catalyst	Ref.
Acids	Sulfuric acid	114, 115
	Solidified sulfuric acid	26
	Alkane sulfonic acid	162
	Phosphoric acid	84, 87, 88, 92, 107
	Solid phosphoric acid (kieselguhr)	35, 37, 92
	Copper pyrophosphate	195
	Phosphorus pentoxide in trialkylphosphate	98
	Boron phosphate	102
	Tetraborohypophosphoric acid	94
	Hydrogen fluoride-acid of phosphorus	112
	Hydrogen fluoride-alkali fluoride	141
	Mono (or di-) fluophosphoric acids	18, 19
	Dihydrofluoboric acid	18
	Silicontetrafluoride	53
Friedel-Crafts Type	Friedel-Crafts catalysts	10, 156, 157
	Aluminum chloride on alumina or bauxite	71, 165
	Titanium chloride-mineral acid	178
	Zinc chloride	119, 157
	Boron trifluoride	23
	Boron trifluoride + mineral acid	44, 46, 143
	Boron trifluoride-ether	180
Clays and Other Oxide Systems	Fuller's earth	57, 119
	Activated clay	21, 79, 80, 81
	Bauxite	68
	Silica-alumina	57
Metals, Metal Salts and Supports	Nickel oxide on SiO_2-Al_2O_3	70, 126
	Molybdena-phosphoric acid-silica gel	126
	Nickel on diatomaceous earth	97
	Nickel on silica gel	149
	Cobalt on charcoal	24
	Copper chloride	58
	Copper acetylide	11
	Copper sulfide	199
	Nickel cyanide	163
	Palladium oxide on silica-alumina	33

references to their use and manufacture. Applications of many of these catalysts will be discussed on the following pages.

Commercial Polymerization Processes in the Petroleum Industry[28]. Polymerization of light hydrocarbons may serve either of two purposes, viz., (1) the removal of undesirable diolefins from gasolines by selective polymerization to higher boiling and easily separable hydrocarbons, and (2) the production of normally liquid hydrocarbons boiling in the gasoline boiling range from normally gaseous hydrocarbons. This may be accomplished by homopolymerization or selective polymerization of a single specific olefin, by hetero or non-selective polymerization of different olefins or by conjunct polymerization which results in the formation not only of higher molecular weight olefins but also of saturated hydrocarbons.

Removal of Gum-Forming Compounds. Substances in gasolines which oxidize in storage, in contact with air, or upon exposure to light, forming high boiling compounds detrimental to motor performance, have been identified as aliphatic and cyclic diolefins and as mono- or diolefins attached to the benzene ring. Mild catalytic treatment which results in a selective polymerization of these diolefins and does not cause reaction of mono-olefins is practiced to convert gum formers and to remove them as polymers by distillation. The Gray process[21] employs a clay, such as Fuller's earth, as catalyst. Gasoline, either in liquid or vapor state, is passed over the catalyst at 140 to 240°C and atmospheric pressure or elevated pressures up to 400 psi. Treating rates of 4 bbl gasoline/ton clay/hr are employed and a catalyst life of 5000 to 6000 bbl/ton is obtained. Spent catalyst can be regenerated by burning with air. The polymerization product may amount to as much as 5 per cent of the gasoline. A modification of the Gray process, the Osterstrom process[21], operates at higher temperatures (290 to 330°C) and pressures (1000 psi) and realizes a catalyst life of up to 72,000 bbl/ton.

Refining of gasolines with dilute sulfuric acid[127] effects considerable improvement in the gum stability of gasolines with small hydrocarbon losses in comparison with those suffered when using concentrated acid. Sulfuric acid is also used in the Stratford process[182] for gum removal, in which the distillate is countercurrently contacted with the acid and passed to a battery of centrifuges which separate acid and hydrocarbon phases. Contact times of the order of one second are employed.

Olefin Polymerization to Gasoline Constituents with Sulfuric Acid Catalyst. Shell Development Company has developed a process for the polymerization of butenes to octenes and dodecenes, and hydrogenation of the octenes to octanes. This process found large-scale application in the production of aviation gasoline components during World War II. Two separate processing schemes are in existence, viz., the "cold acid process" and the "hot acid process".

The cold acid process selectively polymerizes isobutene. A butane-butene (B-B) refinery fraction is countercurrently reacted in two stages with acid of 60 to 70 per cent concentration at 20 to 35°C and at a pressure sufficient to maintain liquid phase operation[114, 120]. In the second stage freshly regenerated acid contacts hydrocarbons from the first stage. Intermediate acid contacts fresh hydrocarbons in the first stage. About 90 per cent of the isobutene present is selectively absorbed. The acid containing absorbed isobutene is passed to a reactor, consisting of a coil, where it is heated to 100°C. The reaction is complete in about one minute. The acid is then separated from the reaction product, which consists of 75 to 80 per cent dimer and 20 to 25 per cent trimer. A processing flow sheet is given in Figure 5.

The hot acid process[114, 120] is applicable to normal as well as isobutene. The hydrocarbons are contacted at 75 to 100°C with acid of 63 to 72 per cent concentration. The higher acid concentration is used at the lower temperature and vice versa. Normal butenes as well as isobutene are absorbed and at once polymerized in the same reactor. The higher molecular weight olefins formed are reabsorbed in the hydrocarbon phase, minimizing further polymerization. Codimers and interpolymers are formed. To promote the cross polymerization of olefins, the more reactive isobutene is kept in low concentration by recycling a stream of hydrocarbon-acid emulsion having a low isobutene content. At a contact time of 10 to 15 minutes, 80 to 90 per cent of the C_4 olefins are converted to polymers containing 90 to 95 per cent octenes.

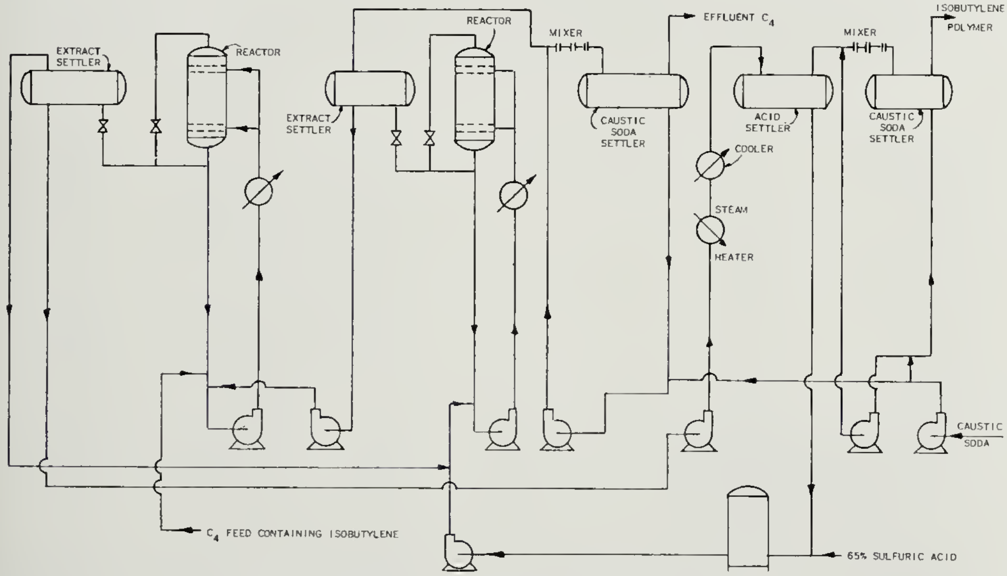


Figure 5. Shell cold-acid polymerization process.

Conversion, yields and polymer composition for the processing of a B-B stream by cold and hot acid methods are shown in Table 6.

Olefin Polymerization to Gasoline Constituents with Phosphoric Acid Catalysts. The great majority of all commercial polymerization units in the petroleum industry utilize phosphoric acid[123] as a catalyst. Ipatieff[84] and others have carried out much of the early development work on phosphoric acid catalysts. Important commercial catalysts currently used are liquid phosphoric acid and solid phosphoric acid-kieselguhr mixtures.

A film of *liquid phosphoric acid* on an inert nonporous carrier, such as quartz, is used in the process developed by Standard Oil Co. of California[75, 107]. The catalyst is prepared in place in the reactor by soaking finely crushed quartz (28 to 35 mesh) with orthophosphoric acid of 70 to 85 per cent concentration. The reactor is drained and the residual film of acid on the catalyst, amounting to three to five pounds of acid per cubic foot, is concentrated by contact with hot feed. Advantages of this process are the simplicity of the reactor design, ease of regeneration, and the high mechanical strength of the catalyst which shows no softening or deterioration. Accidental water admission to the catalyst causes only a temporary activity decline. Extreme ranges of temperature, pressure, water content and feed composition can be used. Catalyst regeneration is carried out by washing the catalyst with cold and hot water, drying the quartz and recoating it with acid. The whole procedure requires less than 24 hours. A catalyst life of about 140 gallons of polymer per pound of 75 per cent phosphoric acid is normally obtained between regenerations. Ammonia and amines poison the catalyst and must, therefore, be carefully removed from the feed, as must sulfur compounds, to avoid high sulfur gasolines.

TABLE 6. POLYMERIZATION OF BUTENES WITH SULFURIC ACID (65% conc.)

	Temperature (°C)		
	30–35	80	90
Feed composition, %			
isobutene	18.5	18.5	9.1
n-butene	28.0	28.0	20.6
butanes	53.5	53.5	70.3
Products, %			
isobutene	2.4	0	0
n-butene	26.6	15.1	11.4
butanes	53.5	53.5	70.3
polymer	17.5	31.4	18.3
Conversion			
isobutene polymerized, %	87	100	100
n-butene polymerized, %	5	46.0	44.5
Total olefin polymerized, %	37.5	67.5	61.5
Composition of polymer			
octenes, %	75	88	92
sulfur, %	0.01	0.03	0.06
Octane No. of hydrogenated octenes	100	99.2	98.8

The feed to the unit may consist of gas from a thermal or catalytic cracking unit or may be a condensed liquid C_3-C_4 cut. The exothermic heat of reaction is controlled by a cold liquid feed quench. The reaction product is passed through a knockout drum packed with limestone to remove traces of entrained acid, and is then stabilized.

The character and properties of the polymer product are affected little by variation of reaction conditions in the normal operating range of 150 to 205°C and 200 to 500 psig. The octane number is virtually constant and the boiling range shows minor variations. Increased temperature and pressure result in a lower boiling polymer. Polymer from propene is higher boiling than polymer from butene. The average molecular weight of the polymer decreases as the catalyst activity declines. Data on a typical polymer from a C_3-C_4 cut are given in Table 7.

The effect of process variables on operation has been well studied for this process[107] but since it is largely applicable to other processes employing phosphoric acid catalysts, it will be briefly discussed. For propene, *n*-butene and mixtures thereof, the dependence of olefin conversion on feed rate can be expressed by the empirical equation:

TABLE 7. POLYMER FROM A C_3-C_4 OLEFINIC FEED[107]

Liquid Phosphoric Acid Film

Gravity, °API	62.9
Reid vapor pressure, psi	7.3
Sulfur, %	0.01
F-1 Clear	98.0
F-2 Clear	84.0
In. B.P., °F	97
10%	162
30	226
50	248
70	280
90	359
End point	392

$$\int_0^c \frac{(1 + Bc)^2\, dc}{(1 - c)^2 + 0.3c(1 - c)} = \frac{k}{S} \qquad (1)$$

where c = fractional conversion of monomer, moles/mole

S = space rate in gas volumes at reaction temperature and pressure per volume of catalyst voids per hour (42% voids)

k = Specific reaction constants, hr^{-1}

B = fractional increase in the number of moles per unit mass for complete reaction of monomer, i.e.

$$B = Nm\left(\frac{Mm}{Mp} - 1\right) \qquad (2)$$

where Nm = mole fraction monomer in feed
Mm = molecular weight of monomer
Mp = molecular weight of polymer

The specific reaction constant k is a function of temperature, composition of feed, acid concentration, particle size of quartz, and its value must be determined in each case. The effect of these variables on rate constants is known for a wide range of reaction conditions. Equation (1) is not valid for feeds containing isobutene.

Effect of Feed Composition. Of the C_3-C_4 olefins, propene reacts most slowly, n-butene twice as fast, and isobutene much faster than either. The rate of reaction of mixtures of n-butene and propene is a linear function of the n-butene content. If isobutene is present in mixtures, it accelerates the rate, especially in the low conversion region. This is shown in Figure 6. The effect of isobutene is not a linear function of the initial isobutene content.

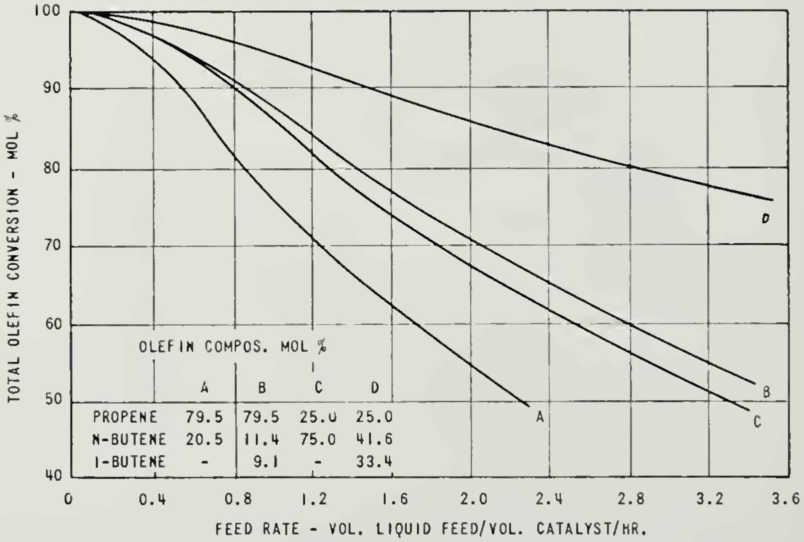


Figure 6. Effect of isobutene on reaction rate[107].

Effect of Acid Concentration. The rate of olefin polymerization is a sensitive function of the acid concentration. The acid should contain less water than orthophosphoric acid. Expressing acid concentration in terms of the water content on a per cent H_3PO_4 scale and speaking of mixtures of ortho-, pyro- and metaphosphoric acid, the effect of acid concentration in the range 97 to 115 per cent H_3PO_4 (pyrophosphoric acid = 110 per cent) is given in Figure 7. The reaction rate increases rapidly in the region 100 to 108 per cent concentration. Acid of any particular concentration has an equilibrium vapor pressure of water. It is necessary to introduce sufficient water in the reactor feed so that the partial pressure of water in the reactor

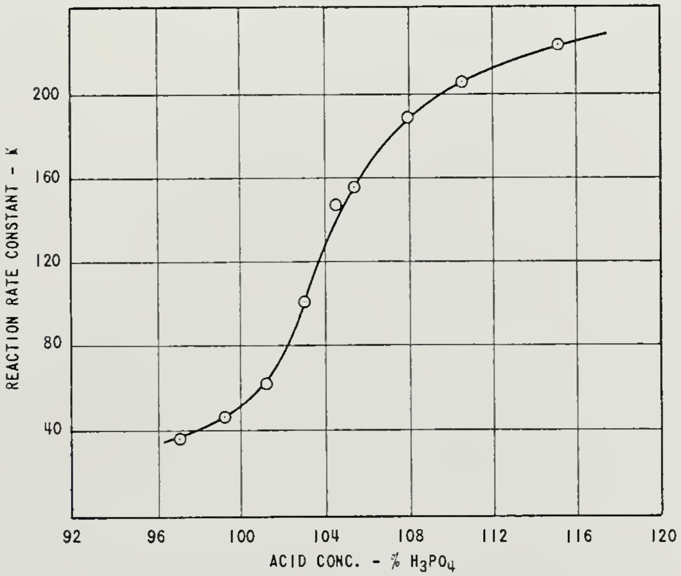


Figure 7. Effect of acid concentration on catalyst activity[107].

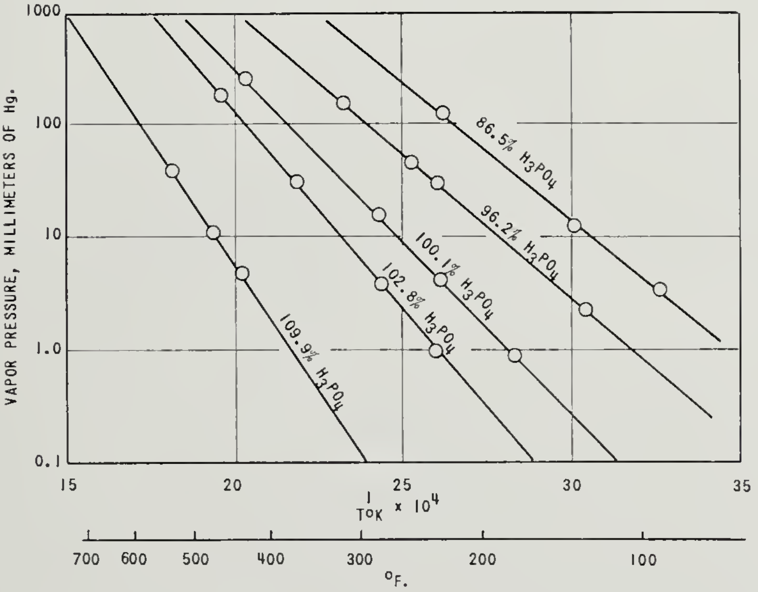


Figure 8. Equilibrium vapor pressure of water over phosphoric acid[107].

is equal to the vapor pressure of the acid. The vapor pressures of several phosphoric acid concentrations are shown in Figure 8. While a very high acid concentration may give maximum activity, the rate of activity decline is higher at these concentrations. Phosphoric acid of 106 per cent concentration gives a satisfactory catalyst life.

More recently, Terres[189] has stated that hypophosphoric acid ($H_4P_2O_6$) is a more active catalyst for propylene polymerization than orthophosphoric acid.

Effect of Pressure. The feed rate necessary to obtain a fixed conversion is directly proportional to the reactor pressure. If the space rate is to be increased at higher pressure, the water content of the feed must be reduced in order to maintain a fixed pressure of water in the reactor.

Effect of Temperature. The temperature coefficient is not large and the reaction rate for propene polymerization about doubles every 39°C. Catalyst activity declines rapidly above 205°C.

Particle Size. Since the area of nonporous spherical particles is proportional to the reciprocal of the diameter, the use of very small particles would be desirable, except for pressure drop considerations.

Most of the considerations developed for the phosphoric acid film system also apply to the most commonly used polymerization process, which was developed by Universal Oil Products Co.[35, 37, 92, 120, 173, 206] (U.O.P.). This process employs a fixed bed of *solid phosphoric acid catalyst* prepared by mixing an acid of phosphorus with diatomaceous earth to form composites which are calcined at 180 to 300°C. The dried composites are crushed and screened to particles of 2 to 10 mm diameter. The catalyst can also be produced by extrusion and calcination. The acids of phosphorus used are those in which P has a valence of 5. The physical strength of the catalysts can be improved by calcination at 300 to 500°C, subsequent steaming at 200 to 300°C, and final drying at 200 to 300°C.

Fresh catalyst exhibits maximum activity and requires the lowest operating temperature. As it gets deactivated by carbonization, the temperature has to be raised, causing in turn more coke lay-down. Water must be present in the feed to prevent catalyst dehydration and deactivation. It is preferable to have a slightly underhydrated rather than an overhydrated catalyst. Underhydration favors coke formation; overhydration results in catalyst softening and eventual plugging of the bed. Free water will leach out acid and cause corrosion problems. The catalyst can be regenerated by burning at 343 to 510°C and regulating the oxygen concentration to control the temperature. The catalyst is rehydrated by steaming at 260°C.

The polymerization of propene and butenes can be accomplished at different *conditions of temperature and pressure*. Non-selective polymerization gives maximum polymer yields and almost complete olefin conversion. Selective polymerization of butenes yields largely isooctenes. Isobutene is easiest to convert, followed by *n*-butene and propene. However, it is easier to polymerize propene in combination with butenes, than in their absence. C_5 olefins tend to form coke and are therefore excluded from commercial feed stocks. Catalyst poisons, such as sulfur compounds, ammonia, amines, oxygen, and butadiene, are removed from the feed by washing or treatment.

The polymerization reaction is exothermic, liberating 670 Btu for a mole of C_3 and 450 Btu for C_4 olefin. The heat of reaction is controlled by recycling a portion of the unconverted gas. Temperatures of 150 to 245°C (300 to 475°F) are employed, with the lower temperatures for C_4 and the higher for C_3 polymerization. High temperature and low pressure both tend to increase coke deposition. Conversion increases with pressure. At relatively high pressure enough hydrocarbon dense phase is present to exert a washing effect on the catalyst and dissolve high molecular weight polymers and tars which otherwise coat the catalyst. The combination of high pressure and low temperature gives clean catalyst surfaces and permits non-regenerative operation of sufficient length to make discarding of spent catalyst more economical than regeneration.

Three operating schemes have been evolved and are compared in Table 8: (1) the low pressure regenerative method used in early units employs a series of reaction chambers operated at 205 to 245°C (400 to 475°F) and 250 psig. Occasional catalyst regeneration is practiced; (2) the newer high pressure chamber process permits yields of 75 to 125 gallons of polymer per pound of catalyst and does not need regeneration facilities. It is operated at 190 to 232°C (375 to 450°F) and 500 to 700 psig. The catalyst is arranged in superimposed beds and the temperature is controlled by injecting cool recycle gas between the beds; (3) the high pressure reactor process (Figure 9) gives yields of 150 to 200 gal/lb of catalyst. Temperatures of 205 to 213°C (400 to 415°F) are employed at 900 psig. The catalyst is contained in a multiplicity of small tubes surrounded by a circulating heat medium. The tubes are 2 to 5 inches in diameter. Better temperature control and higher pressure result in better conversion and in lower boiling polymer (Table 8).

Operation may be *non-selective* or *selective*. Non-selective operation is at 191 to 246°C (375 to 475°F) and the product is a mixed polymer of 95 per cent liquid monoolefins in the gasoline range. At optimum conditions 95 per cent butenes and 90 to 92 per cent propene are converted. Table 9 gives the composition and properties of five fractions of a non-selective polymer gasoline. The diolefin content disappears with increasing boiling point, the monoolefin content increases, and paraffin and naphthene hydrocarbons decrease. Small amounts of aromatics appear in the higher fractions.

Under proper conditions isobutene can be selectively polymerized to form dimers[82]. The term "selective polymerization" usually applies to the polymerization of normal and isobutenes. In the range 149 to 177°C (300 to 350°F), isobutene only is polymerized at the lower temperature, while *n*-butene enters the reaction at higher temperatures. The octane number

TABLE 8. TYPICAL OPERATING CONDITIONS FOR THREE TYPES OF POLYMERIZATION UNITS PROCESSING C_3-C_4 MIXTURE

	Chamber Type		
	Low Press. Regeneration	High Press.	Reactor Type
Pressure (psig)	250	500	900
Catalyst temp., °F			
Inlet	400	375	400
Outlet	475	450	415
Olefin contents, %			
Fresh feed	35	35	35
Combined feed	20	20	35
Spent gas	10	5–7	4
Olefin conversion, %	80	85–90	92
Catalyst life, gal./lb catalyst	50	75–125	150–200

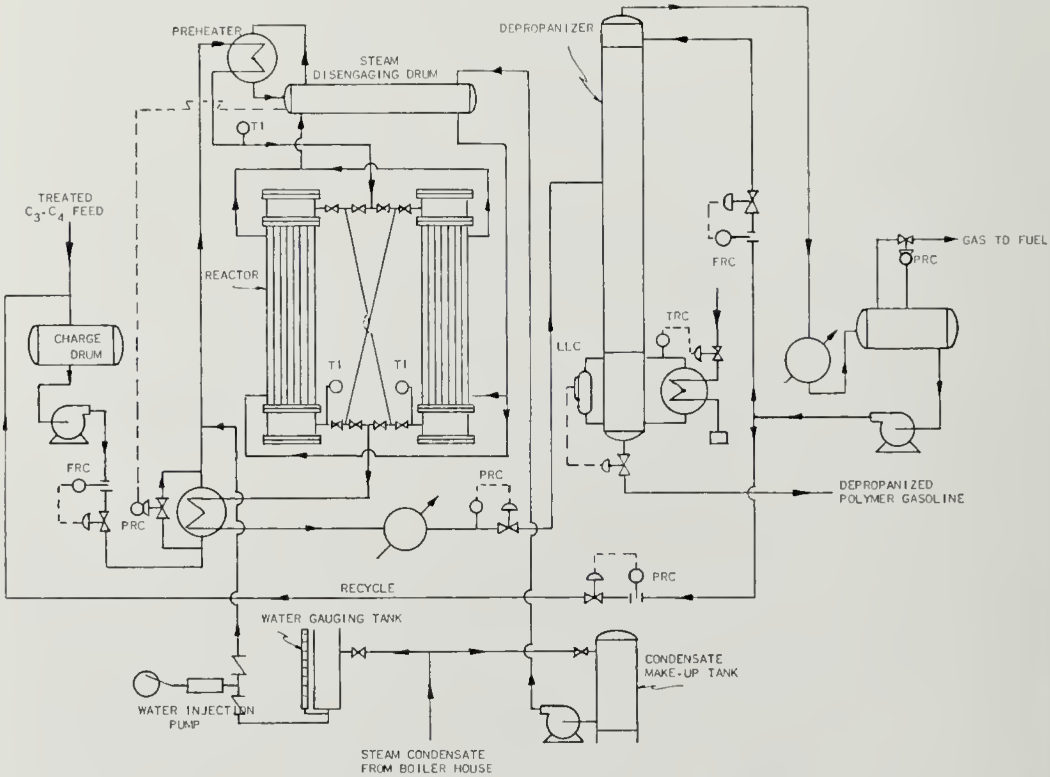


Figure 9. High pressure reactor process.

of the hydrogenated polymer decreases with increasing temperature. Reaction conditions control the relative amounts of dimer and trimer formed. At 165 to 177°C (330 to 350°F) and 900 psig, about 90 per cent dimer and 10 per cent trimer are produced. Table 10 presents a comparison of products from selective and non-selective polymerization.

Table 9. Analysis of a Typical Non-Selective Polymer

Component	Liquid Volume (%)	Cut No.
iC_4	Trace	
nC_4H_8	0.4	
C_5H_{10}	5.8	
C_5	2.6	1
115–140°F	0.6	2
140–250°F	64.2	3
250–338°F	16.3	4
Bottoms	10.1	5

Cut No.	1	2	3	4	5
Molecular weight	72	80	95	120	142
Density	0.6545	0.6683	0.7140	0.7540	0.7948
Bromine No.	169	181	157	127	110
Refractive index	1.37758	1.38874	1.41117	1.42997	1.44786
Dispersion	82.0	85.0	88.9	90.7	94.1
Diene content No.	0.7	0.7			
% Aromatics	0	0	0.5	1.1	2.2
% Olefins	76.2	90.6	93.2	95.4	97.6
% Paraffins and naphthenes	32.8	9.4	6.3	3.5	0.2

Average of C_6 Fraction (cuts No. 2–5 inclusive)

	Per Cent
Aromatics	0.8
Olefins	94.1
Paraffins and naphthenes	5.1

The yield of polymer gasoline obtainable depends upon the olefin content of the feed gas, as follows:

Propenes and Butenes in Feed	Polymer Gasoline (gal/1000 cuft)
14.1	2.4
18.0	3.1
21.3	4.2
27.1	5.3
33.3	7.0
41.0	9.2

In non-selective polymerization a C_3-C_4 olefin content of 20 to 25 per cent (based on total feed) is considered practical, since fresh feed olefin content is reduced in the charge stream by the relatively low olefin content of the recycled gas.

Olefin Polymerization to Gasoline Constituents with Coppery Prophosphate

Catalyst. Polymerization of C_3-C_4 olefin fractions over a solid copper pyrophosphate catalyst[120, 173, 179] proceeds much like in the U.O.P. process. The catalyst can be diluted with charcoal in a 1:1 or 2:1 ratio. The charcoal acts as an adsorbent for phosphoric acid released under operating conditions and distributes the acid over a larger portion of the bed. Operating conditions are 900 psig pressure and 177 to 188°C (350 to 370°F) for codimer production from C_4 olefins or 205°C (400°F) for non-selective polymerization. Catalyst life reaches 100 to 150 gallons of polymer per pound. Olefin conversion is at the 85 per cent level. The conversion of olefins increases with increasing catalyst activity and reactor temperature and with decreasing olefin space velocity, total space velocity, and olefin:paraffin ratio of the feed. The catalyst can be regenerated by conventional methods.

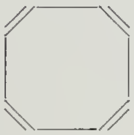
TABLE 10. PROPERTIES OF POLYMER GASOLINE[92]
Solid Phosphoric Acid Catalyst

Type	Non-selective Polymer			Selective Polymer	
	Polymer from C_4 Feed	Polymer from C_3-C_4 Feed	Polymer from C_3 Feed	Polymer	Polymer after Hydrogenation
Specific gravity	0.732	0.708	0.732	0.735	0.717
ASTM distillation					
I.B.P. (°C)	53	41	57	99	99
10	83	63	84	105	105
30	106	86	104	107	107
50	112	110	120	109	109
70	116	122	138	111	110
90	128	176	159	112	112
E.P.	198	206	207	130	128
R.V.P.	2.1	10.0	2.0	2.0	2.0
Sulfur (%)	0.18	0.02	0.05		
ASTM gum mg/100 cc	5	8	9		
Copper dish gum	20	33	35		
Oxygen bomb stability, min., with 0.05% UOP Inh. No. 4	70	70	80		
Copper dish gum	15	12	15		
Oxygen bomb stability, min.	500	450	525		
Molecular weight	108				
Bromine number	144				
F-2 Octane-clear	84.0	83.5	82.2	82.5	94.7
F-2 Octane + 3cc TEL	86.4	86.1	86.0	86.0	106.4
F-1 Octane-clear	97.1	96.0	96.0		

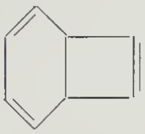
Many modifications of solid phosphoric acid catalysts have been described, particularly in the patent literature. Promoters such as titanium, tin or manganese compounds have been proposed[121, 122]. The addition of a solid diluent consisting of, for instance, adsorbent carbon, impregnated with phosphoric acid[187] helps in preventing agglomeration of particles of the kieselguhr-phosphoric acid catalyst.

Polymerization of Acetylenes, Diolefins and Monoolefins. *Acetylenes and Diolefins.* The polymerization of acetylene to benzene (Berthelot) by either thermal or catalytic reaction over iron or nickel powders is part of classical chemistry. So is the work of Sabatier and Senderens, who polymerized acetylene to cuprene, a mixture of cyclic hydrocarbons, using a copper catalyst. The dimerization of acetylene to monovinylacetylene has been described by a group of Indian workers[58]. Using a catalyst comprising 1000 g of Cu_2Cl_2, 780 g of NH_4Cl, and 1315 cc of water containing a dispersing agent, such as agar-agar, 35 per cent conversion per pass with 75 to 80 per cent yields of monovinylacetylene are obtained at 75°C. The reaction can be accelerated by raising the pressure.

Considerable technological importance attaches to the reactions of acetylene developed by Reppe and his co-workers[163]. Polymerization of acetylene over copper acetylide and nickel cyanide catalysts has been described[11, 63]. Nickel cyanide is prepared from nickel chloride and hydrogen cyanide and is suspended in tetrahydrofurane. The suspension is charged to the reactor together with small amounts of calcium carbide to maintain anhydrous conditions. Reaction with acetylene is carried out at 60 to 70°C, and 250 psi pressure. Cyclo-olefins of eight-, ten- and twelve-membered rings are formed in reasonable yields, with cyclo-octatetraene as the main product. Cyclo-octatetraene is found in three isomeric forms, viz.:



(1)



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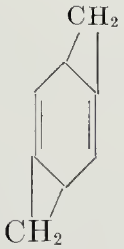

(3)

Polymerization of diolefins to remove gum-forming substances from gasoline has already been discussed (p. 372). Polymerization of isoprene and butadienes to high molecular substances is an important and well covered field, but it is outside the scope of this discussion. While dimerization of 1,3-butadiene to vinylcyclohexene and 1,5-cyclo-octadiene has been investigated by thermal methods[72], this reaction has not been extensively studied with catalysts. Isoprene can be polymerized to low molecular weight polymers using either sulfuric or phosphoric acid catalysts[99]. Dimers and trimers are obtained with the dimer consisting of a mixture of dipentene and an aliphatic dimer, which when hydrogenated gives 2,6-dimethyloctane. Good dimer yields are obtained at 20°C with 48 per cent sulfuric and 70 per cent phosphoric acid, and 20 and 60 min. contact time, respectively. Polymerization of isoprene to a polymer of average molecular weight 270 has been carried out with a catalyst comprising a 35 per cent solution of phosphorus pentoxide in trialkylphosphates at 34°C[98].

Ethylene. Ipatieff, Pines and Schaad[88, 92] have polymerized ethylene over liquid as well as solid phosphoric acid catalysts. Using liquid phosphoric acid of 90 per cent concentration at temperatures in the range 250 to 330°C, and pressures of about 50 kg/m² paraffinic, olefinic, naphthenic and aromatic hydrocarbons are obtained. The yield of isobutane formed increases with temperature and reaches 18.8 wt. per cent of the ethylene reacted at 330°C. Table 11 shows reaction products obtained at various temperatures. The concentration of paraffins is greatest in the lowest boiling fractions, while aromatics appear in fractions boiling above 225°C. No aromatics and only small amounts of paraffins are found in thermal polymers and the catalyst must, therefore, have hydrogen transfer properties. With solid phosphoric acid catalysts, 7 to 8 gallons of liquid hydrocarbons/1000 cu ft ethylene are obtained at 296°C and 520 psi. The product distribution is 13.7 per cent ethylene, 0.7 per cent butene, 11.6 per cent isobutane, 73.7 per cent liquid polymer.

TABLE 11. POLYMERIZATION OF ETHYLENE OVER PHOSPHORIC ACID[88]
50 kg/m²

Boiling Range (°C)	Total Product at Polymerization Temperature of 250°C	280°C	300°C	330°C
(1) Below 110	37	31	42	46[a]
(2) 110–225	26	33	20	14
(3) 225–300	27	23	26	29
(4) Above 300	10	13	12	11

[a] 18.8% of total product is isobutane.

Ethylene polymerization with Friedel-Crafts type catalysts such as aluminum chloride[202] or BF_3-SO_3-HF[87] results in polymers containing up to 50 per cent hydrocarbons boiling in the gasoline range.

Excellent yields of butenes and hexenes have been obtained from ethylene by reaction below 150°C and at 1 to 100 atm. over a cobalt on charcoal catalyst[24, 147]. A conversion of 50 per cent per pass is obtained. The predominantly straight chain polymer has an even number of carbon atoms/mole. The product consists of 75 per cent butenes, 15 per cent hexenes and 10 per cent higher olefins. A catalyst life of better than 165 kg polymer per liter of catalyst is realized. The catalyst is poisoned by carbon monoxide, oxygen, carbonyl sulfide, hydrogen sulfide, and acetylene in the feed. Table 12 gives the composition of butenes and hexenes obtained, while Figures 10 and 11 show the effect of pressure on ethylene dimerization and the influence of feed rate on conversion and production rates. Activity of the catalyst is greatly enhanced by pretreating the coconut charcoal support with nitric acid[146].

Nickel catalysts, supported on diatomaceous earth[97], silica gel[149], and silica-alumina[70, 74a] have also been proposed for the polymerization of ethylene to polymers in the dimer to hexamer range. Dimers and trimers may be obtained from ethylene over a palladium oxide catalyst, supported on silica-alumina gel (containing 1 per cent alumina) at 50°C and 250 psig[33].

Propene. Polymerization of propene with mineral acid catalysts has already been discussed on p. 373 under the heading "Olefin Polymerization to gasoline constituents with Phosphoric Acid Catalysts."

TABLE 12. POLYMERIZATION OF C_2H_4 OVER CO-CHARCOAL CATALYST[24]

50 atm.; 35–40°C

Butene Composition

Feed (g/l/hr)	Avg. Conversion to Polymer (%)	Composition of Butene (Wt. %)	
		1-Butene	2-Butene
72	74	9	91
104	69	6	94
228	58	60	40
360	37	70	30
480	28	54	46

Hexene Composition,%

cis-2-Hexene *cis*-3-Hexene	38
trans-2-Hexene *trans*-3-Hexene	38
1-Hexene	10
trans-3-Methyl-2-pentene	9
2-Ethyl-1-butene	3
cis-3-Methyl-2-pentene	2
3-Methyl-1-pentene	0.2

2,2- and 2,3-dimethylbutenes can be selectively obtained from propene with an aluminum chloride on alumina catalyst at 350°F and 350 psi[71]. Polymers in the C_{12}-C_{24} range are predominant in the reaction over boron trifluoride catalysts activated with hydrogen fluoride[46] or with oxygen containing polar compounds, such as butyl ether, ethyl alcohol, propyl acetate, etc.[23]

Gayer[57] has investigated the activity of clays and silicates for propene polymerization. Dehydrated Floridin is active at 350°C and atmospheric pressure. The catalyst activity can be increased by treatment with hydrogen chloride. Synthetic aluminum silicate is as active as Floridin, but ferric and magnesium silicates and precipitated silica are inactive. Alumina precipitated on silica is the most active of this series of catalysts and its activity and life can be further extended by the addition of traces of chloride (such as 0.3 vol. per cent amyl chloride) to the feed. The polymer produced consists of C_5-C_9 olefins, with the dimer predominating; 90 per cent of the polymer boils in the gasoline range.

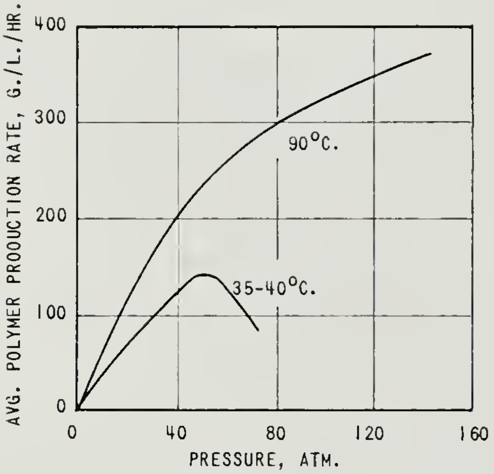

Figure 10. Polymerization of ethylene with cobalt-charcoal catalyst[24].

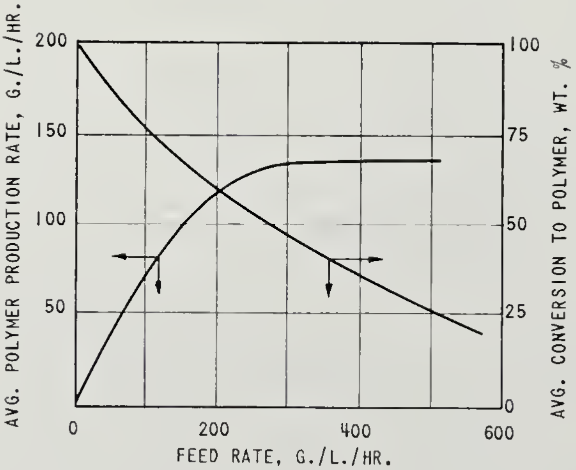

Figure 11. Polymerization of ethylene over cobalt-charcoal catalyst[24].

The use of acid catalysts containing a hydrogenative function has been proposed by Moore and Stewart[126]. Such catalysts may contain 0.25 per cent molybdena and 2 per cent phosphoric acid on silica gel or can be composed of 1 to 10 wt. per cent nickel oxide on alumina containing 5 per cent silica. Propene in a propene-propane mixture is polymerized at 260 to 370°C and about 200 psi in the presence of 300 to 400 cu ft hydrogen/bbl of hydrocarbon charged. The polymer yield, consisting mostly of dimer, is two to three times as great as that obtained without hydrogen.

Butenes. Phosphoric acid and sulfuric acid are the most commonly used catalysts for butene polymerization. Innumerable improvements and modifications have been suggested for the processes which have been discussed on pp. 373–381 under the heading "Olefin Polymerization to Gasoline Constituents with Phosphoric Acid Catlysts." Most of these are concerned with selective polymerization[102,103]. Very pure homogeneous polymers may, for instance, be obtained from isobutene or butene-1 with an alkane sulfonic acid catalyst[162].

Clay, alumina and synthetic alumina-silica frequently are good butene polymerization catalysts. Houdry *et al.*[79, 80, 81] have developed a liquid phase polymerization process operating at 82 to 149°C (180 to 300°F) under about 500 psi pressure using an activated clay as the catalyst. A per pass conversion of 55 to 72 per cent of the butenes charged is reported. Regeneration becomes necessary after 4 to 8 hours on stream. Heinemann, LaLande and McCarter[68, 104] have studied bauxite catalysts and found that their activity increases with increasing bauxite dehydration temperature up to 760°C. By selection of proper operating conditions, such as 205 to 315°C (400 to 600°F) and atmospheric pressure, isobutene can be selectively polymerized in a mixture which also contains the other butenes.

Friedel-Crafts type catalysts can be used to give polymers of isobutene ranging from dimer to molecular weights in excess of 100,000[106]. The catalytic activity of this type of catalyst decreases in the order boron trifluoride, aluminum bromide, titanium chloride, titanium bromide, boron chloride, boron bromide, tin chloride[157]. Paushkin and Topchiev[143] have found that *n*-butene can be polymerized at atmospheric pressure and 50 to 150°C in the presence of molecular compounds of boron trifluoride with phosphoric acid. The individual components alone are inactive under these conditions. Polymers of an average molecular weight of 156 are obtained. Polymerization of isobutene to dimers, trimers and tetramers with boron trifluoride catalyst can be accelerated by adding as little as 0.06 per cent acetic acid vapor to the olefin[44] or by using the catalyst as a complex with ethyl ether[180]. Dihydroxyfluoboric acid is a very interesting copolymerization catalyst[18]. At 0 to 40°C and 50 to 125 psi, 2,3-dimethylpentene is predominantly obtained from isobutene and propene; trimethylpentenes only from 2-butene and isobutene; mixtures of 34 per cent dimethylhexenes and 66 per cent trimethylpentenes from 1-butene and isobutene.

An entirely different catalyst for the dimerization of isobutene has been suggested by Wassermann and Weller[199]. It consists of copper sulfide, part of the surface of which has been activated by conversion to copper sulfate.

Pentenes. Relatively little work has been reported on the polymerization of pentenes. Pentenes, of course, can be blended into gasolines without further processing and are, therefore, of less interest as a polymerization feed stock. Their tendency to lay down coke during polymerization also restricts their usefulness. Ipatieff and Schaad[91, 92] have studied the polymerization of 3-methyl-1-butene and of a mixture of 2-methyl-1-butene and 2-methyl-2-butene over solid phosphoric acid catalyst. Some of their data are contained in Table 13 and show that the pentene polymers consist mainly of branched chain decenes which can be hydrogenated to decanes with an octane number of 94.5. When a liquid phosphoric acid catalyst is used at 60 to 90°C, decenes are again the major product. During polymerization 8 per cent of the 3-methyl-1-butene charged was isomerized to higher boiling pentenes such as 2-methyl-2-butene.

Copolymerization of amylenes with butenes or propene has been investigated. Using sulfuric acid as a catalyst, McAllister has produced isononenes at 70 to 110°C[115]. An octene fraction obtained from copolymerization of isopentene and propene with dihydroxyfluoboric acid[18] consists of 58 per cent 2-methyl-3-ethylpentene and 42 per cent 3,4-dimethylhexene.

TABLE 13. POLYMERIZATION OF C_5 OLEFINS WITH SOLID PHOSPHORIC ACID[92]

	3-Methyl-1-butene			Mixture of 2-Methyl-1-butene and 2-Methyl-2-butene	
Temperature, °C	100	83	84	84	85
Pressure, atm	7.9	7.7	7.7	7.4	7.7
LHSV, V/V/hr	2.3	2.3	3.7	3.7	6.7
Polymer, % of charge	81	65	53	78	70
		n_D^{20}	Br. No.		n_D^{20}
Fractions					
to 148°C	9.1	1.4275	110	11.1	1.4265
148–160°C	67.1	1.4328	104	58.4	1.4343
160–176°C	18.0	1.4380	100	23.9	1.4395
Above 176°C	5.8	1.4490	91	6.4	1.4550
Octane No. of hydrogenated polymer	94.5				94.5

Polymers of Intermediate Molecular Weight

Polymerization of C_2, C_3 and C_4 olefins, as well as copolymerization of these olefins with aliphatic diolefins or cyclic compounds to large molecular liquid and solid compounds, is a well developed industrial art and an enormous volume of work has been published on this subject. The catalysts used for this type of polymerization are either of the free radical chain initiator type, such as organic peroxides, or of the Friedel-Crafts type used at low temperatures. The solid polymers, elastomers, plastics and condensation polymers will not be considered here; this discussion will be limited to the production of hydrocarbons with molecular weights about 250 to 1000. To obtain hydrocarbons in this range from low molecular olefins, Friedel-Crafts type catalysts are employed almost exclusively. The number of modifications of catalysts and promoters, described particularly in the patent literature, is very large, however, and several excellent reviews covering them have appeared over the last fifteen years[161, 167, 190, 211]. Appreciable work has also been done on thermal, non-catalytic polymerization[172].

Relation of Olefin Structure to Product Composition. Sullivan *et al.*[186] have studied the effect of constitution of the charge olefin on

Table 14. Polymerization of Olefins to Lube Oils with $AlCl_3$ at 57°C[186]

Olefin	Yield (Wt. %)	Specific Gravity 60°F	Viscosity S.U.S. at 100°F	Viscosity S.U.S. at 210°F	Viscosity Index
Ethylene	—	0.9465	2769	80	−150
Propene	33.3	0.8579	1083	70	20
Butene-1	46.4	0.8534	1654	92	50
Butene-2	33.3	0.8514	1507	81	21
Isobutene	42.0	—	3706	147	67
Pentene-1	59.8	0.8591	1350	94	82
Pentene-2	38.5	0.8612	1946	93	27
3-Methylbutene-1	50.8	0.8550	3301	108	0
2-Methylbutene-2	34.5	0.8565	1959	89	11
Trimethylethylene	29.3	0.8708	1476	70	−74
Hexene-1	—	0.8534	1155	92	91
Octene-1	—	0.8509	905	88	104
Cetene	85.0	0.8555	1774	201	138
Cyclohexene	—	0.9465	2135	85	−27

the properties of lube oils produced by polymerization with 5 per cent aluminum chloride at 57°C in the presence of a solvent naphtha. The reaction time varied with the olefin used, but was generally about eight hours. The free oil recovered was caustic washed and distilled to remove gasoline and kerosene. Hydrolysis of the aluminum chloride sludge yielded an oil distinctly inferior to the free oil in all respects. The data in Table 14 show the properties of the free oil obtained by polymerization of various olefins in the C_2 to C_{16} range. For normal olefins, the viscosity index (V.I.) improves with increasing length of the chain of the feed olefin. For isoolefins the V.I. becomes poorer with an increasing degree of branching, except in the case of butenes. Cyclohexene yields an oil with physical properties similar to those of highly naphthenic natural oils and with a much lower V.I. than any known natural oil. Better yields are obtained from normal than from isoolefins. Most of the synthetic oils have specific gravities lower than those of natural oils.

In a similar study, Zorn and his co-workers[76] found that only straight chain olefins with a terminal double bond produced satisfactory yields of high V.I. polymers. The yield and viscosity index are both low when the double bond is not in the 1-position or when there is alkyl substitution on a double bond carbon atom. The viscosity, viscosity index, and pour point of the polymer increase and the ease of polymerization decreases as the chain length of the olefin increases. In a homologous series, both the viscosity and V.I. increase with increasing molecular weight of the olefin.

TABLE 15. POLYMERIZATION OF OLEFINS TO LUBE OILS[76]

Olefin	Yield (Wt. %)	Viscosity S.U.S. at 210°F	Viscosity Index	Pour Point (°F)
n-1-Octene	80	98	100	<−22
Methylheptene	20	32	20	<−22
n-4-Octene	5–10	28	−10	<−22
6-Methyl-1-heptene	85–90	290	100	<−22
n-Octa-1-decylene	90	210	140	+15

TABLE 16. PROPERTIES OF SYNTHETIC LUBE OILS[186]

Derivation	Viscosity S.U.S. at 100°F	Pour Point (°F)	Flash Point (°F)	Color NPA	Conradson Carbon (%)	Sligh Oxidation Test, mg sludge/10 g oil
Cracked wax-polymer	850	−20	515	2	0.13	1.8
Cracked wax-polymer	3250	0	615	2.5	0.40	2.8
Natural refined aviation oil	1180	10	490	3.0	0.25	
Natural residual lube oil	3050	20	530	8.0	1.75	

For olefins of the same molecular weight, the viscosity index declines as the number of side chains increases and as cyclization of the carbon chain increases. This is shown in Table 15 for C_8 and higher olefins.

Experiments have been carried out with olefins obtained in the cracking of various feed stocks[186]. The more paraffinic the charge to thermal cracking, the better is the V.I. of the oil prepared by polymerization of the resulting olefins. Wax-bearing stocks are superior and the higher the wax content of the cracking charge, the better is the synthetic lube oil. Stocks containing 70 to 90 per cent wax gave synthetic oils of a V.I. of 100 or better. Properties of oils obtained by polymerization of olefins from the cracking of wax are compared in Table 16 with natural oils. The synthetic lube oils are comparable in behavior to high-grade natural lube oils. The low pour points of the synthetic oils, together with the high V.I., make them outstanding. The synthetic oils are wax free and do not have to be refined. They have little color and can be prepared water-white. After 50 hours of service in a motor, an 85 S.U.S. synthetic oil increased 5.6 true color units to a value of 101, while a Mid-Continent lube oil of the same viscosity went from 163 to 760 color units. The carbon residue of synthetic oils is generally lower than that of highly refined natural oils. When thermal decomposition occurs at high engine temperatures, the synthetic oils decompose and because of their high hydrogen-to-carbon ratio give volatile products without deposition of tar, asphalt or coke. The high quality of the synthetic oils is apparent from the dynamometer tests in Table 17.

Commercial Operations for the Production of Lube Oils from Low Molecular Weight Olefins. The major commercial application of the findings presented in the preceding pages has been in Germany[78, 174] where a considerable portion of the lube oil requirements during World War II was satisfied by synthetic production.

Table 17. Dynamometer Tests of Lube Oils

Oil	Viscosity, S.U.S. at 210°F		Acidity mg KOH/g oil	Combustion Chamber Carbon (g)	Sludge %	
	Original	after 50 hours			Carbon	Asphaltene
Synthetic	108	140	1.0	5.2	0.12	0.003
Natural A[a]	122	195	1.9	15.0	0.93	0.008
Natural B[a]	85	131	1.6	7.9	0.35	0.70

[a] Oils A and B are highly refined commercial oils from different types of crude.

Ethylene was one of the source materials employed. Organic acids, formaldehyde, acetylene, oxygen, carbon monoxide, benzene, and higher hydrocarbons are carefully removed from the ethylene feed. A slurry is made from 5 to 7 per cent aluminum chloride (based on weight of finished lube oil) with light oil from the process. Ethylene is then added to a total reactor pressure of 440 psi. The batch reactor is heated to 70°C, at which temperature the reaction begins; the temperature is permitted to rise to 180 to 210°C and the pressure to 575 psi. The reaction is then quenched and after the temperature has been reduced to 110 to 120°C, ethylene is continuously introduced to maintain a pressure of 882 psi at constant temperature. The reaction is terminated when the reactor is full of liquid. A synthetic oil having a viscosity of 220 S.U.S. at 210°F is obtained. To produce an oil of 105 S.U.S. at 210°F, the polymerization temperature is controlled at 127 to 138°C. A small amount of catalyst complex in the oil is neutralized with methanol and lime. The oil is steam distilled and the aluminum chloride sludge is decomposed with aqueous aluminum chloride solution, yielding a highly unsaturated oil. This raw oil is treated with 6 per cent by weight of aluminum chloride for 3 hours at 120 to 150°C, separated, neutralized and topped to produce a cylinder oil. This process, as practiced in Leuna, Germany, resulted in 74 per cent (based on ethylene) of finished blending stock, 7 per cent of light oil distillate used for slurrying aluminum chloride, and 8 per cent of cylinder oil. The properties of these products are given in Table 18. The synthetic bright stock is blended in equal proportions with a solvent-refined mineral oil to produce an aviation grade lube oil.

TABLE 18. CHARACTERISTICS OF PRODUCTS FROM ETHYLENE POLYMERIZATION AT LEUNA[78]

	Blending Oil	Light Oil	Cylinder Stock
Specific gravity, 20°C	0.852–0.855	0.815	0.857
Viscosity, S.U.S. at 210°F	205–261	33	105
Viscosity index	108–112	>140	100
Pour point, °C	−32 to −35	<−73	−37
Flash point, °C	217–230	121	180
Neutralization No.	0.03–0.06	0	0
Caponification No.	0.08–0.17	0	0.20
Sarbon residue, %	0.03–0.23	0.1	0.20

TABLE 19. EFFECT OF FEED IMPURITIES ON ETHYLENE POLYMERIZATION[212]

Impurity in Feed	Conc. of Impurity (Vol. %)	Yield (1)	Viscosity (99°)	V.I.
None	0	4.0	53.0	89
CO	0.05	4.0	40.9	82
	0.14	3.5	26.8	69
	1.0	2.8	12.2	38
	2.1	2.3	13.6	22
	10.0	2.0	9.1	−11
H_2S	0.2	Polymerization completely inhibited		
CO_2	0.1			
O_2	0.8			

A careful study was made of the effect of impurities in the feed on the quality of the oil produced. No more than 5 volume per cent of nitrogen, methane and ethane can be tolerated in the ethylene. Carbon oxides, molecular oxygen, oxygen-containing compounds and hydrogen sulfide are very harmful in much smaller quantities, as are to a lesser extent monoolefin, diolefins, acetylenes, nitrogen compounds and water. Some of Zorn's data[212] on the effect of impurities on ethylene polymerization are reproduced in Table 19. The aluminum chloride used as a catalyst should not contain more than 2.5 per cent unsublimable residue. Iron-free aluminum chloride yields a high pour point polymer and it is necessary to maintain a level of about 2.5 to 3.5 weight per cent iron in the sublimed aluminum chloride to meet a −34°C (−30°F) to −40°C (−40°F) pour point. The effect of the iron chloride content of the catalyst at different temperatures on yield, viscosity and viscosity index is shown in Table 20, and the effect of unsublimable residue on these properties is shown in Table 21.

Higher olefins, prepared by the thermal cracking of natural wax, gas oil, or wax from the Fischer-Tropsch synthesis, were another source of raw material for commercial lube oil synthesis. A flow diagram for a plant using wax as the starting material is shown in Figure 12. Between 95 and 97 per cent of the unsaturated olefin fraction is polymerized with 6 weight per cent technical aluminum chloride. The temperature is not allowed to exceed 60°C and is controlled by olefin quenching. Ultimate yields obtained on the basis of wax charged for this type of processing are:

TABLE 20. EFFECT OF IRON CHLORIDE CONTENT OF CATALYST ON ETHYLENE POLYMERIZATION[212]

Wt. % Fe in $AlCl_3$	Temp. (°C)	Yield (g)	Viscosity (99°)	V.I.
0.04	120	3850	39.5	92
0.04	110	3200	36.4	92
0.04	100	3270	54.5	94
0.04	90	3700	50.5	94
0.17	110	3700	21.0	62
0.17	100	3900	24.3	74
0.17	90	3770	39.2	74
1.20	100	3250	15.1	64
1.20	90	3820	17.0	62
1.77	110	2975	27.5	54
1.77	90	2680	27.9	59

TABLE 21. EFFECT OF UNSUBLIMABLE RESIDUE IN CATALYST ON ETHYLENE POLYMERIZATION[212]

Unsublimable Residue in $AlCl_3$ (Wt. %)	Yield (Kg)	Viscosity (99°)	V.I.
1.56	34.0	34.9	112.5
2.16	32.2	34.6	111.5
3.80	29.5	42.2	107.5
4.64	28.7	41.6	103.5
5.08	27.0	36.6	97.0

	(%)
Aviation blending stock	45
Cylinder oil	10
Gas oil	15
Fuel gas	28
Loss	2

Operation of the process is essentially the same for natural and for Fischer-Tropsch wax.

Ruhrchemie produced an automotive engine to blend lube oil by poly-

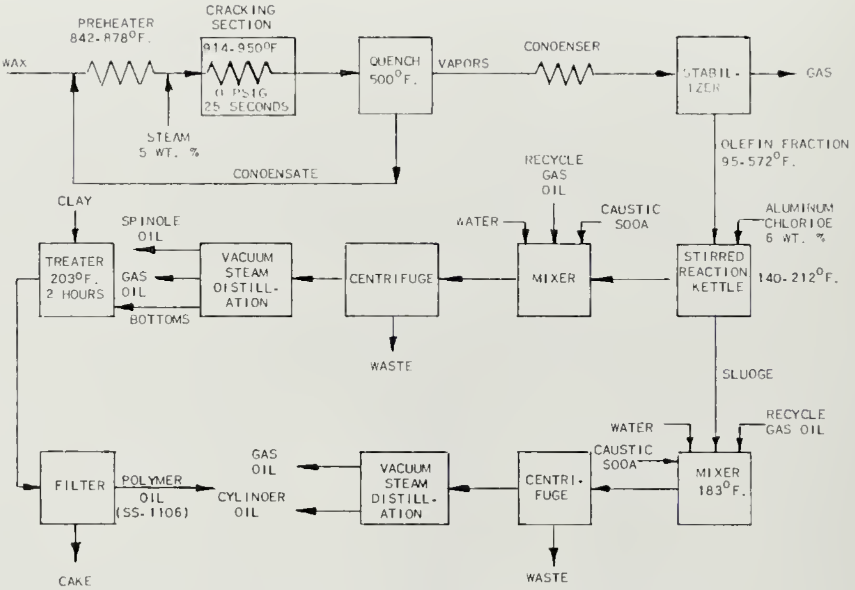

Figure 12. Polymerization of higher olefins (Pölitz).

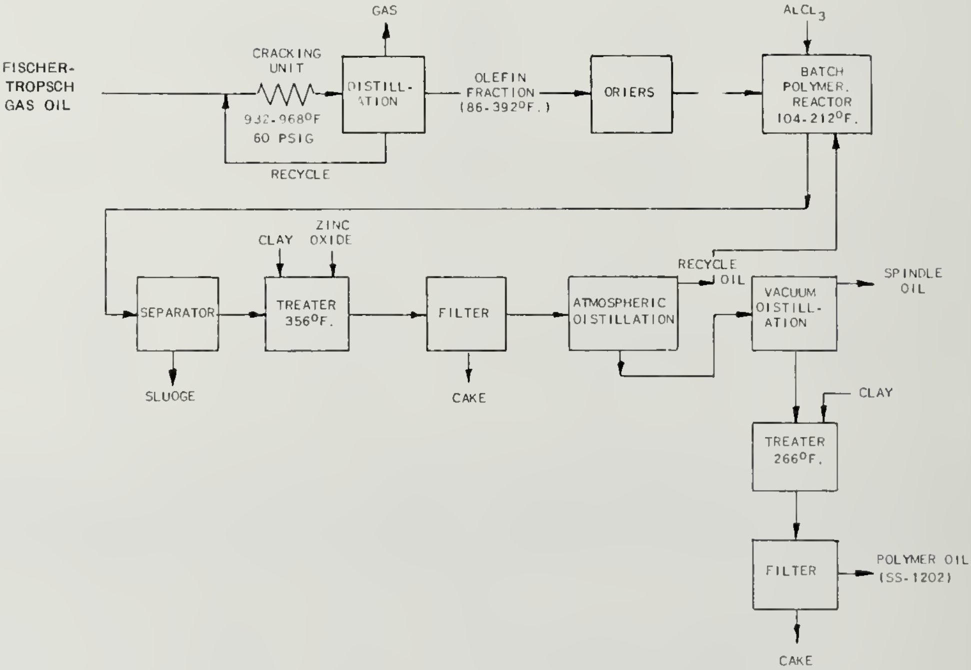

Figure 13. Polymerization of higher olefins (Ruhrchemie-Holten).

merizing olefins from the vapor phase cracking of Fischer-Tropsch gas oil. The processing scheme is shown in Figure 13. The olefins produced are dried to a water content of 0.15 per cent and then reacted with 1.2 to 1.5 weight per cent technical aluminum chloride. The temperature is gradually raised in the course of 14 hours to 100°C. Crude polymer is settled out and treated according to the processing scheme of Figure 13. Vacuum distillation yields a spindle oil and a residual blending oil in a yield of 61 per cent based on olefins charged to polymerization. The properties of these oils are given in Table 22.

Still another commercial process, developed by I. G. Farbenindustrie, produced a mixed polymer. A deasphalted and dewaxed, but not solvent extracted, lube oil distillate is reacted in the presence of an aluminum chloride catalyst with about an equal amount of a synthetic polymer prepared from ethylene or other olefins, for instance, those obtained in the thermal cracking of waxes. An oil of superior quality results in a yield which substantially exceeds that which could be obtained by mixing the olefin polymer and the mineral oil fraction after sufficient solvent extraction to give the mixture the same viscosity index as possessed by the products of mixed polymerization.

TABLE 22. PROPERTIES OF SYNTHETIC OILS FROM CRACKING AND POLYMERIZING FISCHER-TROPSCH GAS OILS[78]

	Spindle Oil	Automotive Blending Oil
Specific gravity, 20°C	0.845	0.855
Viscosity, S.U.S. at 122°F	78	250
Viscosity index	—	~110
Flash point, °C (°F)	193(380)	221(430)
Pour point, °C (°F)	−51(−60)	−46(−50)
Carbon residue, %	0.01	0.04

TABLE 23. COMPARISON OF MIXED POLYMER WITH OTHER LUBE OILS[174]

	Deasphalted and Dewaxed Petroleum Dist.	C_2H_4 Polymer	Mixed Polymer from Equal Parts C_2H_4-Polymer and Distillate
Input, parts by wt.	52.5	47.5[a]	—
Output, parts by wt.	—	—	93.5[b]
Density at 20°C	0.915	0.855	0.870
Viscosity, S.U.S. at 100°F	540	2950	1200
Viscosity, S.U.S. at 210°F	58	205	108
Viscosity index	54	109	108
Flash point, °C (°F)	220(428)	220(428)	220(428)
Pour point, °C (°F)	−17.8(0)	−29.9(−22)	−29.9(−22)
Conradson carbon (%)	1.09	0.08	0.15

[a] 63.5 wts. of C_2H_4 required to produce 47.5 wts. polymer

[b] In addition, 5.1 wts. of low molecular weight material are produced.

In this process, ethylene is first polymerized with aluminum chloride. The resulting reaction product, containing about 5 per cent aluminum chloride, is mixed in an autoclave with an equal weight of mineral oil and agitated for 3 or 4 hours at 99 to 121°C. The reaction occurs primarily between aromatics (and such olefins as are present in the natural oil) and the ethylene polymer. The product is freed of aluminum chloride and neutralized. Oils thus produced have superior ring sticking performance. A comparison of a synthetic oil from this process with an ethylene polymer and a heavily extracted mineral oil raffinate is given in Table 23.

Effect of Modifications of Catalyst and Operating Conditions on the Polymerization of Olefins to Lube Oils. Of the great abundance of proposals employing innumerable modifications of Friedel-Crafts catalysts, only a few shall be mentioned here. Waterman *et al.*[203, 204] studied catalysts such as aluminum chloride, boron trifluoride and aluminum oxide on silica. Temperatures below 20°C were used for all but the last-named catalyst. Excellent viscosity-temperature curves were obtained with hexadecene polymers.

The polymerization of 1-heptene and 1-pentadecene has been carried out with 3 to 5 per cent aluminum chloride at 0 to 20°C without a diluent and at 80°C in a solution of the corresponding paraffin[31]. No sludge is formed at the lower temperature and the products have viscosity indices in the range 108 to 132.

Zinc chloride and ferric chloride as well as aluminum chloride and boron trifluoride have frequently been proposed as catalysts, sometimes in the presence of controlled amounts of water as promoter[2, 6, 177, 184].

Ethylene Polymerization. Nash, Hall and co-workers have made careful studies on the aluminum chloride catalyzed polymerization of ethylene[60, 130, 131], investigating the effect of operating conditions on polymer properties. They found that the yield obtainable was a function of pressure, temperature, contact time and catalyst concentration. They also polymerized ethylene at 150°C, 50 atm. pressure with aluminum chloride containing aluminum turnings, and in the presence of hydrogen, hoping to prevent hydrogen transfer and to obtain higher viscosity index products. The reaction products were quite different from those obtained with the aluminum chloride catalyst alone, but this was so only when metallic aluminum was present with the aluminum chloride, whether or not the reaction was carried out in the presence of hydrogen. The product consists of a solution of aluminum ethyl chloride in a viscous oil. The hydrocarbons have a high viscosity index and the oils are essentially saturated and have a higher hydrogen-to-carbon ratio than oils from low temperature aluminum chloride polymerization. The higher viscosity indices indicate that the individual hydrocarbon species are more paraffinic and contain fewer branched and cyclic compounds. Table 24 presents data on some of these products obtained at three different polymerization temperatures.

The use of aluminum ethyl chloride as catalyst resulted in yields of 67.5 per cent at 250°C. The product had a specific gravity of 0.851, S.U.S. viscosities of 193 and 15.4 at 100 and 210°F, respectively, and a viscosity index of 86. It was shown that this polymerization proceeds in two steps, viz. (1) polymerization of ethylene to long chain olefins by a free radical mechanism, with thermal decomposition of the catalyst providing ethyl radicals as chain initiators, and (2) secondary polymerization with aluminum chloride catalyst to the lube oil range.

A two-step polymerization of ethylene to lube oils has been carried through at the U. S. Bureau of Mines[3]. The first step is thermal and leads to a polymer in the gasoline boiling range, which in turn is catalytically polymerized with aluminum chloride at 25°C to yield oils with a viscosity index range of 50 to 108.

Table 24. Polymerization of Ethylene with $AlCl_3$-Aluminum Turnings

Pressure: 50 atm.

Temp. (°C)	Yield (Wt. %)	Boiling Range	Spec. Grav.	Viscosity, C.S.		V.I.
				100°F	210°F	
100	61	200–250°C/10 mm	0.861	50.2	5.76	35
		250°C/10 mm-280°/2 mm	0.875	247	13.8	30
200	57	200–250°C/10 mm	0.871	34.7	4.86	45
		250°C/10 mm–280°/2 mm	0.885	172.5	12.0	50
300	25	200–250°C/10 mm	0.867	28.9	4.32	35
		250°C/10 mm–280°/2 mm	0.890	217	13.2	40

Propene Polymerization. Early work with propene[139] showed that high pressure is necessary for its polymerization with 10 per cent boron trifluoride as a catalyst at room temperature. Finely divided nickel accelerates the reaction. Some of the many other catalysts proposed are: combinations of an active inorganic halide of the Friedel-Crafts type with a non-hydrocarbon polar compound, such as a nitroparaffin[105]; aluminum chloride in ethyl chloride solution[69] used at −20 to −100°C and carrying out the polymerization in a cycloparaffinic solvent; aluminum bromide, with hydrogen bromide as a promoter[52] and propane as a solvent, operating at −40 to +26°C.

Butene Polymerization. Boron trifluoride, titanium tetrachloride and aluminum chloride have been used for the selective polymerization[128] of isobutene in mixtures containing at least one other olefin at room temperature. Fuming sulfuric acid or halosulfonic acid can be used as isobutene polymerization catalysts at temperatures below −20°C[170]. Evans *et al*,[40] have shown that polymerization of butene with a boron trifluoride catalyst occurs only if a co-catalyst such as acetic acid is present.

Production of V.I. Improvers, Other Lube Oil Additives and Drying Oils. Improvement of the viscosity index of lube oils by the addition of soluble, relatively high molecular weight products is of increasing importance to the petroleum industry. The so-called "viscosity index improvers" are almost exclusively hydrocarbon polymers, varying in average molecular weight from below 1000 to about 30,000 and more. Production of this type of oil-soluble polymer is therefore a borderline field as far as consideration in this chapter is concerned, but will be treated briefly as an adjunct to the synthesis of lube oils.

The effect of the addition of varying amounts of a polyisobutene on the viscosity and viscosity index of lube oils from Coastal or Pennsylvania crude was shown as early as 1934[140]. Both viscosity and V.I. are functions of the polyisobutene concentration and oils of low initial V.I. are most sensitive to improvement. Pour, flash, fire points and color, Conradson carbon and acidity of the oil are not markedly changed by the addition. The V.I. of a Coastal crude lube oil, which is 26, increases to values of 51, 80, 99 and 111 upon addition of 0.5, 1.5, 3.0 and 5.0 weight per cent of polyisobutene. The same amounts of polymer added to a Pennsylvania lube oil raise the V.I. from 100 to 106, 119, 126 and 128.

A detailed study of the production and efficiency of propene and butene polymers as V.I. improvers has been published by Fontana *et al*[51]. The polymers are obtained, employing a hydrogen bromide promoted aluminum bromide catalyst either by a "semibatch" method, wherein the reaction is initiated by simultaneously feeding the olefin-catalyst solution and promoter over a time interval, after which the olefin addition is continued without adding more catalyst until the optimum molecular weight polymer is obtained, or by a "semicontinuous" polymerization of propene, in which a minor portion of the olefin is first polymerized in a continuous stage, after which the reaction is completed in a batch stage. Similar products can also be obtained in a multistage continuous process; each stage is a continuous reactor.

In studying the polymerization of propene and of butene-1 with aluminum bromide catalysts, it was found that promotion of the reaction with hydrogen bromide results in polymers of much higher viscosity than obtained without a promoter. This is particularly pronounced at temperatures in the range of 0 to −40°C. Figure 14 illustrates this effect. An investigation of other process variables shows that while the product is not very sensitive to changes in the oil-to-catalyst ratio, more viscous polymers are obtained at a promoter concentration of 0.1 than at 0.05 per cent and an optimum V.I. is reached at a 1.5 mole ratio of hydrogen bromide/aluminum bromide. Lowering the feed ratios causes viscosity increases. The effect of blending propene polymers of different viscosity into two lube oils is shown in Table 25.

Better V.I. improvers can be obtained from higher 1-olefins. Since direct viscosity determination on these polymers is difficult, they are evaluated on the basis of their thickening power (*TP*), defined as:

$$TP_{210^\circ\text{F}} = \frac{100}{\text{Wt.\% polymer in blend}} \log_{10} \frac{\text{Viscos. 210°F of blend}}{\text{Viscos. 210°F of base oil}}$$

The effect of polymerization temperature on the thickening power of butene-1 polymers obtained with promoted aluminum bromide catalyst is shown in Figure 15. An optimum promoter-to-catalyst mole ratio is reached at about 0.3 and an optimum olefin-to-catalyst mole ratio at about 50. The presence of butene-2, isobutene and butadiene impurities in butene-1 lowers the thickening power of the polymer.

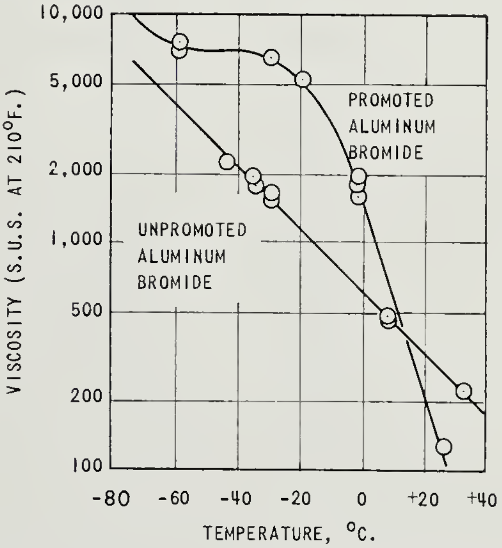

Figure 14. Viscosities of polypropylenes obtained with promoted and unpromoted aluminum bromide[51].

Copolymers of diisobutene and butadiene can be used as V.I. improvers[56]. The polymerization is carried out with aluminum chloride in alkyl chloride solution at −40°C. Liquid refrigerant, such as propane, is added directly to the reaction mixture. V.I. improvers are also obtained by polymerizing a polyolefin of 6–14 carbon atoms, such as 1,3-pentadiene, diisobutene, etc., cyclizing the polymer and finally treating with a halide of phosphorus[74]. A Friedel-Crafts type catalyst is used for the polymerization, tin tetrachloride for the cyclization, and phosphorus trichloride in carbon tetrachloride for final treatment.

Table 25. Blending Properties of Various Polypropylenes in Light Oils[51]

Polymer, Wt. %	Viscosity		Viscosity Index
	SUS at 100°F	SUS at 210°F	
0[a]	113.2	40.85	114
5.00	150.2	44.79	127
15.00	260.4	55.10	131
22.00	393.2	66.51	130
30.00	629.7	85.68	127
100	67,200	1766	115
0[a]	113.2	40.85	114
10.00	168.2	45.66	119
22.22	298.1	54.56	114
28.05	411.2	61.07	109
35.00	613.0	71.54	103
45.00	1126.4	95.43	98
100	237,000	1635	77
0[b]	150.2	40.92	15
5.00	204.3	45.31	74
14.70	377.5	57.06	99
22.00	610.3	72.61	107
23.63	627.7	76.67	107
100	67,200	1766	115
0[b]	150.2	40.88	16
10.00	243.4	46.63	61
25.00	560.9	61.12	69
35.00	1033.0	79.04	67
45.00	2039.7	111.1	67
100	237,000	1635	77

[a] Rodessa neutral base stock.
[b] Light coastal oil.

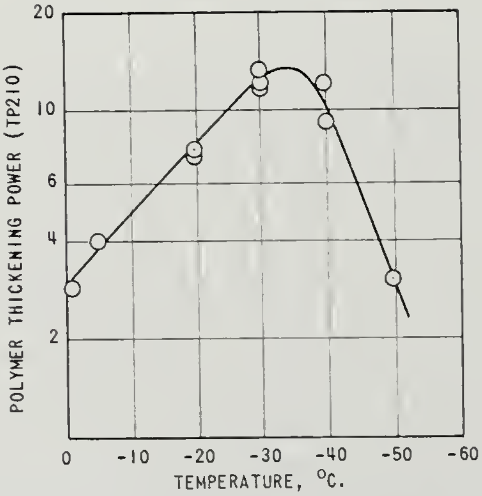

Figure 15. Effect of reaction temperature on molecular weight of 1-polybutene[51].

Waxy ethylene polymers of low molecular weight can find use as lube oil additives[207]. They are prepared by polymerization in the presence of small quantities of a metal of group II of the periodic table, for instance, calcium. A temperature of 250°C and a pressure of 825 to 980 atm. are employed, and anhydrous ammonia is used as the polymerizing medium.

Synthetic liquid drying oils have found some application and considerable literature exists on their production by hydrocarbon polymerization. A typical example is the copolymerization of propene and diolefins with Friedel-Crafts type catalysts[111]. Propene and butadiene in a 6:4 ratio are mixed and cooled to −60°C. Boron trifluoride gas is introduced and the temperature and pressure are permitted to reach their maximum at 85°C and 680 psi. About 80 per cent of the monomer is converted to an oily, soluble polymer and 10 per cent to an insoluble gel.

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CHAPTER 5

CATALYTIC CRACKING

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INTRODUCTION

In the petroleum industry the partial decomposition of hydrocarbons to those of lower molecular weight is of great importance. By means of such decomposition heavy oils are converted to gasoline and hydrocarbon gases. This operation is known as cracking and may be effected by heat alone or with the aid of a catalyst. The former is termed thermal cracking and the latter catalytic cracking.

A wide variety of gaseous, liquid, and solid materials influence the rates of decomposition of hydrocarbons. Some materials with this property have been known for many years but have not led to industrial processes. The present catalytic cracking process was developed largely through the observations of Eugene Houdry from 1924 to 1928[55]. It was found that good quality gasolines were produced by treating heavy oils at high temperatures with certain clays, particularly if they had been treated with acid. The term "catalytic cracking" as used in the petroleum industry and hereafter in this chapter refers specifically to cracking in the presence of clays and other related solid oxide catalysts such as a combination of alumina and silica. These catalysts have acidic properties. Although they increase rates of decomposition relative to those obtained in purely thermal treatment, the reason for their use lies entirely in the more valuable products that are obtained. Thus we may speak of catalytic cracking as being selective. In particular, the gasoline from catalytic cracking has a higher octane number than that from thermal cracking and the gaseous products are in general more useful.

Since the initial large-scale use of catalytic cracking in 1936, it has become a very important refinery process and has been applied in many countries. The capacity of installed catalytic cracking plants in the United States by 1956 was well in excess of three million barrels (of 42 gallons) of charge stock per day. The catalytic cracking process has been described as the largest single forward stride in the development of refining processes that the petroleum industry has made. Indeed, catalytic cracking is now probably the leading industrial catalytic process in terms of moles treated and quantity of catalyst consumed. It has been widely studied from the practical side, and has also been investigated fundamentally to learn the physical and chemical principles that govern the operation. For the catalytic chemist the process is a very interesting one, involving numerous simultaneous reactions, including a rapid deposition on the catalyst of carbonaceous material called coke which must be burned off periodically with air to regenerate activity. The requirement of frequent regeneration is a characteristic feature of catalytic cracking and has led to ingenious engineering developments for practical application, but from the standpoint of the chemist regeneration is decidedly secondary to the cracking reactions that occur. These cracking reactions and the other hydrocarbon transformations that take place form such a complex system that at first glance it appears that anything can happen in this process. It will be seen, however, that this is not so, and that a few principles suffice to explain catalytic cracking quite well.

In this chapter the commercial aspects of the process will be treated but briefly, and prime attention will be paid to basic knowledge about the reactions that occur, and to the theories which explain these reactions. The chemistry of cracking catalysts will be discussed by L. B. Ryland, M. W. Tamele, and J. N. Wilson in a separate chapter in Volume VII of this series.

Catalytic cracking is specifically defined here as the treatment of hydrocarbons over solid catalysts at temperatures above about 300°C for the production of hydrocarbon materials of lower average molecular weight. A wide variety of solid materials that have been employed by various experimenters might be considered within this definition. Actually, however, a limited number of materials have shown the type of activity which makes them valuable for cracking petroleum oils. This activity is associated with acidic properties of the catalysts, and it is the only type considered except for a few special cases which are given for comparison.

The first commercial cracking catalysts were treated clays, such as the acid-treated montmorillonite clays often referred to as "natural" catalysts. Later synthetic catalysts won much favor. They were more expensive, but they gave somewhat superior products and were somewhat more stable with respect to deterioration of activity in use. Recent improvements in catalysts derived from clays have made the competition between the two types quite close. The most common synthetic catalyst is a silica-alumina combination containing 10 to 15 per cent by weight of alumina. Such catalysts are called alumina-silica in this chapter. Since about 1954 alumina-silica catalysts containing 25 per cent aluminum oxide have come into use because of their high stability. A number of other synthetic catalysts give cracking results similar to those obtained with alumina-silica; these include magnesia-silica, alumina-zirconia-silica, and boria-alumina. None of the latter is widely used.

Information on the reactions that occur with cracking catalysts has been obtained by cracking pure hydrocarbons, sometimes over catalysts not commonly used in commercial cracking, such as alumina-zirconia-silica. However, it has been amply demonstrated with certain pure hydrocarbons, as well as with petroleum fractions comprising complex mixtures of hydrocarbons, that the basic reactions which occur are the same over alumina-zirconia-silica as over alumina-silica and many other catalysts of this type. The individual catalysts may emphasize to a slightly greater extent one or another of the complex set of reactions, but the degree of emphasis will depend on methods of preparation and treatment, which determine physical structure and surface properties, as well as on composition of the catalyst. Small differences in the relative amounts of gasoline, coke, or light gas formed at a given conversion are of considerable economic importance, however, and in practical applications all the variations must be carefully followed. Catalyst stability is also of great economic importance.

Commercial Applications

Catalytic cracking is primarily used for the conversion of high-boiling petroleum fractions into gasoline of high octane rating. Besides the fact that it gives a good yield of gasoline of high octane number, about 80 by the motor or F-2 method (ASTM D-357) and about 92 by the research of F-1 method (ASTM D-908), there are other features which make it an attractive refinery process. For example, the gaseous by-products of catalytic cracking are more valuable than those from thermal cracking processes, since they contain more propylene and butenes which may be converted to gasoline or to chemicals and more isobutane which may be converted to "alkylate." Also, the high-boiling "uncracked" fractions from catalytic cracking are usually more suitable for blending with fuel oils than are the comparable fractions from thermal cracking. Although more coke is produced in catalytic than in thermal cracking, there is no need for periodic decoking of equipment, because the catalytic coke adheres to the catalyst and is burned off in regeneration. This feature makes catalytic cracking the more flexible process, for operating conditions are not restricted by equipment limitations on tolerable coke and may be chosen to give the optimum distribution of products.

The feed for catalytic cracking may be any petroleum fraction boiling above about 200°C (400°F). It is usually an overhead fraction since undistilled materials often contain either asphaltic substances giving an excessive coke yield or traces of metals contributing to permanent alteration of the catalyst. As an example of catalytic cracking the data in Table 1 are given. The feed was a Texas gas oil obtained as the overhead from a tar separator, and it had the following properties: gravity 30.3°API (specific gravity 0.874); IBP in ASTM distillation 171°C; 50 per cent point 297°C; EP 404°C. The cracking was a rather mild operation designed to furnish a high yield of good quality fuel oil as well as gasoline. Of particular interest in Table 1 are the small amounts of light gases (C_2 and below), the substantial amounts of propylene and butenes, and the high isobutane to *n*-butane ratio. The coke, 3.2 per cent by weight of the feed, is not entirely wasted, for much of the heat from its combustion is used for heating the feed and for generation of steam. With more extensive cracking, especially at higher temperatures, much higher yields of olefinic gases and of gasoline are possible.

Table 1. Commercial Catalytic Cracking Data

From operation of the TCC plant of the Magnolia Petroleum Company at Beaumont, Texas, as cited by Thornton[109]

Operating Conditions	
Catalyst	Synthetic beads, 15% Al_2O_3 85% SiO_2, 0.003% Cr
Reactor pressure	10 psig
Temperature of oil vapor feed	407°C
Temperature of catalyst to reactor	482°C
Catalyst to oil ratio	3.8 vol/vol
Carbon on spent catalyst	1.12% wt
Carbon on regenerated catalyst	0.04% wt
Feed space velocity	1.7 LHSV[a]
Products, Weight % of Feed	
H_2, CH_4, C_2H_4, C_2H_6	1.1
C_3H_6	1.5
C_3H_8	1.2
C_4H_8	2.1
i-C_4H_{10}	3.7
n-C_4H_{10}	0.9
Gasoline, 33–202°C	32.3
Naphtha, 188–231°C	4.7
Fuel oil, 218–338°C	38.8
Heavy oil, 18.3°API	10.5
Coke	3.2
	100.0

[a] LHSV = Liquid hourly space velocity, volumes of liquid feed per volume of catalyst per hour.

The importance of catalytic cracking as a major refinery process is shown by the following approximate statistics[117] for installed capacity, in barrels per day of feed, for the United States (1955).

Fluidized catalyst plants	2,300,000
Thermofor catalytic cracking (TCC)	570,000
Houdry fixed bed (not all operating)	250,000
Houdriflow	200,000
Total	3,320,000

In addition to the use of cracking catalysts for conversion of heavier fractions to gasolines or gases, there are other possible applications. During World War II some use was made of the hydrogen transfer properties of cracking catalysts in the retreating of olefinic gasolines to make them more suitable as aviation-base stocks. In this way an olefinic gasoline could be converted with relatively little loss in volume into an essentially saturated material rich in isoparaffins, naphthenes, and aromatics, which was blended with alkylate and tetraethyl lead to make high octane gasoline.

Still other possible applications are the isomerization of selected olefins, the depolymerization of olefins, dealkylation of aromatics as in the conversion of cymene to toluene, the cracking of arylethanes to styrenes, and so on. At the present time large-scale use for reactions other than cracking to gasoline does not appear to be made.

Catalytic Cracking Processes

In catalytic cracking the vapors of an oil are contacted with a catalyst at a temperature of about 450 to 550°C. The contact time is usually a few seconds, and the pressure 1 to 2 atmospheres absolute. The conventional gas oil feeds consist of a diversified mixture of paraffins, naphthenes, and aromatics, and many reactions occur simultaneously, as will be noted below.

A deposition of carbonaceous material deficient in hydrogen is characteristic of the process. This material, called coke, is formed within the catalyst particles, and must be burned off periodically to regenerate activity. The burning off need not be complete, for the catalyst has considerable activity even when fairly large amounts of coke are present. Typical curves showing activity at a given coke level, rate of coke formation, and the decline of activity within a process period are presented in Figures 1, 2 and 3 for fixed bed cracking. The burning off of coke, or regeneration, is a characteristic feature of the catalytic cracking process and largely determines the design of the plants. The design problems, which have been met in ingenious ways by the engineers, include:

(1) Securing continuous operation in spite of the fact that a given particle of catalyst must be periodically regenerated,

(2) Maintaining the desired cracking temperature,

(3) Keeping the reaction gases and regeneration gases from mixing,

(4) Avoiding overheating of the catalyst during the highly exothermic regeneration,

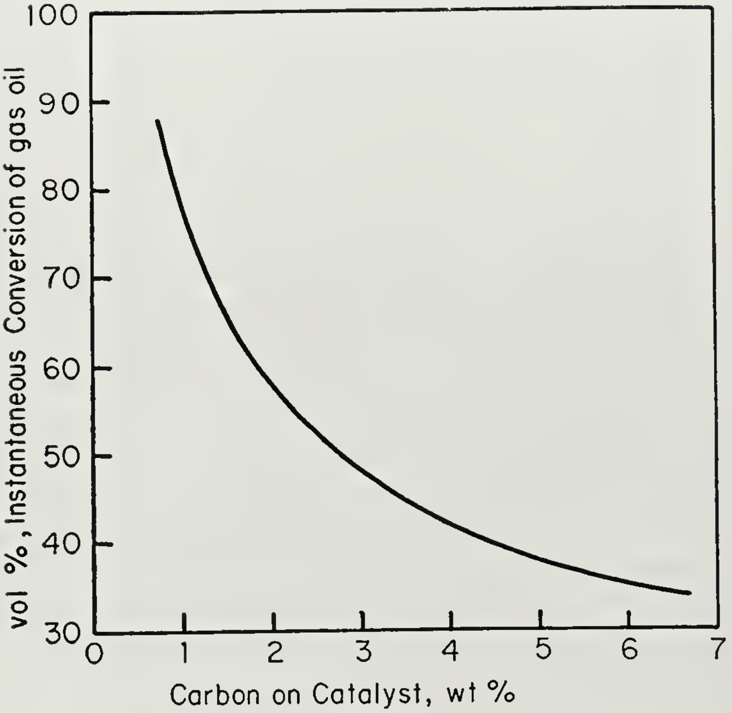

Figure 1. Instantaneous conversion as a function of carbon on catalyst computed from data of Voorhies[118] for East Texas gas oil cracked over alumina-silica at 0.6 LHSV and 454°C.

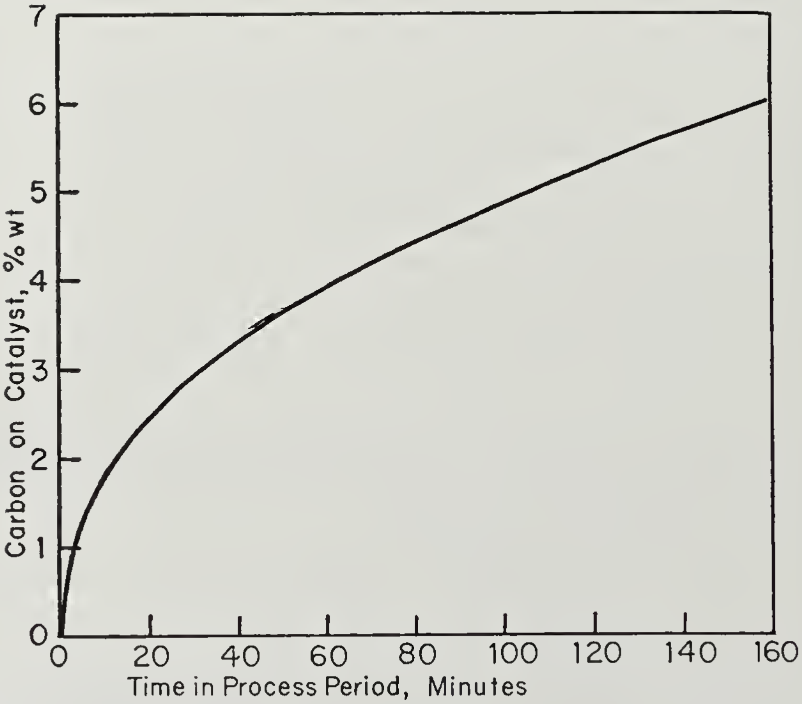

Figure 2. Carbon on catalyst as a function of process period. From data of Voorhies[118] for East Texas gas oil over alumina-silica at 454°C.

(5) Keeping any contact of the catalyst with steam at high temperature to a minimum, and

(6) Making efficient use of the heat liberated in regeneration.

Several highly successful commercial processes for catalytic cracking have been developed. These are briefly described in the following paragraphs. For further references the reviews of Haensel, and Sterba[42, 100], of Appell and Berger[3, 7a] and of Sittig[98] may be consulted, as well as the specific references cited below. An excellent summary of industrial catalytic cracking is that of Shankland[96], which includes many details and diagrams.

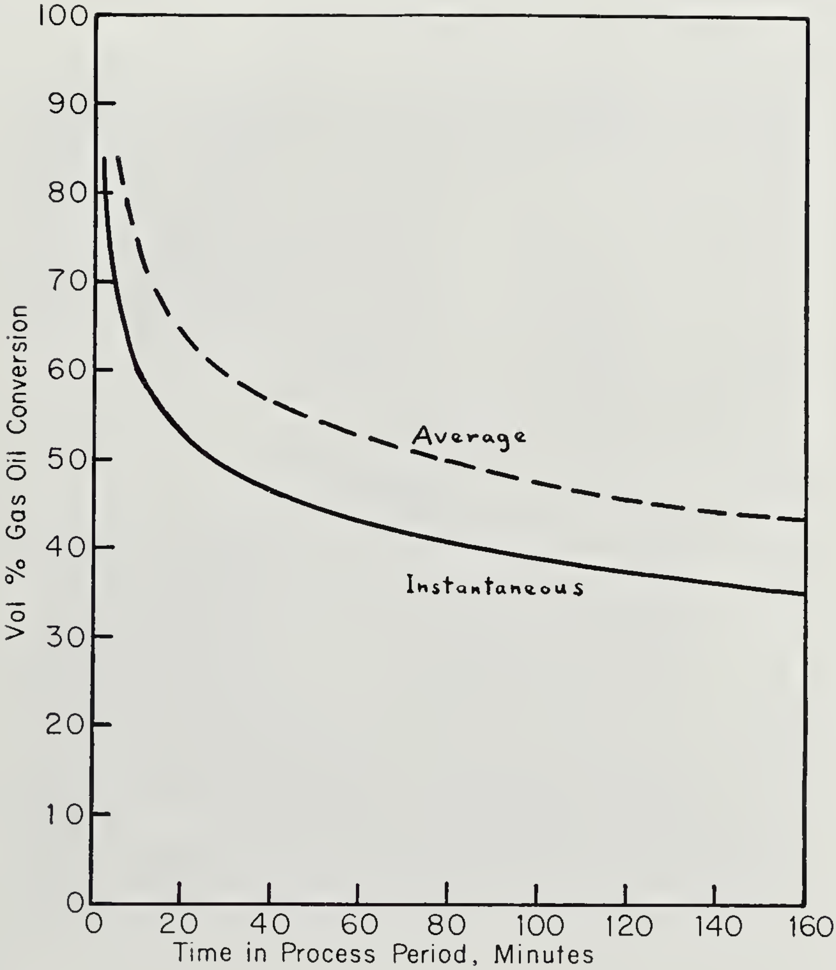

Figure 3. Feed conversion as a function of process period. The solid line gives instantaneous conversion; the dashed line the cumulative average. Data computed from Voorhies[118] for cracking of East Texas gas oil over alumina-silica at 0.6 LHSV and 454°C.

A fixed bed of catalyst is used in the Houdry Process[5, 26, 72]. This was the first catalytic cracking process to reach large scale use. In a Houdry plant several reactors are manifolded together so that a continuous flow of oil can be maintained while individual beds are alternately used, purged, regenerated, and purged. Cracking is carried out at temperatures of about 450 to 525°C, and regeneration is at a somewhat higher temperature, but not ordinarily above 600°C. The catalyst particles are pellets or beads of about 3-mm diameter, and are loaded into cases which are essentially tubular heat exchangers, with catalyst on the shell side. A molten salt mixture is circulated in the tubes to supply heat of reaction or to remove heat of regeneration. Processing and regeneration periods are each of the order of 15 minutes. This fixed bed process has been largely supplanted by those in which there is a continuous flow of catalyst from a reactor vessel to a regenerator and back. In the processes with catalyst flow, greater flexibility is possible, large amounts of expensive heat transfer surface are dispensed with, and an independent heat transfer medium is not required. The prominent processes of this type are fluid catalytic cracking, Thermofor catalytic cracking, and Houdriflow.

Fluid catalytic cracking[72, 74, 75, 97] uses beds of catalyst in the form of a fairly fine powder, with 50 to 80 per cent by weight of the particles in the size range 100 to 300 mesh and the remainder smaller, down to about 10 microns in diameter. The individual catalyst particles may be irregularly shaped or they may be spheroidal; the latter type is called microspheroidal (MS). When gas is passed through a bed of powdered catalyst at a suitable velocity the catalyst becomes "fluidized" and displays many of the properties of a liquid. There is a moderately sharp dividing level between the dense phase and the dispersed phase in such a bed; this level corresponds to the top of the liquid phase in a normal liquid vessel.

In operation the fluidized catalyst is flowed from the reactor vessel to the regenerator vessel and back in a continuous stream. The flow occurs because of gravitational forces akin to hydrostatic heads. Downflowing streams are usually dense mixtures of catalyst and gas, while upflowing streams are usually less dense suspensions obtained by adding more gas to the mixture.

The predominant type of fluid catalytic cracking plant is of the "downflow" design, so named because dense phase catalyst is withdrawn from the vessels for circulation to the other parts of the system. One of the latest examples of this design is shown in Figure 4, in which the catalyst and oil vapors together enter the bottom of the large reactor vessel and form a fairly dense, turbulent phase which constitutes the reaction zone. A stream of catalyst (spent catalyst) is continuously withdrawn from the dense phase of this vessel and after being stripped or flushed with steam for removal of entrained hydrocarbon vapors passes downward through a control valve to meet a stream of air and be carried by a rising conduit to the regenerator vessel where the coke is burned off in another dense phase bed. Hot catalyst (regenerated catalyst) is withdrawn from the dense phase of the regenerator and is mingled with the oil feed stream for introduction into the reactor. As much as 20 pounds of catalyst may be fed to the reactor for each pound of oil fed. The average residence time of catalyst in the reactor is of the order of 2 to 20 minutes.

Much of the heat released by the combustion of the coke is carried by the regenerated catalyst and this may serve to vaporize the oil as well as to supply any heat requirements of the reactor without the necessity of metal heat transfer surface. The gas streams passing through the reactor and regenerator leave most of the catalyst particles behind them in the dense phase, and are separated from the major portion of the remaining suspended particles by means of cyclone separators, and also, sometimes, electrostatic precipitators. Many modifications, mostly simplifications, have been made since the first fluid catalyst plant was built. One of the later designs is called "Orthoflow" cracking, and employs a reactor directly above the regenerator, so that spent catalyst falls in a straight line into the

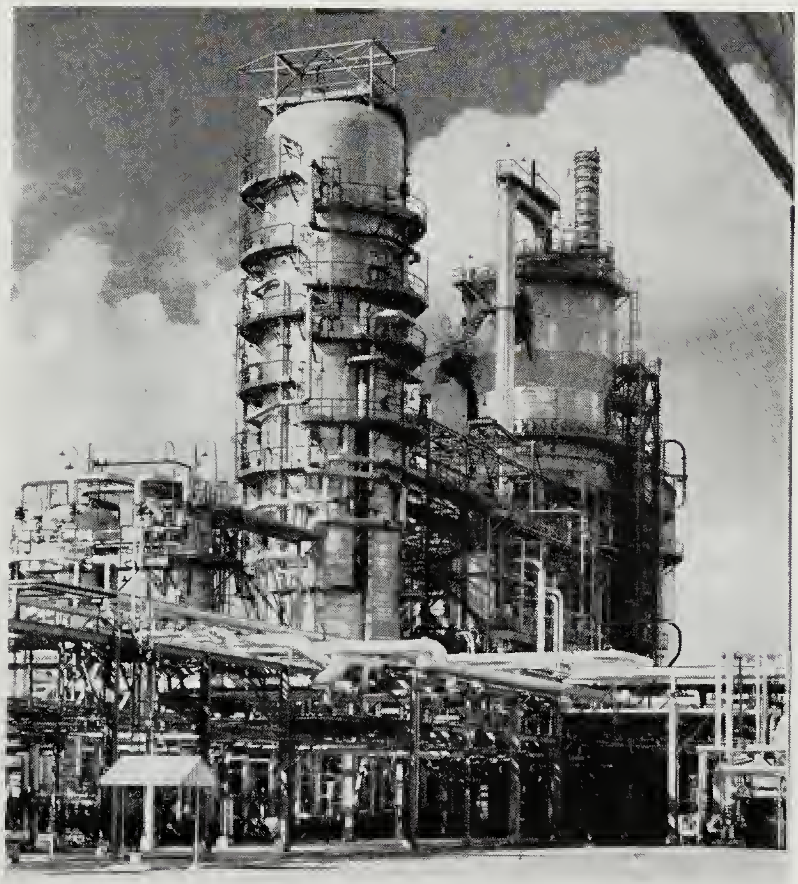

Figure 4. Catalytic cracking unit at Shell Oil Company's Norco, Louisiana, refinery.

regenerator. Recently a "riser" reactor has been described[50] in which the cracking occurs entirely in a dispersed phase. It is the first part of a two-stage process, the first commercial example of which is shown in Figure 5.

The "Thermofor" catalytic cracking process, sometimes called the TCC process[5, 72, 109], uses moving beds of fairly large granules or pellets of catalyst, about 3 mm in diameter. Catalyst is steadily withdrawn from the bottom of the reactor through flushing zones and is lifted by elevator buckets to the top of the regenerator, which is called a kiln. In the kiln, catalyst passes down through alternate burning zones where air is introduced and through cooling zones where the heat of regeneration is removed by coils generating steam. From the bottom of the kiln the catalyst is again lifted so that it may reenter the reactor. The very considerable catalyst circulation rate is indicated by the fact that 1 to 5 pounds of catalyst are circulated per pound of oil entering the reactor. The newer TCC plants employ an air lift for the catalyst rather than bucket elevators, and this makes possible higher circulation rates. To avoid two lifts it is now customary to place the reactor directly above the regenerator.

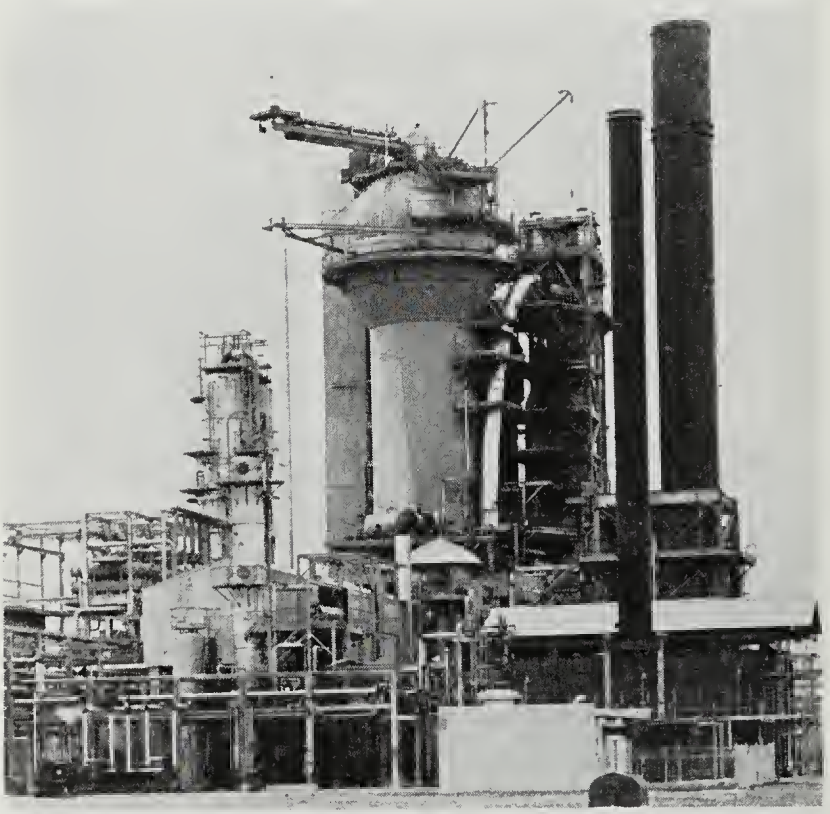

Figure 5. New two-stage catalytic cracking unit with one riser reactor at Shell Oil Company's Anacortes, Washington, refinery.

A recent moving bed process is called "Houdriflow"[5, 26]. It is basically similar to the TCC process in that a moving bed of fairly large catalyst particles is used, but it differs somewhat in kiln and reactor designs. The reactor is directly above the regenerator, and hence the catalyst is lifted only once, from the bottom of the regenerator to the top of the reactor, and this lift is accomplished by flue gas and steam in a pipe. The catalyst to oil ratio may be as high as 7.

In "Suspensoid" cracking, oil containing a small amount of suspended catalyst powder is passed through an externally heated coil at about 565°C and 400 psig. The quantity of catalyst used, about two pounds per barrel of oil, is insufficient to give all the characteristic cracking reactions, and the products are intermediate between those obtained in thermal cracking and those in true catalytic cracking. The catalyst may be a clay or a synthetic material.

"Cycloversion" is a fixed bed process using a bauxite catalyst. It is used chiefly for the desulfurization or reforming of naphtha, although it may occasionally be used for cracking higher boiling oils. Since the bauxite catalyst gives few of the characteristic reactions caused by acidic cracking catalysts, it is not considered further here.

Catalysts for the above processes, except for Cycloversion, have similar properties. These catalysts are for the most part either synthetic alumina-silica or acid-treated clays. They are discussed by Oblad[77] and Shankland[96], and will be considered in detail in the chapter on cracking catalysts. Cracking catalysts are remarkable solids, with surface areas as high as 600 square meters per gram when fresh. They display acid properties with respect to indicators in nonaqueous solvents, and are temporarily poisoned by high-boiling nitrogen bases such as quinoline. They are quite stable up to temperatures of about 600°C unless high partial pressures of steam are present.

Synthetic alumina-silica catalyst ordinarily contains 10 to 25 per cent by weight of aluminum oxide. One method of preparation is to hydrolyze an aluminum salt in the presence of freshly prepared silica hydrogel. The mixed hydrogels are then filtered, washed, dried, and calcined. Forming into beads or microspheres may be done before or during the drying step. It is also possible to prepare active catalysts by a number of other procedures, for instance by blending an alumina hydrogel with a silica hydrogel. In all procedures it is necessary to wash the catalyst well to remove soluble metal compounds, such as those of sodium, for these neutralize the acidity and destroy activity. Natural aluminosilicate catalysts prepared by treating montmorillonite clays with sulfuric acid are also much used commercially. More recently treated clay catalysts based on halloysite and kaolin have been introduced. Other synthetic catalysts such as magnesia-silica and alumina-zirconia-silica are quite active, but have found only limited commercial use. Many other catalysts have been found to have activity for cracking in laboratory experiments but for various reasons have not been commercially used.

Thermodynamics

In some reaction systems thermodynamic data are of great value in predicting the possible extents of reaction and the most suitable reaction conditions. Catalytic cracking is not such a system, for equilibria do not limit the principal cracking reactions in practice. Nevertheless, thermodynamics does tell what reactions are possible under the conditions of catalytic cracking and predicts the equilibria that occur in a few of the secondary reactions. Also, deviations from equilibrium values for observed ratios of isomers have significance for the reaction mechanism. Another application of thermodynamics is calculation of heats of reaction from enthalpy data. For all these purposes the thermodynamic data for hydrocarbons collected and correlated under the American Petroleum Institute Project 44[94] may be used. In this discussion an outline is given of some of the more important conclusions regarding possible hydrocarbon reactions, and a few examples of equilibria are cited. Numerical examples for cracking reactions are to be found in subsequent pages on the reactions of catalytic cracking.

Equilibrium is not attained under the conditions of catalytic cracking for most of the possible hydrocarbon reactions. In fact, a far-reaching equilibrium for cracking reactions would mean almost complete degradation to graphite and hydrogen, as this reaction has a favorable standard free energy change for all hydrocarbons except methane at all temperatures above about 200°C. Equilibrium is observed for many olefin isomerization reactions, however, and is approached for certain other isomerizations and for dealkylation of aromatics.

As a guide to the information available from thermodynamics the following lists are presented showing which reactions are possible or impossible in catalytic cracking at temperatures in the range 400 to 550°C and at about atmospheric pressure. These lists are intended to supply orientation, and it should be noted that exceptions can be found in unusual cases.

Reactions that can go essentially to completion (over 95%)

$C_nH_m \rightarrow n\text{C (graphite)} + (m/2)H_2$	For all hydrocarbons except CH_4
$C_nH_m \rightarrow (m/4)CH_4 + (n - m/4)\text{C (graphite)}$	As above
$C_nH_m \rightarrow CH_4 + C_{n-1}H_{m-4}$	As above
Large paraffin → paraffin + olefin	A few exceptions when olefin is C_2H_4

Large olefin → 2 small olefins	A few exceptions when small olefin is C_2H_4
Hydroaromatic → aromatic + $3H_2$	Dehydrogenation to an aromatic
Paraffin → aromatic + $4H_2$	The dehydrocyclization reaction
Paraffin + H_2 → 2 smaller paraffins	A hydrocracking reaction
Hydroaromatic + olefin → aromatic + paraffin	A hydrogen transfer reaction

Reactions that will be incomplete at equilibrium

Olefin isomerizations, both double bond shifts and skeleton rearrangements
Paraffin isomerizations
Cycloolefin isomerizations
Cycloparaffin isomerizations
Rearrangement of alkyl groups in aromatics
Redistribution of alkyl groups between two aromatics
Dehydrogenation of paraffins to olefins
Dehydrogenation of naphthenes (cycloalkanes) to olefins
Cyclization of olefins to naphthenes
Dehydrocyclization of paraffins to naphthenes
Dealkylation of alkyl aromatics
Some aromatic condensation reactions, such as 2 benzene → biphenyl + H_2
Some hydrogen transfer reactions

Examples of equilibrium constants for some typical reactions of this intermediate group are given in Table 2. For a reaction $A \rightarrow B + C$, $K = (B)(C)/(A)$, where (A), (B), and (C) are equilibrium partial pressures in atmospheres absolute. These K values give some idea of the conversions possible, but for an exact figure a detailed calculation must be made for a specific case, and this is often rather complicated since the amounts of the materials at equilibrium will depend on the temperature, the pressure, the nature and amounts of diluents present, and perhaps also on other simultaneous equilibrium reactions involving one or more of the same molecular species.

Reactions that cannot occur to a significant extent

These are the reverse of the reactions in the first list.
Of particular significance are the following:
Alkylation, i.e., olefin + paraffin → larger paraffin, except to a small extent if the olefin is ethylene.

Methanation, i.e., methane + hydrocarbon → methylated hydrocarbon + H_2
Hydrogenation of aromatics
Polymerization of olefins, except for ethylene

Heats of reaction in catalytic cracking depend considerably on the feedstocks and conditions. Ordinarily the cracking reactions are endothermic, but if extensive hydrogen transfer occurs, as in the retreatment of an olefinic gasoline to produce a saturated product, there may be an over-all production of heat. For a typical cracking reaction

$$n\text{-decane } (C_{10}H_{22}) \longrightarrow trans\text{-2-butene } (C_4H_8) + \text{2-methylpentane } (C_6H_{14})$$

the heat of reaction is $\Delta H_{800°K} = +14{,}200$ cal/mole.

Table 2. Equilibrium Constants for Hydrocarbon Reactions of Interest in Catalytic Cracking

Values computed from free energy data of API Project 44

Reaction	Equilibrium Constant, K	
	at 427°C	at 527°C
1-butene → *trans*-2-butene	1.63	1.24
1-butene → isobutene	2.44	1.72
n-butane → isobutane	0.505	0.435
cyclohexane → methylcyclopentane	9.02	12.6
o-xylene → *m*-xylene	2.13	2.01
propane → propylene + H_2	4.04×10^{-3}	6.45×10^{-2}
n-butane → *trans*-2-butene + H_2	5.53×10^{-3}	7.09×10^{-2}
cyclopentane → cyclopentene + H_2	4.55×10^{-2} [a]	0.544[a]
n-hexane → cyclohexane + H_2	6.90×10^{-2}	0.178
1-hexene → cyclohexane	15.2	2.37
benzene + *m*-xylene → 2 toluene	4.50	4.45
isopropylbenzene → benzene + propylene	1.46	11.1
1-octene → 2 1-butene	29.6	170
1-octene → 1-hexene + ethylene	2.40	33.4

[a] From Ref. 24, corrected for 6,710 cal error in ΔF_f of cyclopentene.

Reactions of Catalytic Cracking

Catalytic cracking is remarkable for the number of simultaneous reactions which occur, although all possible conversions certainly do not take place. Most of the reactions that do occur are desirable, and hence the value of the process. The following discussion is based on evidence found in the cracking of pure hydrocarbons, for the petroleum fractions cracked in refineries contain too many hydrocarbon species to allow the individual reactions to be ascertained. A key to references on the catalytic cracking of pure hydrocarbons is given in Table 3; this is not complete for Russian publications. Data cited in the text below are from Greensfelder and Voge, or from Greensfelder, Voge, and Good, unless otherwise noted. After a discussion of the reactions that occur, based on the data in these references, it will be demonstrated that they can be qualitatively explained by the theory that hydrocarbon transformations on the catalyst surface proceed through the formation, rearrangement, and rupture of electron deficient or polarized hydrocarbon radicals known as carbonium ions.

Cracking

Cracking does not occur indiscriminately, but only in definite ways. The following tabulation describes the principal modes of cracking of important hydrocarbon classes. The types most prominent in petroleum gas oils are paraffins, naphthenes, and substituted aromatics. (Naphthenes are the cycloalkanes or saturated cyclic hydrocarbons.)

Hydrocarbon Type	Mode of Cracking	Products
n-Paraffin	Chain rupture in several places	Olefins and paraffins
i-Paraffin	As above	As above; little methane
Naphthene	Ring and chain rupture	As above; some aromatics
Naphthene-aromatic	Naphthene ring opened, or split from the aromatic ring	Mixed aromatic materials, and olefins and paraffins
Pure aromatic	Little or no cracking	
Alkyl aromatic	Alkyl group sheared off	Olefin and bare aromatic
n-Olefin	Chain rupture in several places	Olefins, with some paraffins

Much detail on the cracking reactions of various hydrocarbons now exists in published literature. Only a brief discussion will be given here, with emphasis on *n*-paraffins that illustrate most clearly the nature of the cracking reactions. The products from the cracking of a *n*-paraffin, *n*-hexadecane (cetane), in a series of experiments[37] are plotted in Figure 6, and it is noteworthy that even at a low conversion there was a total of 340 moles of product for every 100 moles of *n*-hexadecane cracked. These experiments, like most others with pure hydrocarbons, were at atmospheric pressure. The products fall mostly in the range C_3 to C_6 and include prominent quantities of isoparaffins. Yields of isobutane and isopentane are shown in Figure 7. At 11 per cent cracked there were 53 moles of isoparaffins for 100 moles of hexadecane cracked. It has not been possible to explain these products

TABLE 3. GUIDE TO PAPERS ON THE CATALYTIC CRACKING OF PURE HYDROCARBONS

Catalyst component abbreviations are: Al, Al_2O_3; Zr, ZrO_2; Si, SiO_2; Mg, MgO; B, B_2O_3

Class	Members	Catalysts	Authors	Ref.
Paraffin	C_8 and C_{16}	Al-Si	Egloff *et al.*	23
"	C_3 to C_{24}	Al-Zr-Si	Greensfelder and Voge	33
"	C_3 to C_6	Al-Si	Franklin and Nicholson	27
"	C_6 to C_{10}	Al-Zr-Si	Good *et al.*	31
"	C_6 to C_{24}	Al-Zr-Si, C, Al, Si	Greensfelder *et al.*	37
"	C_7 to C_{16}	Al-Si, Mg-Si, B-Al, Clay	Gladrow *et al.*	29
"	C_5 to C_8	Al-Si	Hindin *et al.*	53
"	C_8	Al-Si	Obolentsev	79
"	C_{10}	Al-Si, Mg-Si, F-Al-Si	Plank *et al.*	89a
"	C_{16}	Al-Si	Topchieva *et al.*	111
"	C_{16}	Al-Si, Al-Zr-Si	Voge *et al.*	115
"	C_{16}	C	Grosse	39
"	C_{16}	$AlCl_3$	Potolovsky and Spektor	90
Olefin	C_4 to C_{16}	Al-Si	Egloff *et al.*	23
"	C_2 to C_{16}	Al-Zr-Si	Greensfelder and Voge	34
"	C_4 to C_6	Al-Si, Al-Zr-Si, Mg-Al-Si, Clay	Voge *et al.*	114
"	C_{16}	C	Greensfelder *et al.*	37
"	C_4	Al-Si	Blue and Engle	10
"	C_6 to C_{12}	Al-Si	Obolentsev; Obolentsev and Gryazev	78, 79, 81
"	C_8	Al-Si	Petrov and Frost	88
"	C_8 and C_{12}	Al-Si, Clay	Ciapetta *et al.*	17
Naphthene	C_6 and C_{10}	Al-Zr-Si, Th-Al-Si	Bloch and Thomas	9
"	C_6 to C_{18}	Al-Zr-Si	Greensfelder and Voge	35
"	C_6 and C_{10}	Al-Zr-Si	Good *et al.*	31
"	C_{10}	C	Greensfelder *et al.*	37
"	C_{10}	Al-Si	Topchieva *et al*	111
"	C_{10}	Al-Si	Panchenkov *et al.*	85
"	C_7	Al-Si, Mg-Si, F-Al-Si	Plank *et al.*	89a
Aromatic	C_8 to C_{11}	Al-Si, Al-Zr-Si	Thomas *et al.*	108
"	C_7 to C_{15}	Al-Zr-Si	Greensfelder *et al.*	36
"	C_9, Cumene	C, Al	Greensfelder *et al.*	37
"	*m*-Xylene	Al-Si	Boedeker and Erner	12
"	C_{14}, Diphenylethane	Clay	Morton and Nicholls	73
"	Methyl- and chlorocumenes	Al-Zr-Si	Roberts and Good	93
"	Diarylethanes	Al-Si, Clay	May *et al.*	63
"	C_9, Cumene	Al-Si	Obolentsev and Gryazev	80

TABLE 3—*Continued*

Class	Members	Catalysts	Authors	Ref.
Aromatic (*Continued*)	C_9, Cumene	Al-Si	Ballod *et al.*	6
"	C_9, Cumene	Al-Si	Plank and Nace	89
"	C_9, Cumene	Al-Si	Topchieva and Panchenkov	110
"	C_9, Cumene	Al-Si	Weisz and Prater	119
"	C_8-C_{11}, Alkylbenzenes	Al-Si	Rase and Kirk	91
Nitrogen compounds		Al-Si	Mills *et al.*	69

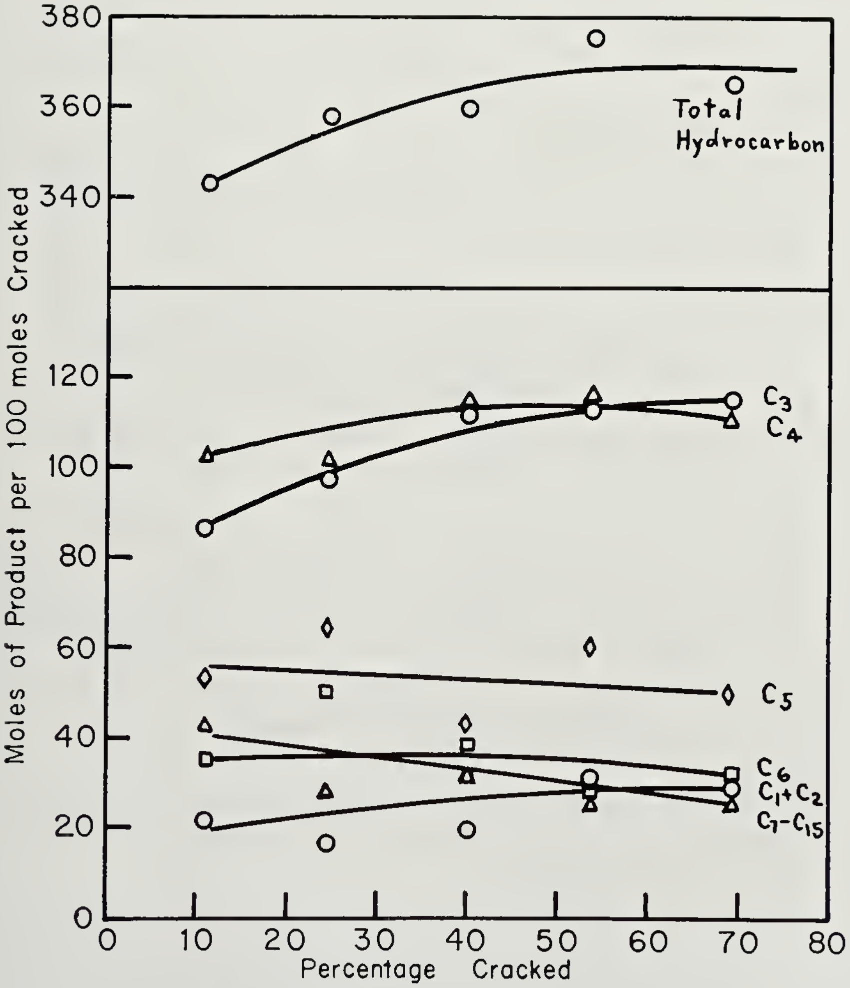

Figure 6. Product distribution from cracking *n*-hexadecane. Alumina-zirconia-silica catalyst, 500°C, LHSV 1 to 24.5, period one hour.

by the hypothesis of secondary reactions following a single initial rupture to a *n*-olefin and a *n*-paraffin. More than one rupture of an activated molecule and the production of isoparaffins as initial cracking products, are necessary to explain the results.

Additional data on the products from cracking *n*-hexadecane are given in Table 4, which includes results with the alumina-zirconia-silica catalyst (UOP-B) and with fresh and used commercial alumina-silica. The compositions of the C_4 and C_5 fractions portray the large amounts of isoparaffins. This table is also of interest in demonstrating that the products with the alumina-zirconia-silica catalyst are essentially the same as those with the alumina-silica catalyst, fresh or used, even though the activities differed considerably. With other cracking catalysts, however, greater differences might well be observed. The cracking of pure hydrocarbons over magnesia-silica, or over acid-treated clay, reported by Gladrow, Krebs, and Kimberlin[29], showed considerably greater differences from alumina-silica than did the alumina-zirconia-silica. A very interesting comparison of three different catalysts for the cracking of methylcyclohexane and decane is that of Plank, Sibbett, and Smith[89a]. Fluoride treated alumina-silica was outstanding for high activity and low coke, alumina-silica was intermediate, and magnesia-silica was at the other extreme. The hydrocarbon cracked had an important effect on comparisons.

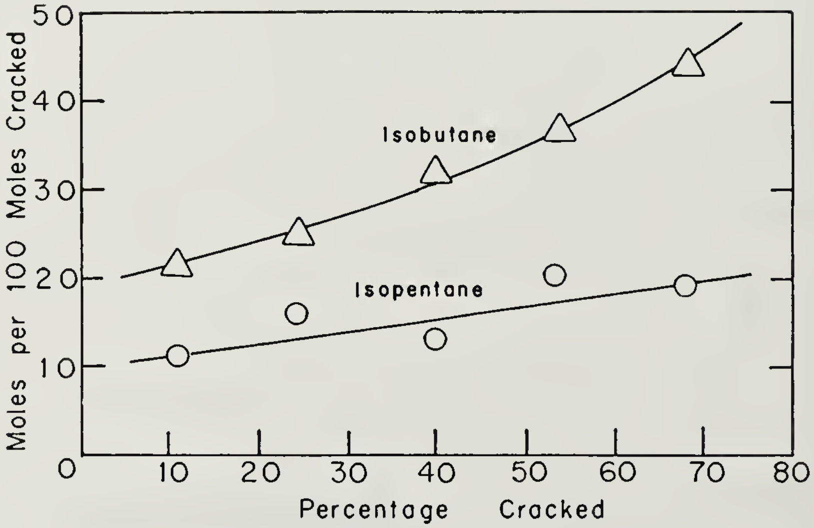

Figure 7. Isoparaffins from cracking *n*-hexadecane. Alumina-zirconia-silica catalyst, 500°C, LHSV 1 to 24.5, period one hour.

The rate of cracking is favored by high molecular weight, the presence of hydrogen attached to a tertiary carbon (hereafter abbreviated to "tertiary hydrogen"), and the presence of a double bond. Aromatic rings greatly favor cracking when side chains are sufficiently long. The effect of molecular weight is shown for *n*-paraffins in Figure 8. The increase in rate of cracking with increasing carbon number is too great to be accounted for by the increased number of carbon-carbon bonds or by the increased number of secondary hydrogens suceptible to attack, and must therefore result from some other influence, such as a greater rate of cracking of the higher members once activated, or a greater adsorption favoring a greater rate of activation per carbon atom.

Table 4. Cracking *n*-Hexadecane

Comparison of alumina-zirconia-silica (fresh) and alumina-silica (fresh and used) catalysts.

Atmospheric pressure; one hour period; 500°C

Catalyst	Al_2O_3-ZrO_2-SiO_2	Al_2O_3-SiO_2	
Catalyst condition	Fresh	Fresh	Used
Flow rate, moles/liter/hour	3.4	6.5	1.7
Conversion (%)	68.0	63.8	65.2
Material Balance (% wt)			
Gas through C_4	36.5	37.1	40.7
Lower boiling liquid	29.2	24.3	23.6
C_{16} and higher	31.9	35.8	34.4
Coke	2.3	1.8	2.4
Loss	0.1	1.0	−1.1
Gaseous Product			
Moles/mole charge (no loss)	1.83	1.95	2.13
Mole % H_2	4.0	3.8	6.9
CH_4	4.0	7.5	4.8
C_2H_4	3.5	5.5	4.8
C_2H_6	3.4	1.8	2.6
C_3H_6	30.2	27.6	28.5
C_3H_8	12.5	13.4	13.0
C_4H_6	0.5	0.2	0.1
i-C_4H_8	7.5	7.4	9.1
n-C_4H_8	11.6	12.1	14.3
i-C_4H_{10}	16.5	14.7	11.9
n-C_4H_{10}	6.3	6.0	4.0
C_5 Fraction			
Moles/mole charge (no loss)	0.34	0.36	0.36
Mole % *tert*-C_5H_{10}	31.2	30.1	34.1
sec-C_5H_{10}	19.8	20.3	23.5
i-C_5H_{12}	38.3	39.0	31.1
n-C_5H_{12}	10.7	10.6	11.3

Some idea of the great differences in cracking rates of various hydrocarbons is conveyed by Figure 9, and by the data in Table 5, for a number of compounds cracked over the alumina-zirconia-silica catalyst at 500°C with a flow rate of about 13 moles/liter/hour and a one hour period. It must be

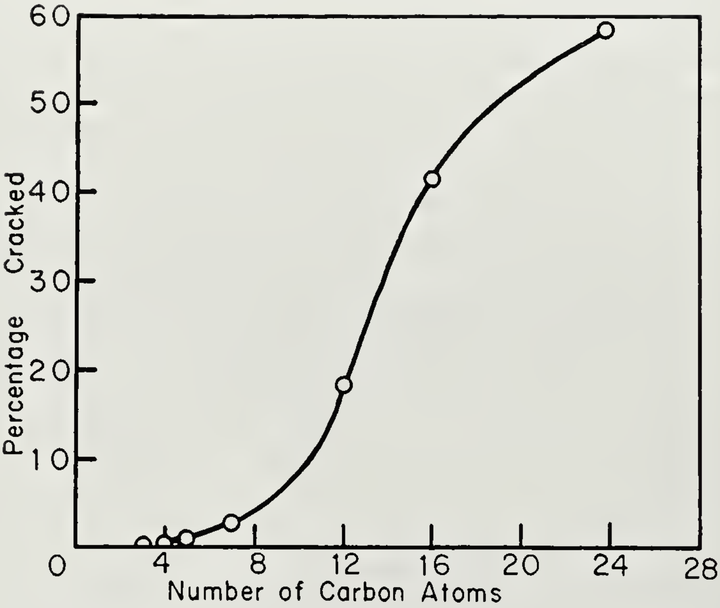

Figure 8. Cracking of *n*-paraffins. Alumina-zirconia-silica catalyst at 500°C; flow rate 13.7 moles/liter/hour.

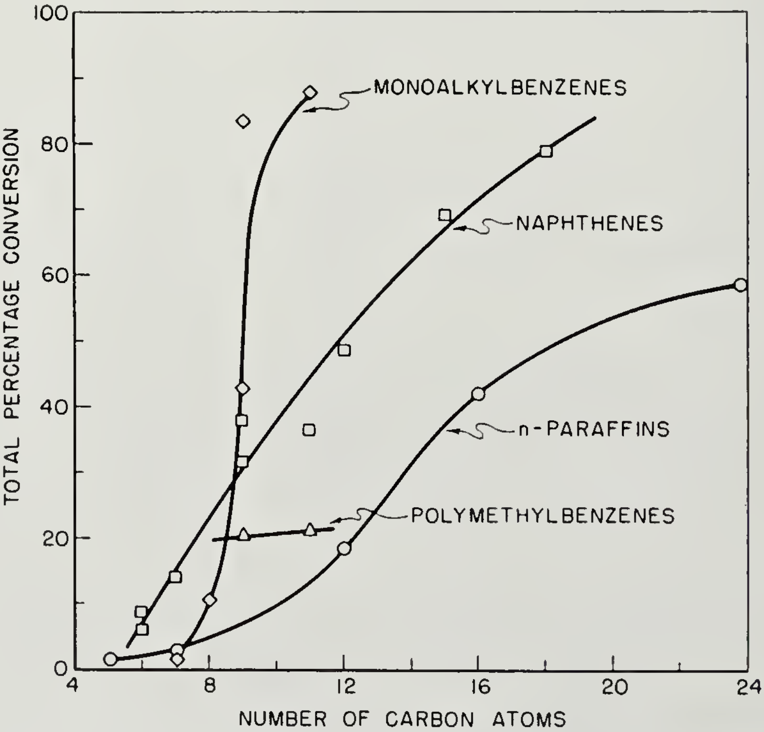

Figure 9. Comparative cracking of various hydrocarbon classes. Alumina-zirconia-silica catalyst; 500°C; flow rate 13.7 moles/liter/hr; one hour period.

noted that these data do not fully represent intrinsic reactivities, for the average activity of the catalyst in the 60-minute period was not constant because of different rates of coke deposition with different hydrocarbons. There is, however, no doubt about the major trends. For example, the activating effect of the tertiary hydrogens in 2,7-dimethyloctane is remarkable (compare *n*-dodecane). The high cracking rate of olefins is also noteworthy. Olefins such as diisobutylene and triisobutylene are extensively cracked or depolymerized at temperatures of about 250°C. For example, Ciapetta, Macuga and Leum[17] reported studies of depolymerization of butylene polymers at 216 to 428°C over Attapulgus clay, which has quite low activity for the cracking of gas oils, and found as much as 50 per cent cracking at 260°C and 2 liquid hourly space velocity (LHSV). *n*-Hexadecene cracks much more readily than *n*-hexadecane, yet the products from both compounds are very similar. This is of considerable theoretical significance.

TABLE 5. EXTENTS OF CRACKING OF VARIOUS COMPOUNDS

Compound	Number of C atoms	Percentage Cracked
n-Heptane	7	3
n-Dodecane	12	18
n-Hexadecane	16	42
2,7-Dimethyloctane	10	46
Decalin	10	44
Mesitylene	9	20
Isopropylbenzene	9	84
Cyclohexene	6	62
n-Hexadecene	16	90[a]

[a] Estimated from data at 450°C.

Naphthenes such as decahydronaphthalene (Decalin) crack at a high rate because of the presence of tertiary hydrogens. An extensive study of the products from Decalin was made by Bloch and Thomas[9]. Table 6 gives data on some of the products. As well as large amounts of propylene, propane, butylenes, isobutane, *n*-butane and methylcyclopentane, there were smaller amounts of liquid olefins and alkylbenzenes, together with some material boiling just below Decalin which was characterized as isomers of Decalin. The products from the cracking of naphthenes are too complex to be discussed in detail here, but it may be said that the majority are explicable in terms of cracking, isomerization, and hydrogen transfer reactions. Because of the efficiency of naphthenes as donors in hydrogen transfer, both gaseous and liquid products from naphthenes tend to be less olefinic than those from paraffins. Cracking of naphthenes occurs in both rings and side chains, but part of the rings are left uncracked. As with paraffins, formation of C_1 and C_2 hydrocarbons is relatively minor.

Aromatic hydrocarbons display a wide range of susceptibility to cracking. Aromatic ring structures are not much affected under usual cracking conditions, and hence unsubstituted aromatics react only slightly. Monoalkylbenzenes crack more readily as the size of the alkyl group increases. Thus, under fixed conditions at 500°C, the reaction of toluene was about 1 per cent, of ethylbenzene 11 per cent, and of *n*-propylbenzene 43 per cent. These values and the effects of isomerism are further reviewed in the discussion on theory. All the alkylbenzenes with alkyl groups of C_2 or larger crack primarily to form benzene and the olefin corresponding to the alkyl group. The methylbenzenes are less reactive, although susceptibility to cracking increases as molecular weight rises; the chief products are benzenes containing fewer methyls, together with methane and small amounts of C_2-C_4 hydrocarbons. Substituted naphthalenes behave in much the same way as substituted benzenes.

Table 6. Products from Decalin and Tetralin

Cracking over alumina-zirconia-silica catalyst at 500°C, as reported by Bloch and Thomas[9]

Hydrocarbon	Decalin	Tetralin
LHSV	3.8	3.8
Process period, min.	30	30
Conversion, %	66	68
Gaseous product		
% wt of charge	13.8	5.0
Moles/mole charge	0.32	0.14
Mole % H_2	14.2	22.0
CH_4	2.6	3.4
C_2H_4	3.9	2.3
C_2H_6	1.8	1.6
C_3H_6	16.2	21.2
C_3H_8	10.3	21.4
i-C_4H_8	2.4	0.7
n-C_4H_8	6.4	6.3
i-C_4H_{10}	29.1	21.2
n-C_4H_{10}	13.0	
Liquid Products, % wt of Charge		
Olefins	4.8	0.1
Paraffins	7.1	1.0
Naphthenes below feed	18.9	7.0
Benzene	0.1	6.8
Toluene	1.4	2.4
C_8 aromatics	1.9	2.6
C_9 aromatics	2.8	1.2
C_{10} aromatics below feed		6.7
Tetralin and isomers	10.5	32
Naphthalene	5.0	28
Higher boiling		7.9

Condensed ring bicyclic hydrocarbons with one aromatic ring, such as tetrahydronaphthalene (Tetralin) crack fairly readily and yield benzene and its homologs as a result of one or more ruptures in the nonaromatic ring. Data for Tetralin are shown in Table 6.

An interesting class of hydrocarbons that has been well investigated[63, 73] in catalytic cracking is the diarylethanes. The 1,2-diarylethanes, as would be predicted from the results with alkylbenzenes, crack rather readily to form mainly styrenes and benzenes. Morton and Nicholls[73] passed 1,1-diphenylethane over activated bentonite of the montmorillonite type at 600°C with a hydrocarbon flow rate of 5 moles per liter of catalyst per hour (5 moles/liter/hour) and a steam flow rate of 50 moles/liter/hour. The chief products, in weight per cent of the feed, were benzene 32.0, ethylbenzene 6.4, and styrene 29.2. The conversion was 67.6 per cent, and the yield of styrene was 74.1 mole per cent. Additional compounds of this class were cracked by May and co-workers[63] over clay and alumina-silica catalysts, with similar results.

In summary the characteristic features of the cracking reactions are:

(1) They are favored by unsaturation, aromatic rings, or tertiary hydrogens.

(2) When possible they tend to produce fragments of three or more carbon atoms.

(3) More than two fragments are often produced from a single molecule.

(4) Methyl groups are not readily cracked off.

(5) Rearrangements of the carbon skeleton often accompany cracking.

Isomerization

Many isomerization reactions occur under the conditions of catalytic cracking. These isomerizations are quite separate and distinct from the nonequilibrium skeletal rearrangements which take place only during the cracking of an individual molecule and which lead, for instance, to the formation of isobutane as a primary product from the cracking of a higher normal paraffin. The true isomerization reactions which tend to approach equilibrium occur with olefins and aromatics in normal cracking, and are usually secondary reactions following initial cracking reactions that produce olefins. Although there may sometimes be some isomerization of saturated hydrocarbons (naphthenes or paraffins) over cracking catalysts, there is no evidence that this is an important reaction under conventional cracking conditions. Hindin, Oblad, and Mills[53] found that at 150°C a one-hour treatment over an alumina-silica catalyst hydrated slightly (0.05 per cent added water) caused isomerization of C_6 or C_7 paraffins containing a tertiary carbon. Isomerizations ranged from 6 to 34 per cent, but no normal or neo structures were formed.

In general olefins are readily isomerized over these catalysts. The shifting of double bonds in *n*-olefins occurs with great rapidity. In one example[114] the conversion of 1-butene to 2-butenes was 79 per cent of equilibrium with an alumina-zirconia-silica catalyst at a flow rate of 68 moles per liter of catalyst per hour at the low temperature of 205°C. Both *cis*- and *trans*-2-butenes were produced. At the usual cracking temperatures, close to 500°C, double bond-shift and *cis-trans* isomerism can always be expected to be at equilibrium. At 500°C the experimental *n*-butene equilibrium is 30 per cent 1-butene and 70 per cent 2-butenes, and the *trans/cis* ratio is 1.30[116]; these are the values usually found in butenes from catalytic cracking. The C_5 and C_6 olefins also show an equilibrium distribution of double bond positions[16].

The chain branching isomerization of olefins is fairly rapid, and often reaches equilibrium in catalytic cracking operations. At 500°C the conversion of *n*-butenes to isobutene or the reverse proceeds at about the same rate as the cracking of a typical gas oil[114]. Side reactions to form products of lower and higher molecular weight take place simultaneously with the isomerization. It has been an experimental observation that butenes from catalytic cracking operations are usually, but not always, at equilibrium. Thus, isobutene is commonly 34 to 40 per cent of the total butenes, compared to the equilibrium value calculated from thermodynamic data of 37 per cent isobutene at 500°C.

The chain branching of pentenes is faster than that of butenes, and an equilibrium value of 58 to 60 per cent tertiary pentenes (2-methyl-1-butene and 3-methyl-2-butene) is readily reached at 475 to 500°C[114]. With pentenes the isomerization is considerably faster than the side reactions of cracking, staturation by hydrogen transfer, and formation of higher molecular weight materials, and at high flow rates a nearly pure isomerization reaction can be obtained. Isomerization is evidently rapid under conditions of commercial cracking. Thus, extents of branching in C_5 and C_6 olefins from the cracking of a Mid-Continent gas oil were reported to agree with equilibria calculated from free energy data[16]. Some deviations for relative amounts of compounds with different locations of methyl groups may well mean that free energy data are not wholly precise. Another example of a relatively rapid chain branching isomerization is the conversion of cyclohexene to methylcyclopentenes, which Bloch and Thomas[9] found to occur to the extent of 29 per cent over a thoria-alumina-silica catalyst at 300°C and 4 LHSV. Here again the isomerization was more rapid than other reactions.

A shifting of methyl groups on the benzene ring can take place, but is rather slow. This was observed in the treatment of *p*-xylene under severe conditions[36]. Isomerization to *meta*- and *ortho*-xylenes occurred together with cracking, disproportionation, and coke formation. The experiment was done at 550°C over alumina-zirconia-silica with a flow rate of 4 moles per liter per hour, compared to the more usual cracking conditions of 500°C and a flow rate of 14 moles per liter per hour. The recovered xylenes, 47.1 per cent by weight of the charge, had the following composition compared to the equilibrium calculated from free energy data[94].

	Product from *p*-Xylene Isomerization	Calculated Equilibrium at 550°C
Para	27.4	23
Meta	47.3	51
Ortho	25.3	26

The isomerization of a fraction rich in *m*-xylene was observed by Boedeker and Erner[12] over a synthetic alumina-silica at 515°C. At atmospheric pressure isomerization, disproportionation and cracking were prominent. At reduced pressure (90 mm abs.) there was nearly as much isomerization but less side reaction. *p*-Xylene was produced more rapidly than *o*-xylene.

Alkyl Group Transfer

An interesting reaction closely related to isomerization of aromatics is the transfer of alkyl groups from one aromatic molecule to another. Two types can be defined:

(a) Transfer to another species

$$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3$$

(b) Disproportionation

$$2C_6H_4(CH_3)_2 \rightarrow C_6H_5CH_3 + C_6H_3(CH_3)_3$$

These two types are closely related and sometimes one is the reverse of the other. Both are found to occur over cracking catalysts under somewhat more severe conditions than are normally employed in cracking. When the alkyl groups are large, with three or more carbon atoms, extensive dealkylation is the predominant reaction, but if they are methyl groups, isomerization and alkyl group transfer are quite prominent. Ethyl groups are mostly removed as ethylene, but may also be transferred to other molecules to some extent; transfer has also been observed for isopropyl groups[80]. The special behavior of methyl groups is connected with the fact that they cannot form an olefin by loss of a hydrogen, as well as with other features to be discussed under the theory of cracking.

Both types of methyl group transfer were clearly demonstrated by Hansford, Myers, and Sachanen[48] who treated xylenes and benzene-xylene mixtures at 15 psig over an alumina-silica catalyst at 538°C and 1 LHSV. The transfer of methyl groups to benzene and to other xylene molecules proceeded at about equal rates. The reactions were rather slow, and with a benzene to xylene molal ratio of two, only 0.27 mole of toluene was produced per mole of xylene charged, which apparently did not represent equilibrium. There was considerable side reaction.

Under higher pressures the methyl group transfer reaction is more rapid and more selective, according to the results of Johanson and Watson[57]. Equimolal mixtures of benzene and xylenes were passed over an alumina-silica catalyst at 500°C, 1 LHSV, and 100 to 450 psig, as well as at other conditions. A typical liquid product contained about 30 mole per cent toluene. There was still considerable side reaction, and the ultimate yield of toluene was about 75 per cent of theoretical. The carbon deposited on the catalyst as coke represented about 10 per cent by weight of the toluene produced.

Dehydrogenation

Dehydrogenation is not a characteristic reaction over uncontaminated cracking catalysts, although hydrogen removal in the molecular form often is somewhat more rapid than it is thermally. Direct dehydrogenation is scarcely appreciable with paraffins or with simple naphthenes like cyclohexane. With higher naphthenes such as bicyclohexyl or Decalin there is observable dehydrogenation to the corresponding aromatic compound. When a saturated or partially saturated ring is connected to an aromatic ring, dehydrogenation becomes quite an important reaction. For example in the cracking of Tetralin, at 525°C, with 28 per cent conversion to gas and lower boiling liquid there was at least 16 per cent conversion to naphthalene[36]. Another example with Tetralin was cited in the discussion on cracking reactions from the work of Bloch and Thomas[9]; naphthalene was 28 per cent of the Tetralin feed. There is much hydrogen in the gas produced from cracking such a compound, although large amounts of hydrogen are not usually produced in cracking. Hydrogen does not all come from direct dehydrogenation, however, but in part derives from material converted to coke or high molecular weight compounds by condensation reactions. Commercial cracking catalysts, if contaminated with nickel, iron, or vanadium by plant use, yield much more hydrogen than do fresh catalysts[68].

Polymerization

The polymerization of olefins is the reverse reaction of the cracking of the higher molecular weight product. It was noted in the discussion on thermodynamics that polymerization of olefins, with the exception of ethylene, cannot be a prominent reaction under the usual cracking conditions. At lower temperatures and higher pressures where equilibrium is more favorable it has been shown that cracking catalysts are quite active for polymerization. It is thus reasonable that polymerization may serve as the first step in the formation of aromatics and coke from olefins, even under conditions where the equilibrium concentration of simple polymer cannot be high.

An example of polymerization accompanied by other reactions was given by Egloff and co-workers[23] who treated *n*-butenes over an alumina-silica catalyst at atmospheric pressure and 400 to 600°C with a flow rate of about 10 moles per liter per hour. The maximum production of liquid boiling above the C_4 range was 24.3 per cent by weight, and was obtained at 450°C. This liquid could not have been a simple polymer, for the equilibrium dimerization of *n*-butene is considerably less than this, and in fact cannot exceed about 20 per cent at 400°C, and is even less at 450°C. Polymerization of 1-butene at 250°C and a flow rate of 95 moles per liter per hour over a magnesia-alumina-silica catalyst at atmospheric pressure was reported to reach 23 per cent by weight of the feed, and the liquid product consisted chiefly of C_8 material[114]. Although such polymerization is a fairly rapid reaction, exceeding the rate of chain-branching isomerization, it is much slower than the double-bond shift. Polymerization under elevated pressures was reported by Thomas[106] for propylene and butenes over several cracking catalytsts.

Alkylation

The alkylation of paraffins with olefins over cracking catalysts has not been reported. This reaction is thermodynamically less favorable than olefin polymerization. Even under elevated pressure it would not be expected to be at all rapid because of the inertness of lower paraffins like isobutane. Alkylation of aromatics with olefins does occur, especially if the temperature is not too high and the pressure is elevated[41, 81a].

Hydrogen Transfer

The transfer of hydrogen from naphthenes or other hydrocarbons to olefins is an important and characteristic reaction. It in part accounts for the large amounts of isobutane and other valuable isoparaffins that contribute to the high antiknock rating of catalytically cracked gasoline, and plays a part in the balance of reactions that produce such a high yield of liquid products. Some of the hydrogen that is transferred to olefins comes from compounds that are dehydrogenated to aromatics, while some comes from molecules that are condensed to coke. In fact, catalytic cracking has sometimes been called catalytic decarbonization because in effect it removes carbon from a heavy oil to leave products of higher average hydrogen to carbon ratio. Very little molecular hydrogen is released in this decarbonization, however, since the hydrogen atoms are transferred to olefins and other unsaturated species.

Hydrogen transfer usually occurs somewhat more slowly than cracking of gas oils at about 500°C. At lower temperatures it is relatively more rapid, but is still a reaction requiring considerable contact with fairly fresh catalyst. To produce a saturated gasoline such as is used as aviation base stock, preferred conditions are a fairly low temperature (about 400 to 450°C), a residence time for the vapors of about 10 seconds, and a high catalyst to oil ratio (or a rather brief process period in fixed bed). This type of operation was used about 1938 in Houdry plants, and was rather widely employed in 1941–1945 for aviation gasoline production.

Much of the chemistry of the hydrogen transfer reaction was elucidated by Thomas[105], who published results in 1944 which showed that transfer occurs between aliphatic olefins in the absence of cycloparaffins. In the case of *n*-octenes treated at 375°C and a pressure of about 8 atmospheres, he found that at least 50 per cent of the hydrogen needed to account for the paraffins formed arose from the conversion of octenes to coke. Prominent side reactions accompanying hydrogen transfer to the octenes were cracking, olefin isomerization, cyclization, polymerization, and condensation. The extent of some of these side reactions under more usual hydrogen transfer conditions is shown by data on the self-saturation of mixed hexenes given in Table 7. A maximum efficiency for the production of hexanes was indicated at about 1 liquid hourly space velocity and 400°C.

TABLE 7. SELF-SATURATION OF HEXENES OVER ALUMINA-ZIRCONIA-SILICA CATALYST WITH 15-MINUTE PERIOD[114]

Hexenes from propylene polymer

Temperature, °C	350	400	400	400	450
Flow rate, LHSV	2	0.5	1	2	2
Conversion of hexenes, % wt, to:					
Cracked material	8	21	20	16	21
Saturated C_6	25	46	45	26	28
Higher boiling	15	14	17	18	20
Coke	4	17	10	5	5
Hexenes	48	2	8	35	26

It has been clearly demonstrated that the hydrogen transfer reaction over cracking catalysts is not a dehydrogenation followed by catalytic hydrogenation as is observed with catalysts such as nickel and platinum. The fact that dehydrogenatable naphthenes such as Decalin are effective materials for the saturation of olefins might lead one to suspect a dehydrogenation hydrogenation mechanism. However, treatment of the naphthene alone under the same conditions produces little moleclar hydrogen. Furthermore, the addition of molecular hydrogen in the treatment of an olefin alone has the same effect as the addition of an inert diluent[114].

One of the most interesting features of the hydrogen transfer reaction is the way in which it contributes to the high ratio of isoparaffins to normal paraffins in catalytically cracked or treated products. This comes about through a selective saturation of tertiary olefins which are thus converted to isoparaffins. In the treatment of butenes, alone or in the presence of cyclohexene as a hydrogen donor, it was found that isobutene was saturated by hydrogen transfer at a rate 7 to 10 times that for *n*-butenes[114]. With Decalin as the donor, the corresponding rate ratio for the butenes was given as 5[10]. Petrov and Frost[88] observed more rapid self-saturation of 2-ethyl-1-hexene than of 1-octene at 250°C. This selective saturation, when coupled with the chain branching isomerization of olefins, can lead to isoparaffin/*n*-paraffin ratios which exceed greatly the equilibrium ratio. Thus, in the treatment of normal pentenes in the presence of Decalin at 400°C[114] the recovered pentanes were over 95 per cent isopentane, whereas equilibrium among either pentenes or pentanes gives only about 65 per cent of mono-branched structures at this temperature.

Although hydrogen transfer is quite appreciable from one olefin molecule to another (self-saturation) it is greatly favored by certain hydrogen donors. From the rather limited published work on this subject[10, 114] it appears that the most effective hydrogen donors are large naphthenes such as Decalin, naphthene-aromatic such as Tetralin, or unsaturates such as cyclohexene. *cis*-Decalin, which carries the two tertiary hydrogen atoms on the same side of the molecule, transfers hydrogen to butenes about ten times as fast as does *trans*-Decalin[10], while Tetralin, although free from tertiary hydrogens is a still more active hydrogen donor, presumably because of the strong adsorption caused by the presence of the aromatic ring. Experiments with butene containing radioactive carbon were reported by Blue and Engle[10] and indicated that under conditions of extensive hydrogen transfer from a donor to the butene very little of the catalyst coke was derived from the butene.

The rate of hydrogen transfer from Decalin to isobutene is sufficiently high to make diffusion into catalyst pellets a limiting step, according to the data of Blue and co-workers[11]. In experiments at constant coke level on the catalyst it was found that the rate constant for saturation of isobutene was about twice as great with 20 to 40 mesh TCC (Thermofor catalytic cracking) beads as with 4 to 5 mesh beads. Rough granules of 20 to 40 mesh obtained by crushing the 4 to 5 mesh beads were even more active. This effect of particle size is considered further in the discussion on kinetics.

Hydrogen Exchange

Although the exchange of hydrogen atoms between hydrocarbons or between a hydrocarbon and the catalyst is not a reaction that alters the products of catalytic cracking for practical purposes, the study of it with the aid of deuterium has given valuable information on its mechanism. The first work of this type was done at Princeton in 1941 to show that activation or breaking of C—H bonds could occur and was probably precedent to C—C cracking reactions. Results were reported in detail in 1948[86]. The exchange between CH_4 and CD_4 over an alumina-silica catalyst at a pressure of 150 mm and a temperature of 345°C to form CHD_3 was observed. The reaction mixture contained 20.2 per cent CD_4, 2.8 per cent CHD_3, and 76.2 per cent CH_4. After six hours of exposure of the gas in a 100-ml vessel to 0.45 gram catalyst, the ratio of mass 20 to mass 19 observed in a mass spectrometer had dropped from 6.25 to 3.75. This result definitely showed activation of the C—H bond, even in a compound as inert as methane. It may be noted, however, that this reaction was not rapid compared to catalytic cracking, for although it was observed at a temperature well below that used for cracking, the reaction time was quite long. The measured temperature coefficient of the reaction, represented by an activation energy of 13 kcal, permits calculating the rate of exchange between methane molecules at 500°C, and this turns out to be of the order of 1/40 of the known cracking rate of a paraffin like *n*-dodecane, when rates are expressed in terms of moles reacted per gram of catalyst per hour. The difference in rates does not invalidate the argument of attack through the C—H bond, for any of the twenty secondary C—H bonds in dodecane is more reactive than the C—H bonds in methane.

Exchange of hydrogen between hydrocarbons and an alumina-silica catalyst deuterated by treatment with deuterium oxide occurs quite readily at temperatures of about 0 to 300°C. It should be kept in mind that the resulting moist catalyst, containing up to 1 per cent added water, is different from the usual fairly dry cracking catalyst. If the deuterated catalyst is partially dried at 525°C the exchange reaction becomes very slow, although deuterium is still present in the catalyst[44, 52]. The exchange reactions tell much about the way in which hydrocarbons can react, but they do not give data directly applicable to a catalyst operating under normal cracking conditions.

The first exchange experiments with a hydrated catalyst were made by Hansford[45]. Of particular interest was the rapid exchange of an isoparaffin as compared to a normal paraffin. Exchange was also rapid with an olefin. Later more precise data were presented by Hansford and co-workers[49] which are summarized in the following list. Here the approximate temperatures required for introduction of at least one deuterium atom into 2 per cent of the molecules of various hydrocarbons contacted for one hour with successive freshly deuterated portions of the catalyst are listed.

Hydrocarbon	Temperature for 2% Deuteration
2-Butene	−20°C
Isobutane + 0.5% isobutene	65
Benzene	80
Isobutane	120
Methylcyclohexane	115
Hydrogen	210
n-Heptane	250
Cyclohexane	270
n-Butane	285
Neopentane	310

These results demonstrate a much more facile exchange with olefins and with hydrocarbons containing hydrogen attached to a tertiary carbon. The presence of a small amount of olefin increased the rate of exchange between isobutane and the catalyst; this has theoretical significance. An increase of olefin content from 0.02 to 0.5 per cent increased the rate by a factor of 15. Apparent activation energies for the various hydrocarbons varied from 10 to 34 kcal, but were not directly related to exchange rates. Addition of olefin did not change the activation energy for isobutane exchange.

The exchange between isobutane and the catalyst was examined in more detail, and was found to be about first order in isobutane pressure. It was found that products from the isobutane exchange tended to be abnormally rich in deuterium, with a preponderance of the exchanged molecules containing 7, 8 or 9 deuterium atoms, but hardly ever 10 deuterium atoms. After long times of contacting the butanes tended to approach a statistical distribution.

Experiments on exchange between butanes and deuterated catalyst were also described by Hindin, Mills, and Oblad[52]. With the exception of a much smaller effect of added olefin, the results resembled those of Hansford and co-workers in those tests that were similar. The effect of water content of the catalyst was observed, and tests were made of deuterium exchange between isopentane and an isobutane containing deuterium in the tertiary position. The most significant findings were as follows:

(1) In exchange between hydrocarbons and deuterated catalyst for one hour at 150°C, 1 per cent of the product molecules from *n*-butane contained deuterium and 34 per cent of the product molecules from isobutane contained deuterium.

(2) Particularly when there was a fairly large amount of deuterium on the catalyst, the product from isobutane tended to contain polydeuterated species, especially $C_4H_2D_8$ and C_4HD_9. There was almost no C_4D_{10}.

(3) Although isobutane was apparently not deuterated in the tertiary position when contacted with a dueterated catalyst, isobutane containing

deuterium in this position readily exchanged it with isopentane, giving isopentane molecules containing chiefly only one deuterium. This is a highly significant observation which fits in well with the carbonium ion theory and will be discussed in the theoretical section, together with other exchange results.

In another study, Hindin, Mills, and Oblad[51] contacted C_5-C_8 paraffins with deuterated alumina-silica at 150°C for one hour. Paraffins containing one or more tertiary carbons showed extensive exchange, close to statistical redistribution of H and D atoms. Exchange extended down the chain at least 4 carbon atoms from the tertiary carbon. There appeared to be some D at the tertiary position in the products from 2-methylpentane. The exchange was much faster than isomerization. Paraffins without tertiary carbons did not exchange.

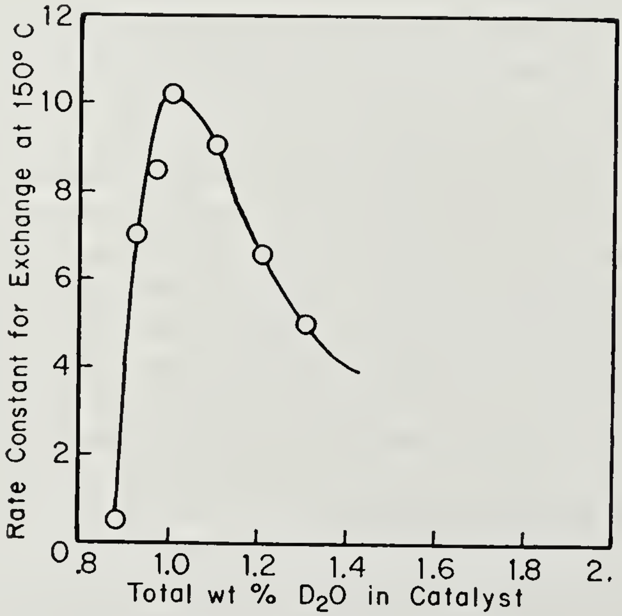

Figure 10. Rate constant for exchange between isobutane and deuterated catalyst, (After Haldeman and Emmett[44]). Catalyst was evacuated at 500°C to 0.89 per cent D_2O and then increments of D_2O were added at 150°C.

Haldeman and Emmett[44] made a careful study of the effect of catalyst water content (D_2O) on the exchange between deuterated alumina-silica catalyst and isobutane. Their results verified those of previous workers, and also showed some of the complexities of this system. The rate of exchange was very dependent on the amount of water added as well as on the prior history of the sample. After evacuation at 500°C, addition of 0.13 per cent deuterium oxide at 150°C caused a sharp maximum in the rate of exchange, as shown in Figure 10. About the same maximum rate was reached by cooling the catalyst from 500 to 150°C in 20 mm of water vapor and evacuating one hour at 150°C. Relative exchange rates after such treatment were observed for several materials. The numbers shown below indicate that the exchange rate was only rapid for the alumina-silica and not for catalyst containing K or Ba ions or for alumina or silica. The latter materials are known to have low cracking activities.

Material	Exchange Rate
Alumina-silica (12.5% Al_2O_3) of 249 m^2/g	10.0
Same, treated with K^+; 0.58 meq.K^+/g	0.2
Same, treated with Ba^+; 0.46 meq.Ba^{++}/g	0.8
Alumina, 80 m^2/g	0.2
Silica, 320 m^2/g	0.0

Still more information on reactions of an isoparaffin over a hydrated (deuterated) catalyst was obtained by Burwell and Porte[15]. They observed the racemization, exchange, and isomerization of +3-methylhexane over an alumina-silica catalyst in the presence of water at 200°C. They found that exchange, isomerization, and racemization proceeded at about the same rate. The agreement of exchange and isomerization rates is contrary to the finding of Hindin, Mills, and Oblad, but it is partly accounted for by the fact that the use of an optically active material enabled Burwell and Porte to observe isomerization from the 3rd to the 4th carbon. However, a puzzle was posed by results at lower temperatures (56°C) where there was racemization but no isomerization. This racemization suggests an activation of the hydrocarbon of a different type than that which leads to isomerization.

The exchange between H_2 and D_2 proceeds rather slowly at 300°C over a cracking catalyst containing 25 per cent alumina[54]. At much higher alumina contents, and particularly with pure alumina, this exchange reaction is more rapid. It is also favored by calcining the catalyst at 650 to 800°C. From the facts that this reaction depends on the degree of dehydration and on alumina contents in much different ways from catalytic cracking it may be concluded that it results from catalyst characteristics somewhat different from those responsible for catalytic cracking. It appears to be related to the known dehydrogenation activity of alumina. The hydrogen-deuterium exchange reaction is a very sensitive test for contamination of a cracking catalyst by metals[54] such as nickel or vanadium, which are often present after prolonged use in a plant.

Condensation

Condensation may be defined as the formation of new carbon-carbon bonds of such type that the molecular weight is increased. Polymerization is thus a condensation reaction, but is a special case that is considered separately. No detailed examination of the condensation reactions occurring in catalytic cracking has been published, yet there is much evidence that such reactions play a significant role. They certainly participate in coke formation, but in addition they are responsible for some recovered products.

In the cracking of most pure hydrocarbons minor amounts of high boiling, highly aromatic liquid or solid products that are not retained on the catalyst are found. Such materials are very noticeable when reactive hydrocarbons such as styrene, indene, or butadiene are treated over cracking catalysts. They are commonly produced from aromatics, evidently by elimination of hydrogen and the linking together of two or more aromatic rings. For example, in the cracking of mesitylene (b.p. 165°C) at 500°C[36] there was produced 6.3 per cent of material boiling above 185°C which had a refractive index, n_D^{20} of 1.5305. This could not have been entirely mononuclear aromatics. Prominent amounts of condensation occur with olefins as well as with aromatics, and since olefins are universally produced in catalytic cracking, some condensation is inevitable. The treatment of *n*-butenes at 500°C[114] gave 20 per cent of a liquid product which was nearly one-half aromatic and included some wholly aromatic material boiling above 174°C.

Coke Formation

The formation of a carbonaceous residue that remains on the catalyst is characteristic of all catalytic cracking reactions. A coked catalyst is easily distinguished from a fresh catalyst by its dark color, and visual observations of catalysts at about 500°C in glass tubes customarily show a darkening within a minute after exposure to a gas oil vapor. Only in reactions occurring at very low temperatures, such as the double-bond shift isomerization of butenes at 150°C, or with unreactive hydrocarbons, does the catalyst stay white for some time.

Coke formation is a complex process, and little information regarding the reactions occurring has been published. Coke is not carbon but consists of a mixture of hydrocarbons of low volatility. The average atomic ratio of hydrogen to carbon may vary from about 0.3 to 1.0 or even higher, depending on the conditions of formation of the coke. All available evidence points to condensation reactions as the major contributors to coke formation. Although some hydrogen is removed in condensation, and although further hydrogen may be removed or transferred to other hydrocarbons as the incipient coke molecules reside on the catalyst, it is quite clear that coke is not simply carbon remaining after hydrogen is stripped from a hydrocarbon.

A portion of the coke may be extracted from a spent catalyst with solvents. Thomas[105] extracted with benzene 27 per cent of the catalyst deposit remaining from the treatment of *n*-octenes over an alumina-zirconia-silica catalyst at 375°C and about 8 atmospheres. The extract was separated into acetone soluble and insoluble portions; these had molecular weights of about 210 and 410, respectively, and hydrogen to carbon atomic ratios of 1.10 and 0.875. The acetone soluble part, 40 per cent of the extract, was a dark oil, while the insoluble part was a dark solid melting at 195 to 210°C.

Hydrocarbons differ in the amount of coke they produce under standardized cracking conditions. In general aromatics and olefins form the most coke. Figure 11 shows relative amounts of coke formed from various hydrocarbons under constant conditions[115].

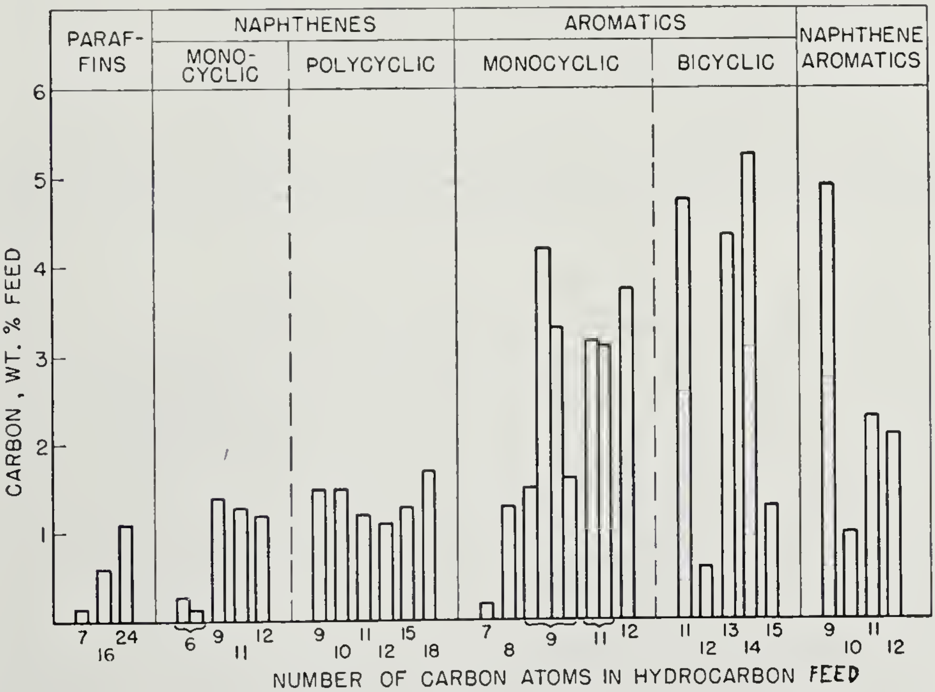

Figure 11. Carbon formation in the catalytic cracking of pure hydrocarbons.

McMahon[65] observed the radioactivity of coke produced in cracking *n*-heptane containing one radioactive carbon atom. From the results he concluded that all carbon atoms were equally involved in coke formation. The same conclusion was reached with *n*-octane and a *n*-octene.

Reactions not Catalyzed

There are a few reactions of hydrocarbons, thermodynamically possible under the usual cracking conditions, that occur to only a minor extent. In order to show whether these are catalyzed or are in reality thermal reactions it would be necessary to compare carefully rates in the absence and presence of cracking catalysts, and this would require many experiments that have not yet been done. The following list, therefore, is really one of reactions which are possible but do not play a significant part in determining the composition of the products. Some of them may actually be accelerated to a slight extent by cracking catalysts.

Dehydrogenation of paraffins to olefins
Dehydrogenation of simple cyclohexanes to olefins or aromatics
Dehydrogenation of simple cyclopentanes to olefins
Dehydrocyclization of paraffins to naphthenes or aromatics
Hydrogenation of olefins with molecular hydrogen
Isomerization of saturated hydrocarbons (paraffins or naphthenes)
Decomposition of hydrocarbons to carbon and hydrogen
Decomposition of hydrocarbons to methane and carbon
Hydrocracking, with molecular hydrogen entering the reaction

It may be noted that one group of workers reported that ethylene was rapidly hydrogenated over a synthetic alumina-silica catalyst at 345°C[86], but this has not been verified in similar tests by others.

POISONING BY NITROGEN BASES

Typical cracking catalysts are remarkably insensitive to materials that poison many catalysts. They are little affected by moderate amounts of gaseous sulfur compounds, carbon monoxide, oxygen, hydrogen, organic acids, alcohols, phenols, or water at cracking temperature[a]. They are, however, temporarily poisoned by certain nitrogen compounds of types which may be present in petroleum[b]. The deactivation so caused is severe, but activity is restored by burning in air in the usual fashion for regeneration. Study of the poisoning by nitrogen compounds has given evidence regarding the nature of the active surface.

Table 8 illustrates the inhibiting effects of various nitrogen compounds on the cracking of Decalin. The experiments summarized in this table were done with feeds containing sufficient added nitrogen compound to bring the total nitrogen content to 0.10 or 0.11 per cent by weight. Since fresh catalyst was used at the start of a run there was always some cracking during the first few minutes of the process period before sufficient nitrogen compound had reached the catalyst to poison it. This mode of operation,

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[a] If there is prolonged exposure to water vapor at high temperature, cracking catalysts suffer an irreversible loss of surface area and activity. Air, carbon dioxide, sulfur dioxide, and ammonia have little effect below about 620°C[68]. Sulfur compounds have a progressive deleterious effect on clay catalysts containing iron, causing increased coke formation and lowered activity[68].

[b] Permanent poisons are represented by compounds of sodium, potassium, or other metals which can neutralize the acidic surface. Contamination with heavy metals (Fe, Ni, V, Cu) does not destroy activity but increases formation of hydrogen, light gases and coke[68, 71]

however, corresponds to industrial cracking of petroleum fractions in a regenerative system.

The greater effectiveness of quinoline as a poison when it is added before the hydrocarbon to be cracked, rather than with it, is shown by data from Mills, Boedeker and Oblad[69] for isopropylbenzene cracking.

Case	Benzene plus Gas, % wt
No quinoline	40.1
Quinoline in feed	15.3
Quinoline pretreatment of catalyst	3.1

In the experiments with Decalin at 500°C, little or no inhibiting effect was exerted by ammonia and aliphatic amines, while quinoline and acridine were extremely effective[115]. Mills and co-workers did observe some inhibition of cumene cracking by ammonia at 425°C. In other experiments the cracking of cetane was inhibited by quinoline to about the same extent as that of Decalin[115]. It is of interest to note that the less basic heterocyclic nitrogen compounds do not inhibit quite as strongly as their similar, more basic relatives. Thus inhibition by indole is less than that by quinoline, and that by carbazole is less than that by acridine. At equal basicity, inhibition increases with molecular weight. Basicity alone is relatively ineffective, judging by results with ammonia.

TABLE 8. INHIBITION OF CRACKING OF DECALIN BY NITROGEN COMPOUNDS

Results from cracking Decalin containing 0.11 per cent nitrogen in various forms. Catalyst alumina-zirconia-silica; atmospheric pressure; flow rate, 13.7 moles/liter/hour; 500°C; one-hour period. Inhibition = percentage reduction of total conversion. Data from Ref. 115.

Compound Added	Conversion, %	Inhibition, %
None	41.9	—
Ammonia	42.0	0
Methylamine	42.0	0
Diamylamine	42.3	0
Dicyclohexylamine	28.0	33
Pyridine	26.8	36
Indole	25.1	40
α-Naphthylamine	21.8	48
Quinoline	8.5	80
Acridine	8.2	81

In another series of tests[69] various nitrogen compounds were listed in the order of their effectiveness in inhibiting the cracking of isopropylbenzene. Starting with the most effective poison these are: quinaldine, quinoline, pyrrole, piperidine, decylamine, and aniline.

Inhibition of the cracking of Decalin by quinoline was not appreciably diminished by the addition of steam or ammonia with the feed[115]. A higher temperature of cracking did reduce the inhibition, and at 575°C the percentage reduction of cracking caused by 1 per cent quinoline was only 30 instead of the value of 80 found at 500°C. Inhibition by nitrogen bases can be minimized by (a) removal of the nitrogen bases; (b) use of short process periods or high catalyst to oil ratios; and (c) cracking at a higher temperature.

Quite small amounts of quinoline are sufficient to reduce the cracking reaction to a low rate. According to the data of Mills and co-workers[69] an amount of quinoline which will cover 2 per cent of the surface of an alumina-silica catalyst destroys most of the activity. This quinoline is held strongly by the catalyst and is desorbed only very slowly, yet it is apparently held as such and is not converted to coke, at least at 425°C. It has been termed chemisorbed quinoline and is somewhat arbitrarily distinguished from physically adsorbed material by the rate of desorption. It is significant that a pure silica gel, which has a low cracking activity, chemisorbs almost no quinoline although the surface area is high. The correlation between the amount of quinoline chemisorbed and the cracking activity appears to be much superior to the correlation between surface area and activity[69].

Miesserov[66] found activity of aluminosilicate catalysts to be inversely proportional to the amount of adsorbed pyridine at low concentrations.

THEORY OF CATALYTIC CRACKING

An acceptable theory for catalytic cracking should explain:

(1) The catalysis of carbon-carbon bond rupture.

(2) High susceptibility to cracking of compounds containing tertiary hydrogens.

(3) The extremely high cracking rates of C_6 and higher olefins and alkyl aromatics (C_3 or larger alkyl groups).

(4) Preferential formation of fragments of three or more carbon atoms from straight chains.

(5) Formation of more than two C_3 or higher fragments from a single large molecule.

(6) Isomerization accompanying cracking.

(7) Selective cracking at the bond to the ring in alkyl aromatics.

(8) Hydrogen transfer.

(9) Selective saturation of tertiary olefins.

(10) Isomerization of olefins.

(11) The formation of aromatics from straight chain compounds.

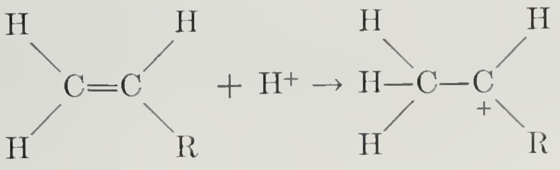
(12) Certain observations on hydrogen exchange and paraffin isomerization.

The so-called "carbonium ion" theory does a fairly satisfactory job in these respects and is rather generally accepted. This theory views the oxide cracking catalysts as belonging to a group of acidic catalysts, and relates catalytic cracking to the reactions occurring in the presence of other acidic substances like sulfuric acid, aluminum chloride, and many more, although recognizing specific characteristics of the various acids determined by physical form, chemical nature, and the temperature range of appreciable activity. The theory has been developed in the period 1944 to 1952 from the original carbonium ion theory of Whitmore[124], which grew from studies of the polymerization of olefins. The chief advocates of the carbonium ion theory of cracking have been Bremner[13], Hansford[45, 46, 47], Ciapetta, Macuga and Leum[17], Thomas[107], and Greensfelder, Voge and Good[32, 37]. This theory became well established as soon as it was clearly shown that cracking catalysts are indeed strong acids when dry. Evidence for the acidity will be given in the chapter on cracking catalysts in Volume VII of this series. Applications of similar carbonium ion theory to various other reactions in the field or organic chemistry are well discussed in several texts[1, 122].

A few other theories of catalytic cracking, more physical in nature, have been set forth. For example, Grosse[38] supposed that cracking catalysts were effective because they physically adsorbed hydrocarbons and slightly lowered the energy necessary for thermal cracking. Davidson, Ewing, and Shute[22] stressed the close agreement of the oxygen-oxygen distance in clays with the distance between alternate carbon atoms in a straight chain and thought that this might cause sufficiently strong adsorption to promote cracking. Turkevich and Smith[112] proposed a "unitary theory" whereby a hydrocarbon is attacked at two places by complementary zones of a catalyst; for example in olefin isomerization, a proton may be added at one point while one is removed at a different point. Although these theories may be in part correct, none of them has demonstrated the broad correlating power of the carbonium ion theory.

Carbonium Ions

The carbonium ions which according to the present theory are the intermediates in catalytic cracking reactions are electron-deficient entities comprising a positively charged carbon atom with three monovalent atoms or the equivalent attached. These carbonium ions may be formed in several ways, but the basic steps are the addition of a proton to an olefin or an aromatic, or the removal of a hydride ion from a saturated hydrocarbon. For the addition of a proton to an olefin the following equation represents the now classical picture. Here the proton becomes a hydrogen atom bonded to one carbon atom, and the positive charge of the carbonium ion resides



on the other carbon. This is the structure preferred by the majority of chemists, although bridged and resonating structures, or π complexes are sometimes pictured. Winstein and Morse[125] have discussed the various proposed structures and have presented experimental evidence favoring the classical form. Brown and Brady[14] reached the same conclusion; they believe that a π complex is a looser bonding found in certain association compounds, and that a classical carbonium ion structure is the intermediate in acid-catalyzed olefin reactions. A further argument in favor of bonding the hydrogen to one of the carbon atoms is found in ionization potential data which show large energy differences between ions formed by bonding hydrogens to one carbon or another in propylene or isobutylene.

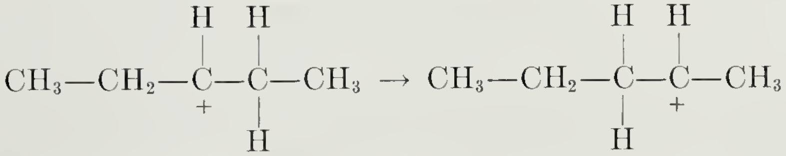
Although free carbonium ions are pictured and discussed in treating hydrocarbon cracking reactions in the following paragraphs, it should be kept in mind that this is an abbreviation and that the carbonium ion is always associated to some degree with a complementary negative ion. Thus carbonium ions are encountered only in highly polar solvents or on polar surfaces, and may be thought of as polarized intermediates rather than as isolated ions. The negative ion plays a vital role, like that of the nucleophilic reagent in Swain's[101] "push-pull" theory of displacement reactions. The necessity for stabilization by association is evident from the fact that the energy required to form a free carbonium ion from a paraffin in space is of the order of 250 kcal, which is far too great to make such a species a possible reaction intermediate (see also Ref. 15). Besides being tied to negative charges, the carbonium ions of catalytic cracking presumably have only a transient existence, and are not as stable or plentiful as the aryl carbonium ions of the type $(C_6H_5)_3C^+$ found in 100 per cent sulfuric acid[76].

A carbonium ion, like a hydronium ion, H_3O^+, is a form characteristic of an acidic medium, and is made only with the aid of an acidic catalyst; that is to say, with the aid of a material that can donate protons or accept electron pairs. Such materials are aluminum chloride, sulfuric acid, phosphoric acid, hydrofluoric acid, fluoboric acid, porous solids impregnated with acids, nonaqueous solutions of aluminum chloride or bromide, acid-treated clays of certain structures, and acidic oxide mixtures like alumina-silica. The various acids are not alike or equally active, and may bring to the fore more strongly one or another of the typical carbonium ion reactions. Schmerling[95] has described ionic mechanisms for a number of these acid-catalyzed hydrocarbon reactions, including polymerization, alkylation, isomerization, and cracking.

The nature of the acidity of alumina-silica catalysts has been described in various ways[46, 59, 67, 70, 77, 103, 107]. Further discussion will be found in the chapter on cracking catalysts to appear in Volume VII of this series.

As applied to catalytic cracking the carbonium ion theory consists of specific rules for the formation, rearrangement, and reaction of carbonium ions. These rules are not arbitrary, but follow consistently from a large body of experimental data, and in addition have been given considerable theoretical support. The rules for catalytic cracking are in the main the same as those for other acid-catalyzed hydrocarbon reactions. They are quite different in detail from those governing the behavior of hydrocarbon free radicals[62], although from the standpoint of logical development the free radical and carbonium ion concepts have much in common. The principal rules, with illustrating reactions, are:

(1) A carbonium ion is a labile structure which readily rearranges by methyl or hydrogen shifts (1,2-shifts) to form an isomerized ion.



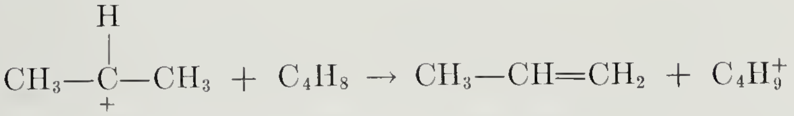
$$CH_3{-}CH_2{-}\underset{+}{\overset{H}{\overset{|}{C}}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}CH_3 \rightarrow CH_3{-}CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{+}{\overset{H}{\overset{|}{C}}}{-}CH_3$$

(2) A carbonium ion is highly reactive, and during its lifetime may undergo many single-step reactions, such as hydrogen shifts or exchanges.

(3) It can remove a hydride ion from a neutral molecule to form a new carbonium ion and a new neutral molecule.

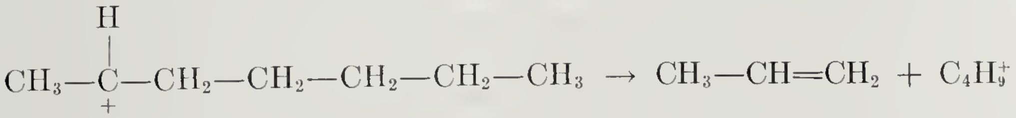
$$R^+ + R'H \rightarrow RH + R'^+$$

(4) It can donate a proton to a base or an olefin and thus become converted to an olefin.



$$CH_3{-}\underset{+}{\overset{H}{\overset{|}{C}}}{-}CH_3 + C_4H_8 \rightarrow CH_3{-}CH{=}CH_2 + C_4H_9^+$$

(5) If it is large it may undergo beta splitting to an olefin and a small carbonium ion.



$$CH_3{-}\underset{+}{\overset{H}{\overset{|}{C}}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH{=}CH_2 + C_4H_9^+$$

(6) The relative stabilities of carbonium ions decrease in the series *tert* > *sec* > prim > ethyl > methyl. The more stable ions participate in reactions to a far greater extent than the less stable ones when there is a choice of forming more than one ion. The more stable ions form more rapidly and lead to faster reactions.

Basis of Carbonium Ion Rules

Before applying these rules to the reactions of catalytic cracking it will be well to review some of the supporting theory. The lability or ease of rearrangement of a carbonium ion (Rule 1) is a natural consequence of the postulate of a localized positive charge. As Szwarc[102] has pointed out, this positive charge attracts the electrons from bonds to a neighboring atom and this makes the potential energy surface for rearrangement relatively flat. In addition the considerable energy release in going to a more stable ion, such as to a tertiary from a secondary, often acts to further lower the activation energy.

Rule 2 implies that the rate of formation of the carbonium ion is the slow step, and that once it is formed it may rapidly undergo a number of changes. This rule is necessary to explain many observations on hydrogen exchange in various acid systems. Rule 3 is a propagation step in a chain of carbonium ion reactions. It finds strong support in the specific exchange of deuterium atoms in tertiary positions, as noted later. Rule 4 follows logically from the postulate that carbonium ions are formed by addition of protons to olefins. It may be that the proton is first transferred from the existing ion to the catalyst and then from the catalyst to the other olefin, but this gives the same result.

Rule 5, the beta scission rule, represents the only manner of molecular splitting that will give a neutral olefin and a smaller carbonium ion without the rearrangement of carbon or hydrogen atoms during the process. Only electrons are shifted, and thus the "Principle of Least Motion" for elementary chemical reactions is maintained. The energy of activation for beta scission is vastly lowered by the presence of the positive charge of the carbonium ion for the same reason that energy of isomerization is lowered. The beta splitting is closely allied to the beta cracking of free radicals[62]. In conjunction with the rules for ease of hydrogen shifting and the relative energies of different carbonium ions it gives a very good explanation for the relatively small amounts of methane, ethane, and ethylene in the products of catalytic cracking.

Regarding rule 6, which lists relative stabilities of different types of ions, some quantitative data are at hand from appearance potentials of ions in mass spectrometry. From appearance potentials observed by D. P. Stevenson the proton affinities of olefins to give carbonium ions of various structures have been derived by Greensfelder[32]. The results, together with values proposed by Evans and Polanyi[25] are tabulated below. These proton affinities are the $-\Delta H_{298}$ values in kcal/mole for the reactions of the type olefin + proton → carbonium ion. P_1 and P_2 are for addition to the first and second carbon atom of the double bond, respectively.

Olefin	Evans and Polanyi[25]		Greensfelder[32]	
	P_1	P_2	P_1	P_2
$CH_2{=}CH_2$	152	152	—	—
$CH_2{=}CH{-}CH_3$	175.5	168.5	181	165
$CH_2{=}C{-}(CH_3)_2$	189	168	196	166

These values clearly show the enhanced stability of the tertiary butyl carbonium ion formed by adding a proton to the first carbon of isobutene.

By combining the ionization potential data with conventional thermodynamic data, Greensfelder obtained data which may be recast to show heats of cracking of various carbonium ions. For the reactions

$$\text{(1)} \qquad R{-}CH_2{-}\underset{+}{CH_2} \rightarrow R^+ + CH_2{=}CH_2$$

$$\text{(2)} \qquad R{-}\underset{+}{CH}{-}CH_3 \rightarrow R^+ + CH_2{=}CH_2$$

$$\text{(3)} \qquad R{-}CH_2{-}\underset{+}{CH}{-}CH_3 \rightarrow R^+ + CH_2{=}CH{-}CH_3$$

The values of ΔH_{298}, in kcal/mole, are given as

Ion, R^+	Reaction 1	Reaction 2	Reaction 3
CH_3^+	69.5	85.5	90.5
$C_2H_5^+$	35.0	61.0	59.5
n-$C_3H_7^+$	22.5	47.5	45.0
sec-$C_3H_7^+$	8.5	33.5	30.5
tert-$C_4H_9^+$	−7.5	17.5	14.5

The most favoarble reaction is thus one in which a primary ion is cracked to yield a tertiary ion with $\Delta H_{298} - 7.5$. It is clear from these series why it is not likely that methyl or ethyl ions will be obtained as fragments in cracking, since reactions producing the *sec*-propyl and *tert*-butyl ions are energetically more favorable by at least 26.5 kcal. Essentially the same energy differences were shown by Szwarc[102] by listing the ionization potentials, in kcal/mole, necessary to produce carbonium ions from the corresponding free radicals: Methyl 232, ethyl 200, *sec*-propyl 172, and *tert*-butyl 159. As Szwarc notes, differences in this series are much greater than the differences in the energies required to form the corresponding free radicals R from the paraffins, RH. The dissociation energy to form an ethyl radical from ethane is about 96 kcal, and that to form a *tert*-butyl radical from isobutane is 88 kcal, with a difference of 8. In forming the corresponding ions from the paraffins an energy difference of 47.5 kcal is encountered. This is the basic reason for the great importance of tertiary hydrogens in catalytic cracking and other conversions involving carbonium ions.

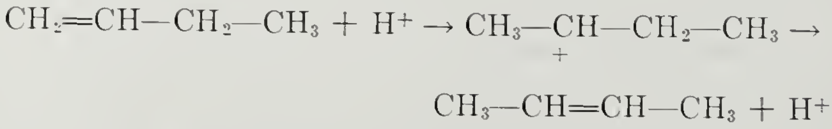
An acceptable qualitative explanation of the great effect of structure (neighboring methyl groups, say) in carbonium ion reactions has been given by Szwarc[102] who points out that the electronic interaction between a positive charge and the electrons in neighboring bonds is much greater than the interaction between the "free" electron of a free radical and the electrons in neighboring bonds, while this, in turn, is considerably greater than the interaction between bonded electrons. In an ion the interactions are much more powerful with neighboring carbon atoms than with neighboring hydrogen atoms because of the greater polarizability of carbons; hence the favored position of the *tert*-butyl ion.

At this point it is well to remember, again, that the energy values discussed above are for free ions, whereas in practice the ions are always associated with complementary charges. The large but unknown association energies will very considerably diminish the important differences in energies of different carbonium ions. Such a qualification is absolutely necessary, however, to reconcile the enormous ionization energies and the very large differences between them with the facts of catalytic cracking which the theory is to explain. For example, cracking of isomeric C_6 paraffins indicated that tertiary hydrogens reacted about 20 times as fast as the primary at 550°C[37], which corresponds to an activation energy difference of 5 kcal rather than the 30 to 35 kcal difference for the energies of formation of primary and tertiary free ions.

Application of Theory

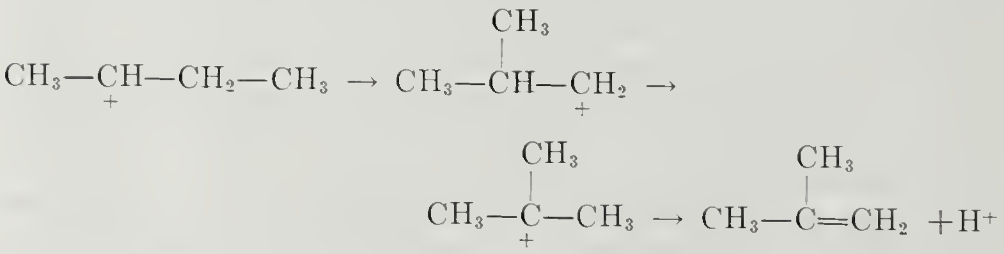
Several examples will demonstrate the reasonably satisfactory manner in which the carbonium ion theory explains the reactions of catalytic cracking.

Olefin Isomerization. By the addition of a proton from the catalyst a carbonium ion is formed from an olefin. Removal of a proton elsewhere gives a new olefin, which has the double bond shifted from the position in the first olefin.



$$CH_2{=}CH{-}CH_2{-}CH_3 + H^+ \rightarrow CH_3{-}\underset{+}{CH}{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH{=}CH{-}CH_3 + H^+$$

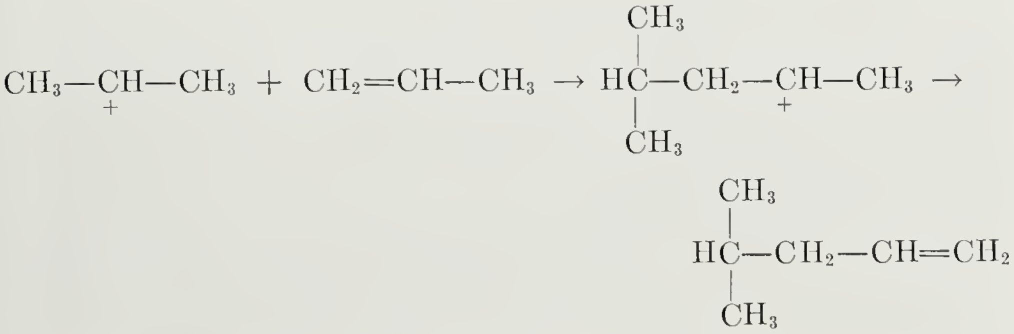
If methyl and hydrogen shifts occur in the carbonium ion an isomerized ion results which can release a proton to give a chain-isomerized olefin.



$$CH_3{-}\underset{+}{CH}{-}CH_2{-}CH_3 \rightarrow CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}\underset{+}{CH_2} \rightarrow CH_3{-}\underset{+}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \rightarrow CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + H^+$$

Olefin Polymerization. The carbonium ion formed from the initial olefin adds to the double bond of another olefin to give a large carbonium ion. When this loses a proton, an olefin polymer results. As Whitmore[124] showed, the carbonium ion rules applied to this process explain the usual polymer structures.

$$CH_2{=}CH{-}CH_3 + H^+ \rightarrow CH_3{-}\underset{+}{CH}{-}CH_3$$



$$CH_3{-}\underset{+}{CH}{-}CH_3 + CH_2{=}CH{-}CH_3 \rightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{HC}}{-}CH_2{-}\underset{+}{CH}{-}CH_3 \rightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{HC}}{-}CH_2{-}CH{=}CH_2$$

Olefin Cracking. The cracking of an olefin is essentially the reverse of the olefin polymerization reaction. A detailed consideration makes clear, moreover, why fragments are at least C_3 or larger. Suppose a primary carbonium ion is formed from a large olefin. The energy data discussed above show that secondary ions are much more stable than primary, and the very rapid double bond shifts observed over cracking catalysts signify that the conversion of the primary ion to a secondary must be rapid. Now the beta cracking of the secondary ion with the charge nearest the end of the chain will produce propylene and a new primary ion.

$$CH_3{-}\underset{+}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH{=}CH_2 + \underset{+}{CH_2}{-}CH_2{-}CH_3$$

Other secondary ions will produce larger olefins, while alternative beta scissions to produce methyl or ethyl ions that will be converted to C_1 and C_2 products will be rare, because of the larger energy requirements. The rather likely prior isomerization of a secondary ion to a tertiary ion by methyl shift will lead to branched olefins like isobutene as cracked products.

Hydrogen Transfer. The saturation of an olefin by hydrogen transfer is considered to be initiated by the formation of the carbonium ion from the olefin, as in the examples given above. This carbonium ion then abstracts a hydride ion (hydrogen atom with two electrons) from the "donor" molecule, thus becoming a paraffin. The donor molecule is now a carbonium ion, and may undergo the usual reactions.

$$CH_3{-}\underset{+}{CH}{-}CH_3 + RH \rightarrow CH_3{-}CH_2{-}CH_3 + R^+$$

This mechanism explains the more rapid selective saturation of tertiary olefins, for since tertiary ions are more stable they will form more rapidly or exist in higher concentration on a surface, and will thus give the high rates of formation of isobutane, isopentane, and others that are observed.

Cracking of Paraffins. In contrast to the olefins, whose high rate of cracking may be explained by the rapid addition of a proton to form a reactive carbonium ion, the paraffins are relatively inert. Thus it is evident that a slower step is involved in the formation of the hypothesized carbonium ion from a paraffin. A number of possible steps have been proposed[37], but further research is required to decide which come closest to the truth. Some proposals are:

(1) A small amount of olefin is formed by thermal cracking, and this is converted to carbonium ions which remove hydride ions from paraffins, and thus sets up a chain of reactions causing cracking.

(2) Removal of a hydride ion is effected by means of a proton from the catalyst. This would lead to traces of molecular hydrogen, as often observed.

(3) Dehydrogenation of a small amount of paraffin is brought about by means of traces of oxygen or by reactive carbon on the catalyst (Grosse[39]) to form olefins which react as in (1).

(4) A catalyst proton attacks a paraffin to cause splitting into a smaller paraffin and a carbonium ion.

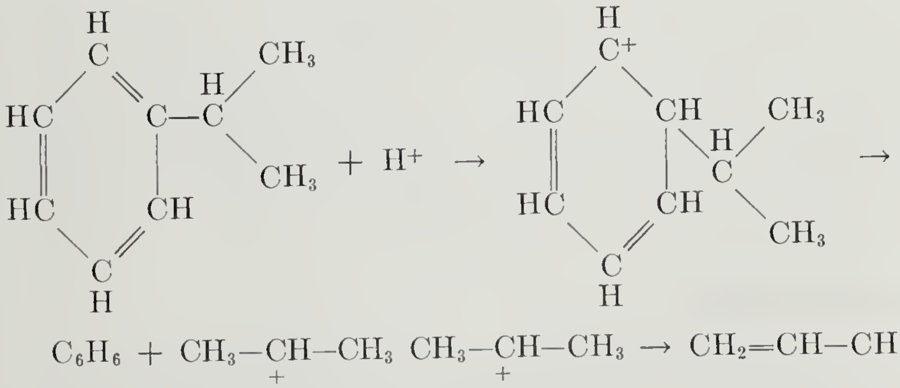
(5) A proton adds to form a complex CR_4H^+, which then breaks up as in (4). This has been implied by Weyl[120].

(6) An electron is transferred from a hydrocarbon to the catalyst to form a positive molecule ion, which may then react to form a carbonium ion. This view has been proposed by Franklin and Nicholson[27] on the basis of a correlation between activation energy for cracking and ionization potential for C_3 to C_6 *n*-paraffins. The correlation does not hold for branched paraffins or cyclohexane.

Once carbonium ions are formed, it is assumed that a number of steps follow, including isomerization of the ions, rupture to form olefins and smaller ions, rupture of the smaller ions, and removal of hydride ions from fresh paraffin molecules to form new ions to continue the sequence. Though olefins may be needed for the initial formation of carbonium ions the supply does not appear to be ordinarily limiting, for olefins are of course produced in abundance by the cracking, and, moreover, admixture of olefins with paraffins like hexadecane does not produce an appreciable acceleration of cracking. However, Hansford and co-workers[49] found olefins accelerated exchange of hydrogens between hydrated catalyst and paraffins. Much more needs to be known before satisfactory quantitative calculations can be made of carbonium ion concentrations. Nevertheless the rules that govern the behavior of these hypothetical ions explain nicely the products of paraffin cracking, as will be demonstrated in later examples.

Cracking of Naphthenes. The formation of carbonium ions from naphthenes evidently occurs in the same manner as with paraffins. The subsequent cracking is complicated by the existence of rings, which means that the first rupture may not produce two molecules, and by more extensive hydrogen transfer. Naphthenes often contain tertiary hydrogens and are therefore rather easily cracked. It has been shown, however, that when paraffins and naphthenes of equal carbon numbers contain the same number of tertiary hydrogens they crack at about the same rate. Thus Decalin and 2,7-dimethyloctane showed similar conversion[31].

Cracking of Aromatics. Aromatic compounds with alkyl groups attached are not as reactive as olefins over cracking catalysts, but are more active than paraffins. An attack of a proton or an acidic reagent on the aromatic ring must be involved in the cracking of an aromatic. There have been two hypothetical formulations of such attack, the first involving addition of a proton to form a conventional carbonium ion and the second involving a displacement of the attached group by an approaching proton[37], with the approach perhaps aided by the formation of a π complex. Brown and Brady[14] have presented evidence to show that a π complex is formed in association compounds, but that a true bond with the ring, or a σ complex, is the reaction intermediate in acid catalyzed reactions of aromatics. This point of view is preferred here, and the conventional carbonium ion formulation is used for aromatics since it explains the results as well as the other formulation does and in addition has the virtue of being uniform with the formulation used for olefins. The cracking of isopropylbenzene may be written as follows:



$$C_6H_6 + CH_3{-}\underset{+}{CH}{-}CH_3 \quad CH_3{-}\underset{+}{CH}{-}CH_3 \rightarrow CH_2{=}CH{-}CH_3 + H^+$$

The aromatic carbonium ion has other resonance forms which increase its stability over that expected for the form drawn.

In the cracking of alkyl aromatics the reaction is almost exclusively a severance of the entire alkyl group from the ring. This follows logically from the carbonium ion theory, once it is admitted that activation occurs through the ring, for only by the removal of the entire side chain can the stable aromatic ring be restored. Furthermore, data on the relative rates of cracking of different substituted benzenes have supplied three independent series, all of which agree beautifully with the carbonium ion concepts. (a) Under constant cracking conditions at 500°C methyl-, ethyl-, and isopropylbenzenes were decomposed to the extent of 1, 11, and 84 per cent, respectively[36]. These values are in the order expected from the relative stabilities of the carbonium ions that must break away from the aromatic ion in the rupture. (b) Normal, secondary, and tertiary butylbenzenes cracked to the extent of 11, 52 and 84 per cent at 400°C[36]. Again the relation of ease of cracking to the differences in energy of the intermediate carbonium ions is evident. (c) In a study of the effect of nuclear substitution on the rate of depropylation of cumenes over alumina-zirconia-silica catalyst, Roberts and Good[93] found that rates were in the order calculated for an electrophilic attack such as occurs in the addition of a proton to form an aromatic carbonium ion. Any substitution which tended to increase the electron density on the carbon atom holding the isopropyl group increased the reaction rate; and chlorine substitution, which decreases that density, decreased the rate. In the work of Roberts and Good it was assumed that the rate-limiting step was an electrophilic displacement by a proton, but the calculated order would be the same if the rate-limiting step were the formation of the ion.

In summary, the carbonium ion theory explains the chief characteristics of catalytic cracking except for the formation of aromatics from straight-chain compounds and the dehydrogenation of naphthenes like Decalin to form molecular hydrogen. These are not glaring misfits. Aromatic formation is in part understandable as a result of polymerization and dehydrogenation by hydrogen transfer. The dehydrogenation to molecular hydrogen observed with larger naphthenes implies the existence of a small activity for catalytic dehydrogenation, like that displayed by gamma alumina of high surface area. Similar aromatization and dehydrogenation reactions are observed with aluminum chloride, and are not well understood there either. Perhaps the weakest feature of the theory is the lack of definite knowledge about the mode of initiation of paraffin cracking. This requires further experimental evidence for clarification.

Hexadecane Cracking

Using the principles outlined above, the cracking of a typical normal paraffin, *n*-hexadecane, will be discussed in some detail. This will bring out more clearly certain features of the carbonium ion mechanism, and will show that the products obtained are indeed in good agreement with theoretical expectations.

An exact prediction of products would require careful consideration of all the secondary reactions of olefins, including saturation by hydrogen transfer which is much influenced by temperature and degree of conversion.

Since the purpose is to understand the primary cracking reactions, the products may be grouped together according to carbon number, thereby largely removing the effects of these secondary reactions from view. Table 9 presents a series of five experiments with hexadecane up to a twenty-five-fold increase of flow rate; other conditions were constant, and the percentage cracked varied from 11 to 68 per cent[37]. Excellent consistency of product distribution by carbon number is seen to hold, with only 5 per cent deviation from the average total 361 moles of hydrocarbon product per 100 moles hexadecane cracked. These data indicate that a uniform mechanism of primary cracking prevails, and that it should be possible to apply definite rules with the aim of predicting product distribution.

Table 9. Catalytic Cracking of Hexadecane

Temperature: 500°C
Pressure: Atmospheric
Catalyst: Al_2O_3-ZrO_2-SiO_2
Process Period: 1 hour

Flow rate, moles/liter/hr Conversion, % (through C_{14})	85.2 11.0	34.0 24.2	13.6 40.0	6.8 53.5	3.4 68.0
Moles Product/100 Moles Cracked[a]					
C_1	5	5	4	12	11
C_2	17	12	16	18	18
C_3	87	97	112	113	115
C_4	103	102	116	116	113
C_5	53	64	43	60	50
C_6	35	50	38	29	32
C_7	17	8	7	9	7
C_8	9	8	8	5	5
C_9	7	3	7	4	5
C_{10}	3	3	4	3	4
C_{11}	3	2	3	3	3
C_{12}	2	2	1	2	2
C_{13}	1	2	1	1	1
C_{14}	1	1	1	1	1
Total hydrocarbon	343	359	361	376	367
Hydrogen	12	12	14	9	12

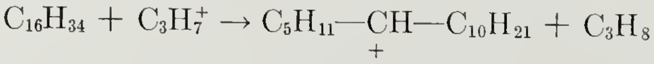
[a] C_{15} was not determined in these tests. In some similar experiments one mole of C_{15} product was obtained per 100 moles of hexadecane cracked.

The following mechanism[37] based on the properties of carbonium ions explains the cracking. The stepwise process in a certain formalistic sense shows parallelism to the Kossiakoff-Rice mode of thermal cracking[62, 113]. Thus, hydrogen is first removed from the molecule, leaving a hydrogen deficient entity, which then cracks at a carbon-carbon bond beta to the hydrogen deficient carbon atom, producing an alpha olefin and a new hydrogen deficient entity. The latter repeats the process until a small uncrackable group is left, which then becomes saturated by acquisition of hydrogen. However, applied to this generalized process are the definite, special properties of carbonium ions, which (A) govern the primary cracking reactions by (1) the preferential formation of certain initial carbonium ions, (2) the rearrangement of most primary to secondary ions, and some secondary to tertiary ions, and (3) the cracking of these ions into fragments not smaller than three carbon atoms each, and (B) govern many of the secondary reactions by (4) the almost complete equilibration of olefin double bonds, (5) the extensive skeletal isomerization of olefins, and (6) the saturation of olefins by hydrogen transfer. The product distribution with respect to (a) carbon number, as well as (b) paraffin/olefin ratio, and (c) paraffin and olefin isomers is thereby greatly altered from that of thermal cracking, and in a very characteristic and definable manner.

The cracking of *n*-hexadecane may be viewed as occurring in four stages.

Stage I: The hexadecane molecule first reacts with a proton or small carbonium ion at the surface of the catalyst to form hexadecyl carbonium ion by the loss of a hydride ion. Secondary hexadecyl carbonium ions immediately predominate, since there are twenty-eight secondary and only six primary hydrogen atoms, and the primary hydrogens are more slowly removed. Furthermore, any primary ions formed may rearrange to secondary ions before cracking.

Example:

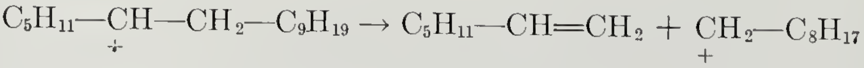


$$C_{16}H_{34} + C_3H_7^+ \rightarrow C_5H_{11}\text{—}\underset{+}{CH}\text{—}C_{10}H_{21} + C_3H_8$$

For simplicity, the important rearrangement of secondary to tertiary carbonium ions is here omitted.

Stage II: The carbonium ion splits at a carbon-carbon bond in a beta position to the carbonium ion carbon atom. The two electrons from this bond move to the original carbonium ion carbon atom and neutralize the single positive charge, simultaneously forming an ethylenic double bond. Thus, an alpha olefin is produced, and the other fragment becomes a primary carbonium ion.

Example:



$$C_5H_{11}\text{—}\underset{+}{CH}\text{—}CH_2\text{—}C_9H_{19} \rightarrow C_5H_{11}\text{—}CH\text{=}CH_2 + \underset{+}{CH_2}\text{—}C_8H_{17}$$

The olefin leaves the catalyst, perhaps first undergoing isomerization.

Stage III: The primary carbonium ion derived from cracking rearranges to a secondary carbonium ion and cracks "beta" to the carbonium ion carbon atom as before. This process continues until a carbonium ion which cannot yield fragments of three or more carbon atoms is produced, for example, a normal secondary C_5 carbonium ion. Methyl and ethyl carbonium ions are relatively hard to produce, as judged by their high electron impact appearance potentials from the parent paraffins, and although some methane and ethane may form, the amounts will be small, as found experimentally.

Table 10. Experimental and Calculated Products from Cracking of Hexadecane over Al_2O_3-ZrO_2-SiO_2

Product	Moles per 100 Moles Cracked															
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	Total
Experimental[a]	5	12	97	102	64	50	8	8	3	3	2	2	2	1	—	359
Calculated	0	0	95	97	72	41	7	6	5	4	4	4	4	0	0	339

[a] Conversion 24.0% at 500°C and 10 LHSV. 12 moles H_2 were obtained.

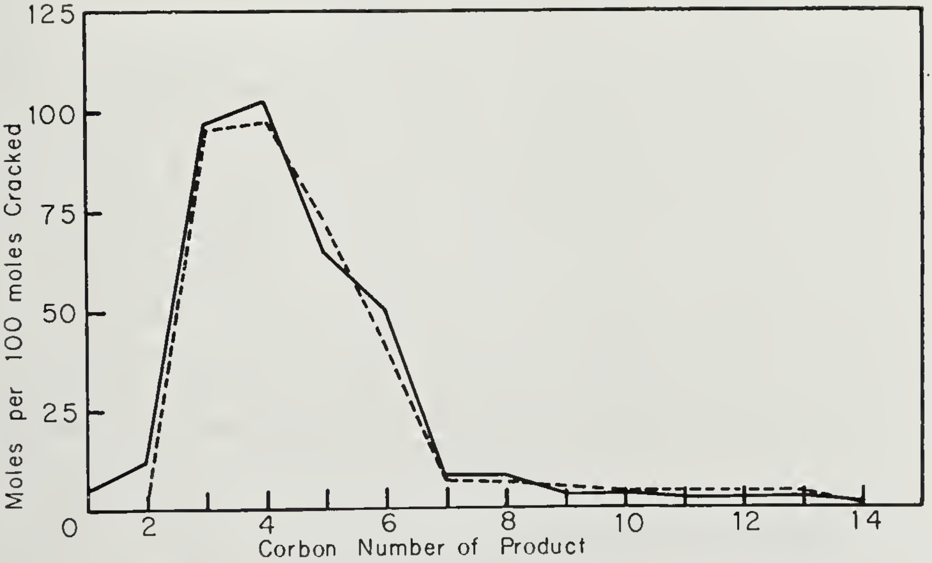


Figure 12. Catalytic cracking of *n*-hexadecane. Solid line: experimental products, 24 per cent conversion over alumina-zirconia-silica at 500°C. Dotted line: Calculated products, carbonium ion mechanism.

Example:

$$\underset{+}{CH_2}—C_8H_{17} \rightarrow CH_3—\underset{+}{CH}—C_7H_{15} \rightarrow CH_3—CH{=}CH_2 + \underset{+}{CH_2}—C_5H_{11}$$

Stage IV: The final carbonium ion from Stage III reacts with a new hexadecane molecule by hydride ion exchange to produce a small paraffin and a new hexadecyl carbonium ion as in Stage I, thereby propagating the reaction chain.

To illustrate the applicability of these rules to hexadecane the experimental and calculated product distributions by carbon number are shown in Table 10 and Figure 12. Good agreement is evident. Calculations were made on the following basis:

(a) Hexadecane forms carbonium ions by random loss of hydride ion from any secondary position.

(b) The secondary carbonium ion cracks at a bond beta to the carbonium ion carbon, forming an olefin, C_nH_{2n}, and a primary carbonium ion, $C_{16-n}H_{33-2n}$. Whenever alternative bonds are available for cracking, all are considered equally, providing that fragments C_3 or larger are formed. The primary carbonium ion then isomerizes by proton shift to an equal distribution of all possible secondary ions. Continued cracking and isomerization proceed as above until all ions are reduced to C_6 or smaller. These become small paraffins by acquiring a hydride ion.

(c) The olefins formed in the above cracking steps (b) react about to the extent expected from cracking tests with pure olefin feeds. Accordingly, half of the C_7 and higher olefins are assumed to form carbonium ions which then crack according to the rules outlined above.

The theory for the cracking of *n*-hexadecane as outlined here is not specific for the alumina-zirconia-silica catalyst, and might equally well be applied to other acidic oxide catalysts. When this is done the agreement is not always as good as shown in Table 10. For example, Gladrow, Krebs, and Kimberlin[29] found that the product distribution from the cracking of *n*-hexadecane over magnesia-silica was significantly different from that with an alumina-silica catalyst, especially in the smaller relative quantity of C_3 and C_4 and the larger relative quantity of C_6-C_{15} material. The results for material through C_5 from both catalysts, recalculated as moles per 100 moles of hexadecane cracked, are shown in Table 11, together with comparable results with clay, boria-alumina, and alumina-zirconia-silica. The alumina-silica gave somewhat more C_3 and C_4 than alumina-zirconia-silica, even after taking into account the different conversion level. The acid-treated clay and boria-alumina catalysts gave product distributions intermediate between those of the magnesia-silica and the alumina-silica. The products from magnesia-silica were explained by the supposition that the catalytic action was less intense so that there was less secondary cracking of primary products. This was borne out by the lower production of aromatics with magnesia-silica and by the low relative activity for cracking of *n*-heptane.

A fairly good theoretical calculation of the products from the cracking of *n*-hexadecane over magnesia-silica can be made by the present method by alteration of the somewhat arbitrary assumption, used with alumina-zirconia-silica, that one-half of the olefins above C_6 suffer secondary cracking. Thus, with magnesia-silica it may be assumed that less than one-half of the olefins above C_6 recrack, or that only those above C_8 are one-half recracked. With alumina-silica the adjustment must be made in the opposite direction to explain the results. Still, without any such adjustments the theory correctly predicts the large amounts of C_3, C_4 and C_5 material, the formation of isoparaffins, and the occurrence of more than one bond rupture per molecule cracked, features which are so characteristic of the decomposition of large *n*-paraffins with all cracking catalysts.

Effects of altering the cracking temperature are qualitatively predicted by the theory, inasmuch as higher temperatures would be expected to increase the further cracking of higher products and also to somewhat increase the less favored modes of rupture to form more methane and C_2 material.

TABLE 11. AMOUNTS OF LIGHTER PRODUCTS FROM *n*-HEXADECANE OVER VARIOUS CATALYSTS

Data from Gladrow, Krebs, and Kimberlin[29], except for Al-Zr-Si which is from Ref. 37. Catalyst component abbreviations are: Al, Al_2O_3; Si, SiO_2; Mg, MgO; Zr, ZrO_2; B, B_2O_3 .

Catalyst	Al-Si	B-Al	Clay	Mg-Si	Al-Zr-Si	Al-Zr-Si
Temperature, °C	510	510	510	510	500	500
LHSV	2	2	2	2	10	2
Period, hr	2	2	2	2	1	1
Conversion, %	45	57	42	51	24	54
Moles product per 100 moles hexadecane converted						
H_2	12	35	11	7	12	9
C_1	23	21	27	17	5	12
C_2	24	26	51	26	12	18
C_3	124	91	85	63	97	113
C_4	130	106	90	92	102	116
C_5	57	56	51	58	64	60
Weight % of converted hexadecane						
C_6-221°C	18.0	29.5	35.3	40.8	32.2	24.4

Cracking of Hexanes

Cracking data for the five hexane isomers over alumina-zirconia-silica make possible calculation[37] of the relative reactivities of primary (P), secondary (S), and tertiary (T) hydrogens. The resulting coefficients are P = 0.62, S = 1.29, and T = 12.3 per cent of charge. These coefficients, when multiplied by the number of C—H bonds of corresponding type, add up to the extent of cracking of a given hexane isomer under the particular conditions applied.

Hexane Isomer	Number and Type of C—H Bonds	Percentage Cracked
2,3-Dimethylbutane	12 P + 2 T	32
n-Hexane	6 P + 8 S	14
2,2-Dimethylbutane	12 P + 2 S	10

The relative values for the three coefficients are close to 1, 2, and 20 for P, S, and T at 550°C. For comparison, the Kossiakoff-Rice thermal values at 500°C are 1, 3.66, and 13.4[62].

These data lead to the conclusion that the relative rates of removal of hydride ions fall in the same order as those for the removal of hydrogen atoms, but the values are different. Of particular significance is the high value for tertiary hydrogen for cracking with an acidic oxide catalyst, which is in line with the relatively easy formation of a tertiary carbonium ion.

TABLE 12. CATALYTIC CRACKING OF HYDROCARBONS AT 550°C OVER Al_2O_3-ZrO_2-SOi_2

Hydrocarbon	Percentage Conversion Experimental	Percentage Conversion Calculated[a]	Numbers and Types of C—H Bond Present
a) 2-Methylpentane	25	23	9 P, 4 S, 1 T
b) 3-Methylpentane	25	23	9 P, 4 S, 1 T
Ratio a/b	1.0	1.0	
a) Isooctane	49	24	15 P, 2 S, 1 T
b) *n*-Octane	42	19	6 P, 12 S
Ratio a/b	1.2	1.3	
a) *n*-Dodecane	35	30	6 P, 20 S
b) Isododecane	32	31	21 P, 4 S, 1 T
Ratio a/b	1.1	1.0	

[a] Feed space rates were not the same for the different groups of isomers, and also the effect of molecular weight enters for C_8 and C_{12} so that only the ratios a/b are expected to agree for these.

Applying these numbers to the cracking of the two other hexane isomers, good agreement is obtained, as shown in Table 12. In addition, data for the cracking of two octanes and two dodecanes are shown, with good agreement of relative rates. The effect of molecular weight on the extent of cracking is not simple and thus has not been considered in Table 12.

The determinative influences of the numbers and types of carbon-hydrogen bonds on the extents of cracking provide strong evidence that the carbon-hydrogen bond is the point of attack in paraffins. The hexanes also supply evidence on rearrangement of the carbonium ions prior to cracking. The production of large amounts of C_3 from 3-methylpentane[31] can be explained only in this way.

Evidence from Hydrogen Exchange

Very strong support for the carbonium ion theory comes from the exchange experiments described in the discussion on reactions of catalytic cracking. These hydrogen exchange experiments, followed by means of deuterium, were of two types, namely those between hydrated catalyst and hydrocarbons and those between two hydrocarbons. The occurrence of hydrogen exchange at temperatures well below cracking temperatures proves that hydrogen atoms are removed from, and added to, hydrocarbon molecules as required by either carbonium ion or radical mechanisms. A more rapid exchange when tertiary hydrogens are present in the molecule is again in agreement, especially with a carbonium ion mechanism. The interesting data on isobutane exchange merit more detailed theoretical discussion, even though the hydrated catalysts employed differ somewhat from the usual drier catalysts.

With isobutane both the experiments of Hansford and co-workers[49] and those of Hindin and co-workers[52] showed that various deuterated butanes were formed when isobutane was contacted with a catalyst that had been treated with deuterium, but that there were never (except in merest traces) more than nine deuterium atoms in the exchanged isobutane. This evidently means that deuterium atoms never occupy the tertiary position. Now this can be nicely explained by the theory, as has also been pointed out by Hansford[46] and by Hindin, Mills, and Oblad[52]. Hansford has supplied a quite detailed picture of the exchanges in terms of polarized olefin, an initiating catalyst-hydrocarbon complex, adsorbed isobutane, and a propagating catalyst-hydrocarbon complex. A somewhat modified explanation is given here. It is presumed that a hydride ion is removed from the tertiary position of the isobutane, leaving a positive charge on the tertiary carbon. This *tert*-butyl carbonium ion is activated for exchange, and as it resides on the catalyst rapidly exchanges its nine primary hydrogens for the deuteriums already on the catalyst. In these exchanges it may be considered that protons leave the butyl ion and are replaced by deuterons, for the beta rupture of the butyl ion would produce a proton and isobutene, while the catalyst deuterium, probably present in hydroxyl groups, is strongly ionic and can readily go off as a deuteron. The positive tertiary carbon of the carbonium ion cannot accept a positive deuteron, nor will a deuteron add to this position in transiently formed isobutene, for this would form the less stable primary ion. Hence no deuterium appears in the tertiary position in the final product. Instead, the tertiary carbon extracts a hydride ion from an isobutane molecule. Thus the deuterium atoms come to occupy the nine primary positions in the methyl groups, while only hydrogens are to be found in the single tertiary position.

A beautiful confirmation of this picture is seen in the experimental result of Hindin, Mills, and Oblad[52] on the exchange between isobutane containing a deuterium atom in the tertiary position and ordinary isopentane. This exchange occurred readily over alumina-silica (degree of hydration not specified) and produced isopentane containing essentially only one deuterium, as would be expected for the hydride ion transfer from one tertiary position to the other. It is gratifying to note that the exchange reactions between isobutane and deuterosulfuric acid[82] display much the same characteristics as do those between isobutane and a hydrated cracking catalyst.

Later studies by Hindin, Mills, and Oblad[51] gave some evidence for deuteration of the tertiary position in 2-methylpentane after one hour over a deuterated catalyst at 150°C. This might be explained by some removal of secondary hydride (deuteride) ions in the neutralization of the tertiary carbonium ion, or perhaps also by some reversible isomerization to dimethylbutane with accompanying exchange.

Adsorption and Active Sites

Zabor and Emmett[126] measured the adsorption of *n*-butane, *n*-heptane, and *n*-octane on an alumina-silica catalyst from room temperature up to and above the temperature at which decomposition began to be appreciable. There was considerable physical adsorption of all three paraffins at temperatures around 50°C, but at the incipient cracking temperatures (424° for butane, 215° for heptane), and at higher temperatures as far as could be judged, there was very little if any adsorption, the upper limit being placed at 0.1 cc of vapor per gram of catalyst. There was no sign of any acitvated adsorption. It may be asked whether this finding is consistent with the present theory of cracking, for the theory demands that reacting molecules be held on the catalyst surface. The answer is that there is no real inconsistency, since the amount of hydrocarbon (other than coke, which forms slowly) that needs to be present on the catalyst at any one time to satisfy minimum theoretical requirements is very small, of the order of 10^{-10} millimoles per gram, even if it is assumed that the residence time on a site for an activated, reacting molecule is of about the duration between ten collisions with that site. The upper limit on the amount of adsorbed gas found by Zabor and Emmett is 5×10^{-3} millimoles per gram. These investigators recognized that this small adsorption was compatible with a surface reaction, and pointed out that if the carbonium ion theory is to explain the cracking, then the slow step in the mechanism must be that of the formation of the carbonium ion.

The number of acid sites in a cracking catalyst can be estimated in various ways. One way is to suspend the catalyst in benzene and titrate with *n*-butylamine, using *p*-dimethylaminoazobenzene as indicator[59, 113]. This determination gives values of about 0.5 milliequivalents of acid per gram of catalyst for a fairly active catalyst. It appears, however, that all these acid sites are not equally active. Mills, Boedeker, and Oblad[69] found a chemisorption of 0.022 millimoles of quinoline per gram on a cracking catalyst of 12.5 per cent aluminum oxide and 273 m²/g surface area at 427°C. A presumably similar chemisorption of quinoline prior to cracking a gas oil lowered the gasoline yield from 45 to 15 per cent. The poisoned activity may be estimated to be about one-tenth of the original on the basis of relative LHSV's for equal cracking. The quinoline causing this deactivation was only enough to cover 2 per cent of the surface. This is strong evidence for the existence of a limited number of active sites.

Haldeman and Emmett[44] calculated the following quantities for a 10 per cent aluminum oxide-90 per cent silica catalyst treated with deuterium oxide and used for isobutane exchange. The catalyst area was 249 m²/g.

Amounts in millimoles/gram of catalyst

Total silica, SiO_2	15
Total aluminum, Al	1
Water left after evacuation at 500°C	0.5.
Calculated H^+ sites after evacuation, from exchange rate	0.0015
Added water to then give maximum exchange rate	0.03
Assumed acid sites from added water	0.03
Quinoline to give complete poisoning, from data of Mills *et al.*[69]	0.01[a]

[a] The amount of quinoline for complete poisoning is not clearly given by Mills, Boedeker, and Oblad[69]. For a 12.5 per cent aluminum oxide catalyst of area 273 m²/g, one may estimate from their data an amount of about 0.02–0.04 millimoles/g.

It is evident that each aluminum atom does not produce an independently active site. Haldeman and Emmett concluded that small amounts of water (0.03 millimoles/g) activated Lewis acid sites and made possible activated adsorption of isobutane. They also pointed out that an isobutane molecule undergoing exchange was equilibrated with the 30 deuterium atoms on 1000 A² of catalyst surface.

A calculation of the number of molecules of isopropylbenzene cracked by a single active site was made by Mills, Boedeker, and Oblad[69]. They calculated the number of active sites per gram from the amount of quinoline that could be chemisorbed. In a 30 minute experiment at 8 LHSV and 425°C about 35 per cent of the isopropylbenzene was cracked. This corresponds to 340 molecules cracked, on the average, for each active site.

KINETICS

Quantitative expression of rate data for catalytic cracking is difficult because of the many reactions and the gradual decline of catalyst activity through coke formation. A complete knowledge of kinetics would supply data on the rates of all of the reactions (including coke formation) as functions of vapor composition, temperature, pressure, and the amount of coke on the catalyst at any given time. From such data over-all average conversions could be computed for a feed of known composition passed through a fixed bed reactor at a given space velocity and process period. Likewise an average conversion could be computed for a fluidized catalyst reactor provided the degree of mixing in the reactor were known. Corrections might have to be made for temperature gradients and for the rate of access of gas to the interior surfaces of catalyst particles. Data of such scope do not yet exist, but a goodly amount of valuable information has accumulated.

In this discussion emphasis is placed on the kinetics of cracking in small fixed bed apparatus, since such equipment has been employed in most studies designed to test catalysts and to find the physical and chemical laws governing reaction rate. Large scale commercial reactors and pilot plants using fluidized or moving beds of catalyst have indeed been the subjects of many practical studies with petroleum fractions as feeds, and valuable correlations regarding products and the effects of operating variables have been obtained. The annual reviews of Haensel and Sterba[42, 100], Appell and Berger[3], and the articles of Shankland[96] and Sittig[98] are excellent guides to this literature.

The experimental methods used for testing of catalyst activities or for determination of rates are described in many articles, including those of Conn and Connolly[18], Grote, Hoekstra and Tobiasson[40], Hansford[46], Ivey and Veltman[56], Rescorla, Ottenweller and Freeman[92], and Shankland and Schmitkons[97].

Variables Governing Rate

The principal variables which determine the extent of a given reaction in fixed bed catalytic cracking are:

(1) The intrinsic catalyst activity. This may be further broken down, if desired, into catalyst type, particle size, porosity, age, surface area per unit weight, activity per unit area, and other catalyst characteristics.

(2) Flow rate or contact time. The hydrocarbon flow rate (moles per liter per hour or volumes per volume per hour) is considered to be more definite and perhaps more fundamental than contact time, which may be calculated in a number of ways. Contact times are useful, however, in estimating the amount of concurrent thermal cracking. Contact times in catalytic cracking usually fall in the range from 2 to 20 seconds.

(3) Temperature.

(4) Total pressure.

(5) Diluents or inert materials.

(6) The average amount of coke on the catalyst. With given feed and operating conditions, this is chiefly governed by the initial coke content and the process period or catalyst holding time.

(7) Composition of the hydrocarbon feed, including inhibitor content. In fluidized catalyst systems or with moving catalyst beds the variables are much the same, but the weight ratio of catalyst feed rate to oil feed rate may be used rather than catalyst holding time to define the variable governing average coke content of catalyst.

Catalyst activity has a decisive influence on reaction rates. Catalysts of widely varying activities per unit area and of widely varying areas per gram have been tested. This subject will be further discussed in the chapter on cracking catalysts in Volume VII of this series.

Total pressure does not have a large effect on cracking rate. Some data with a gas oil are given by Whitaker and Kinzer[123]. The rate, expressed as moles converted per unit weight of catalyst per hour at constant feed rate, increased about 20 per cent when the pressure was increased from one to two atmospheres absolute. In another case of gas oil cracking the rate was half order in oil pressure, according to the kinetic analysis of Blanding[8]. Weisz and Prater[119] showed for cumene cracking that the pressure coefficient depended on temperature, diluents, and inhibitors. Very high pressures (100 to 1250 atm.) were found by Gonikberg and co-workers[30] to accelerate heptane cracking over an alumina-silica catalyst.

Temperature rise invariably increases the rates of reactions over cracking catalysts, but the temperature coefficients of the different reactions vary considerably. Apparent activation energies range from about 10 to about 35 kcal per mole.

Considerable evidence is available on the effects of flow rate and process period. For the conversion of a gas oil to gas, lower boiling products, or coke, Voorhies[118] presented empirical kinetic equations that are useful. If V is the inlet flow rate, volumes of oil per volume of catalyst per hour (same as LHSV), θ is the process period in minutes, and x is the total fraction converted, then the cracking of East Texas Gas Oil over fresh alumina-silica catalyst at 850°F in a fixed bed is described by the equation of Voorhies as

$$x = 0.96(V)^{-0.34}(\theta)^{-0.19} \tag{1}$$

This x is the average conversion for the process period θ. Since the catalyst activity has been declining from the start, the instantaneous conversion at the end of any given process time is less than the average for that process time. Let $f(\theta)$ be the instantaneous conversion. Then

$$\int_0^\theta f(\theta)\, d\theta = x\theta \tag{2}$$

By substituting the value of x from Eq (1) and differentiating both sides with respect to θ it may be seen that the instantaneous conversion is 0.81 times the average conversion.

$$f(\theta) = 0.81\,x = 0.78\,(V)^{-0.34}(\theta)^{-0.19} \qquad (3)$$

These equations and others from Voorhies for the amount of carbon on the catalyst have been used for the construction of Figures 1, 2, and 3 previously presented. These equations were based on values of θ and V such that x was between 0.3 and 0.7. Although specific for a particular case, they furnish an example of the rate of decline of activity with time.

Voorhies made the important observation that the carbon deposited on the catalyst after a given period at a given temperature was relatively independent of the feed rate for gas oil, hexadecane, or Decalin. This means that when a given feed is cracked at various flow rates, with constant temperature and process period, the coke on the catalyst is relatively constant and meaningful kinetic equations may be derived, as in the following paragraphs.

Conversion Equations for Fixed Beds

An empirical equation like (1) has limitations. It is natural to seek an equation based on an integral order of reaction, though it is clear that heterogeneously catalyzed reactions need not have integral orders. Also, for kinetics, a pure hydrocarbon feed is more suitable than a gas oil because the composition of the uncracked material does not change with conversion. A few examples of cracking kinetics for pure hydrocarbons are reviewed here and in the following section.

Some data for cracking of n-hexadecane at 500°C and atmospheric pressure with a one-hour process period over alumina-zirconia-silica are[37] tabulated below.

RATE DATA FOR HEXADECANE CRACKING

S = flow rate, moles/liter/hour	x = fraction converted
85	0.11
34	0.24
13.6	0.40
6.8	0.535
3.4	0.68

These data may be fitted moderately well by the equation for a reaction first order in the presure of undecomposed hexadecane. For a flow system at constant pressure and a reaction of the type $A \rightarrow nB$ the basic differential equation may be taken as $-dN_A/dt = kWP_A$, where N_A is moles of A, t is time in hours, k in the rate constant in moles/kg/hr atm., W is catalyst weight in kg, and P_A is partial pressure of A in atmospheres. To obtain an over-all conversion equation the differential equation is applied to a small increment of catalyst volume, dV, and integration is performed over the whole volume. Let g = catalyst density, kg/l. Then in the increment dV the catalyst weight is gdV, and the rate is $-dN_A/dt = kWP_A = kgP_AdV$. A material balance on feed reacted in the increment of volume then gives $kgP_AdV = Fdx$. Here F is the inlet flow rate in moles per hour, and dx is the incremental fractional conversion. After substituting $P_A = (1 - x)P/[1 + (n - 1)x]$, integration gives $kgVP/F = -n \ln (1 - x) - (n - 1)x$ or, substituting $S = F/V$ = inlet space velocity in moles per liter of catalyst per hour,

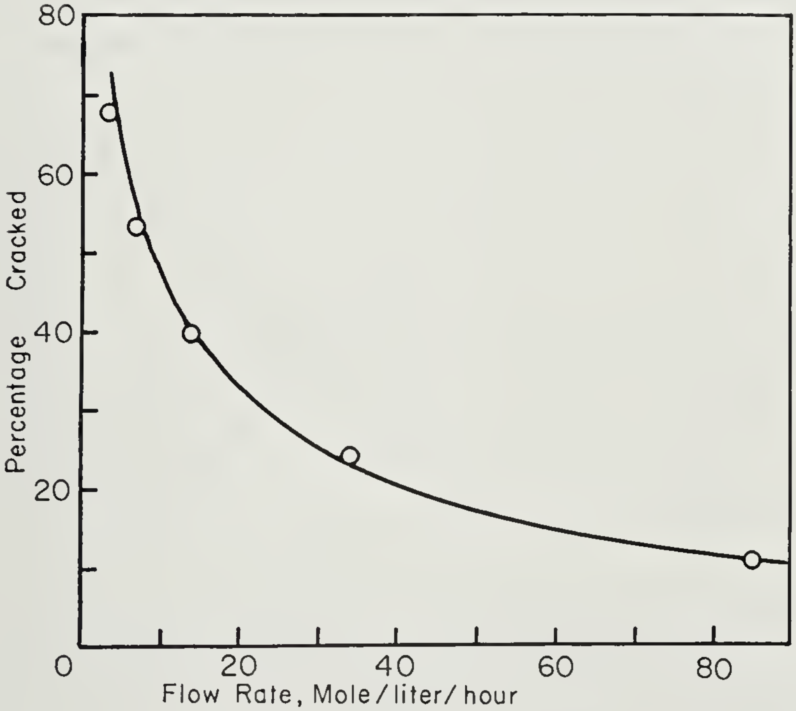


Figure 13. Approximate fit of hexadecane cracking rate by first-order equation. Points experimental[27]; line calculated for first-order equation for n = 4 (see text Eq. 4).

$$kgP/S = -n \ln (1 - x) - (n - 1)x \tag{4}$$

The derivation and use of such an equation for flow systems were discussed in 1931 by Benton[7], and later by many others. Figure 13 shows the experimental points for the cracking of n-hexadecane and the curve calculated by means of Eq. (4) with n = 4 and k chosen to fit at x = 0.4. Agreement is fair.

A somewhat better fit without additional empirical constants is obtained with an equation for a first-order reaction inhibited by the first power of one product. Taking the rate law as $-dN_A/dt = kWP_Ab_A/P_Bb_B$ and integrating for a flow system gives

$$kgb_A/b_BS = k'g/S = -\ln(1 - x) - x \tag{5}$$

where the symbols are as before and b_A and b_B are adsorption coefficients. Such an equation has been used by Topchieva and co-workers[111] to represent the cracking of hexadecane and Decalin. It is considered to be a useful simple equation. An equation of this form has also been used by Panchenkov and co-workers for the cracking of gas oils, Decalins (*cis*, *trans*, and mixed), cetene, and cumene over alumina-silica catalysts of a range of compositions. This work has been summarized by Panchenkov[84] in French. Agreement with the equation is fairly good, as the example for *trans*-Decalin in Figure 14 shows. The straight line of the plot should have unit slope; in Figure 14 it is too great.

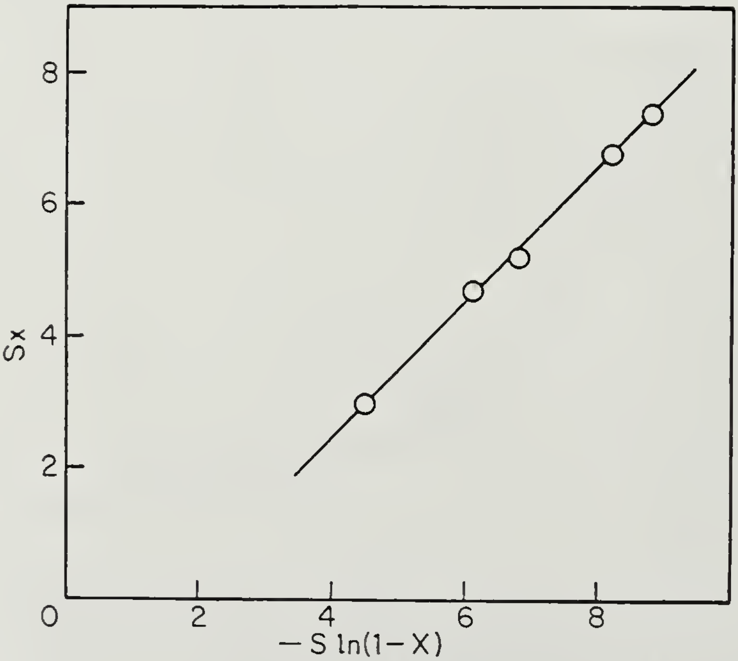


Figure 14. Rate data for cracking of *trans*-decalin at 450°. (After Panchenkov and Krasivichev[84, 85]). Flow rates, *s*, in relative units only.

The next step in setting up a more exact theoretical rate equation is to assume a certain type of adsorption, say Langmuir, and express the rate of reaction in terms of rate constant and all adsorption coefficients, assuming that the reaction rate is proportional to the amount of reactant adsorbed on the catalyst surface. When this is done for a flow system with a fixed bed of catalyst, using the same terminology employed above, the differential equation for a reaction of the type $A \rightarrow nB$ is

$$-dN_A/dt = kP_Ab_A/(1 + P_Ab_A + \sum P_ib_i)$$

and for a flow system this integrates to

$$\alpha P/S = -\ln (1 - x) - \beta x \tag{6}$$

where

$$\alpha = kb_A g/(n + P\sum b_i)$$

and

$$\beta = (n - 1 - Pb_A + P\sum b_i)/(n + P\sum b_i).$$

The b's are adsorption equilibrium constants in the units of 1/atm, A represents the reactant and the i's the products. Equation (6) contains one more adjustable constant than Eqs. (4) or (5) and naturally gives better agreement with the data.

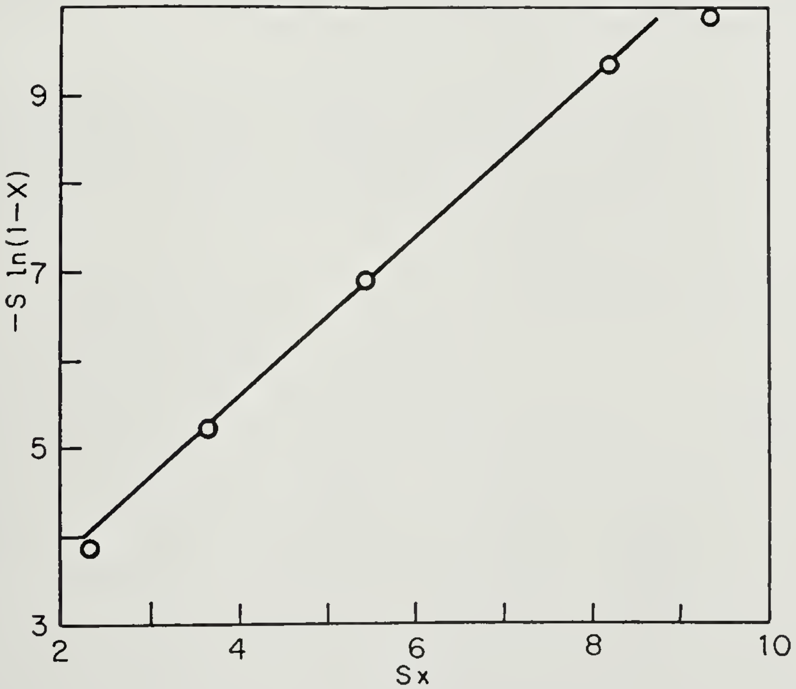


Figure 15. Test of kinetic Eq. (6) for n-hexadecane cracking.

Equation (6) is identical with the one proposed by A. V. Frost[28] for catalytic cracking. The data for hexadecane given above fit this equation fairly well, for when $-S \ln (1 - x)$ is plotted against Sx a nearly straight line results, as is seen in Figure 15. The line drawn gives a value of $\beta = 0.91$. If all the b's were small, β would be 2.8/3.8 or 0.74. The fact that it is greater means that $\sum b_i$ is greater than b_A, and this in turn means inhibition by the products, which is reasonable since olefins and aromatics in the products will be more strongly adsorbed than a saturated hydrocarbon feed. Numerical data on quantities which should be constant for exact fits of Eqs. (4), (5), and (6) are listed in Table 13.

A special case of kinetics governed by adsorption of the product is met in the polymerization of propylene. This is a simple reaction for testing activity. In propylene polymerization over a series of alumina-silica catalysts at 200°C in a constant volume system, Johnson[59] found the rate was that of a first-order reaction retarded by products. Thus, if $y = P_0 - P =$ pressure drop, $dy/dt = k(P_0 - y)/(1 + by)$, where P_0 is the initial pressure and b is an adsorption coefficient. On integration over t and y there results

$$kt = (1 + bP_0) \ln P_0/(P_0 - y) - by \tag{7}$$

Activities measured by k's obtained from this equation were linearly related to titratable acidity in the series of catalysts.

Table 13. Kinetics of Cracking of n-Hexadecane

Experimental data from Greensfelder, Voge and Good[37], for cracking at 500°C, 1-hour period, atmospheric pressure, and Al_2O_3-ZrO_2-SiO_2 catalyst. S is the inlet flow rate in moles/liter/hour, x is the fraction converted, and n is moles of product per mole of n-hexadecane converted. For an exact fit the calculated quantities in a given column would be constant.

Experimental Data			Calculated Quantities		
S	x	n	First order, $S[-4 \ln (1 - x) - 3x]$	First order inhib., $S[-\ln (1 - x) - x]$	Langmuir $S[-\ln (1 - x) - 0.91x]$
85	0.11	3.6	11.6	0.55	1.40
34	0.24	3.7	12.9	1.18	1.92
13.6	0.40	3.8	11.4	1.48	1.97
6.8	0.535	3.8	9.9	1.57	1.90
3.4	0.68	3.8	8.5	1.56	1.77

A few other examples of kinetic studies with pure hydrocarbons may be found in the literature. For example, Blue and Engle[10] observed hydrogen transfer from Decalin to butenes and found it to be approximately first order in unconverted butenes, with an activation energy of about 10 kcal. Coke formation rates and the effects on hydrogen transfer rates were described.

Often rate data are desired for comparing activities of a series of different catalyst samples. To reach this end it is not necessary to know the order of the reaction or even to have an empirical equation relating conversion to flow rate. All that is required is an experimentally determined curve of conversion vs. flow rate for the standard catalyst of the series. An experimental determination of the conversion at a single flow rate with another catalyst under the same conditions then enables one to compute the activity of this catalyst relative to the standard catalyst, for both theory and experiment agree in saying that the activities are proportional to the flow rates required for a given conversion, provided the reaction kinetics are the same. Such a comparison, however, ignores any difference in the average effects of the coke deposits.

Rate of Cracking of Alkylbenzenes

Isopropylbenzene (cumene) has frequently been used for testing the activity of catalysts as well as for studies on kinetics because of the ready and simple cracking to benzene and propylene. Ballod and co-workers[6] have fitted rate data for a flow system by the equation $\alpha/V = -\ln(1 - x) - \beta x$ which is essentially like Eq. (6). Here α is proportional to the rate constant, and V is the inlet LHSV, and β is an inhibition constant. Topchieva and Panchenkov[84, 110] have fitted rate data for the cracking of isopropylbenzene by an equation like (5), while Obolentsev and Gryazev[80] use a more empirical equation with the integrated form

$$\ln(m) - \ln(m - x) = at^b \tag{8}$$

Here m is the maximum fraction that can be dealkylated at the temperature, x is the fraction actually dealkylated, t is the contact time (proportional to $1/V$), and a and b are constants.

The kinetics of cracking of isopropylbenzene were studied intensively by Corrigan, Garber, Rase, and Kirk[19], using an almina-silica catalyst. Seven possible mechanisms were considered and examined for individual rate-controlling steps. Evidence indicated a single site surface reaction was controlling, and a rate equation of the type of Eq. (6) above was derived. Pressure effects on rate were measured, but, as Weisz and Prater[119] have pointed out, these are largely a result of the diffusion limitation in the 4–6 mesh beads. Corrigan and co-workers themselves showed that only the outer half millimeter or so was fully effective for reaction.

In a later article Rase and Kirk[91] reported kinetic data on the cracking of 8 monoalkylbenzenes with C_2 to C_5 alkyl groups. The critical step in the mechanism was assumed to be the reaction of adsorbed alkylbenzene to give adsorbed benzene and an olefin. Adsorption constants were estimated from rate data.

Plank and Nace[89] added much new knowledge about the cracking of isopropylbenzene. They showed that cumene hydroperoxide is an inhibitor of cracking and also causes increased coke formation. The coke itself causes little or no inhibition, for as shown in Figure 16 activity levels out in a steady state of inhibitor adsorption though coke continues to increase. Nitrogen bases and styrene are also strong inhibitors.

A kinetic scheme was developed by Plank and Nace[89] and also by Weisz and Prater[119] on the basis of a competition between cumene, C, and inhibitor, P, for adsorption on the active sites. Adsorbed inhibitor was presumed to react in part to form non-inhibitory coke. The cracking rate in the presence of inhibitor is $R_p = [dC/dt]_p = kC_A$, where C_A represents adsorbed cumene. In the absence of inhibitor it is $R_0 = [dC/dt]_0 = kN$, where N represents active sites. Then it may be shown that at the steady state

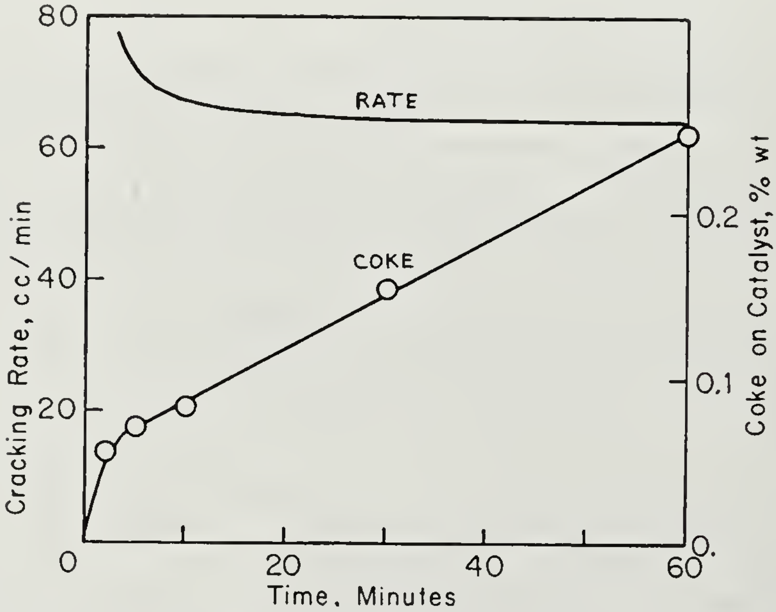


Figure 16. Cracking rate and coke formation with purified cumene over an alumina-silica catalyst of 212 m²/g area. (After Plank and Nace[89].)

Table 14. Relative Strengths of Inhibitors for Cumene Cracking, from Plank and Nace[89]

Compound	Inhibitor adsorption ratio (K)
Imidazole	9250
Quinaldine	3100
Quinoline	2900
Pyridine	1200
Piperidine	900
Indole	850
n-Butylamine	200
Cumene hydroperoxide	200
Styrene	40

$$R_0/(R_0 - R_p) = 1 + C_0(1 - x)/KP_0, \tag{9}$$

where C_0 and P_0 are mole fractions of cumene and inhibitor in the charge, x is the fraction of cumene converted, and K is

$$\frac{k_3/k_4}{k_1/(k + k_2)}.$$

Here k is the reaction rate constant, and k_1, k_2, k_3, and k_4 are adsorption and desorption rate constants in the adsorption reactions

$$C \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_A \qquad \text{and} \qquad P \underset{k_4}{\overset{k_3}{\rightleftarrows}} P_A$$

Equation (9) fits the data quite well. Some values of the inhibitor strength ratio, K, are shown in Table 14.

Effect of Process Period

The previous Eq. (1), cited from Voorhies, included a factor for the effect of process period. A more extensive treatment was given by Blanding[8] in an important paper on the kinetics of catalytic cracking. For the present purpose the most interesting thing in Blanding's paper is the curve relating instantaneous activity to process period (cycle time, as he calls it). He first introduced a method for approximating total conversion of a feed of wide boiling range, called "20+ conversion." This is

$$\text{“}20 + \text{conversion''} = 100 - \left[\begin{matrix}\%\text{ on feed of liquid product}\\ \text{boiling above feed }20\%\text{ point}\end{matrix}\right] \Big/ 0.8$$

Using such conversions he derived a rate law showing rate at constant pressure and process period to be proportional to the second power of unconverted feed. This led to an integrated equation of the form

$$kP/V_w = kgP/Vd = 1/(1 - x) \tag{10}$$

where k is a rate constant, P is pressure, V_w is the weight of oil per hour per weight of catalyst (WHSV), g is catalyst density, d is oil density, V is volume of oil per hour per volume of catalyst (LHSV), and x is fraction converted. This equation applies to catalyst beds with piston flow of reactants. Like other simplified conversion equations it is only an approximation to the truth.

Using Eq. (10), Blanding obtained cumulative and instantaneous rate constants for the cracking of a gas oil over a clay catalyst and a synthetic alumina-silica. By including data obtained by flowing oil and catalyst together through a heated coil he was able to cover a range of process periods from one second to 200 minutes. Activity declined rapidly with time. Figure 17 shows the instantaneous activity of a fresh alumina-silica catalyst as a function of process period in the cracking of an East Texas gas oil at 850°F and atmospheric pressure. This is a log-log plot, and a straight line is obtained in functional agreement with Eq. (3) above. (To get a quantity comparable to a rate constant from Eq. (3), compute values of V for an instantaneous conversion of 0.5).

Blanding plotted instantaneous activity in a different way, and extrapolated to an initial activity of 1500, relative to a 60 minute activity of about 2.5. The initial value is not well established, but there is no doubt about the rapid change with time. Because the change with time will vary, depending on the catalyst, feed, and cracking conditions, many comparisons made in the past contain a hidden and variable catalyst fouling factor. Blanding noted the importance of this effect, and showed that correcting for it changed the apparent activation energy for gas oil cracking from 20 to 10 kcal. The hidden fouling factor also affects comparisons of crackabilities of feeds and of activities of different catalysts.

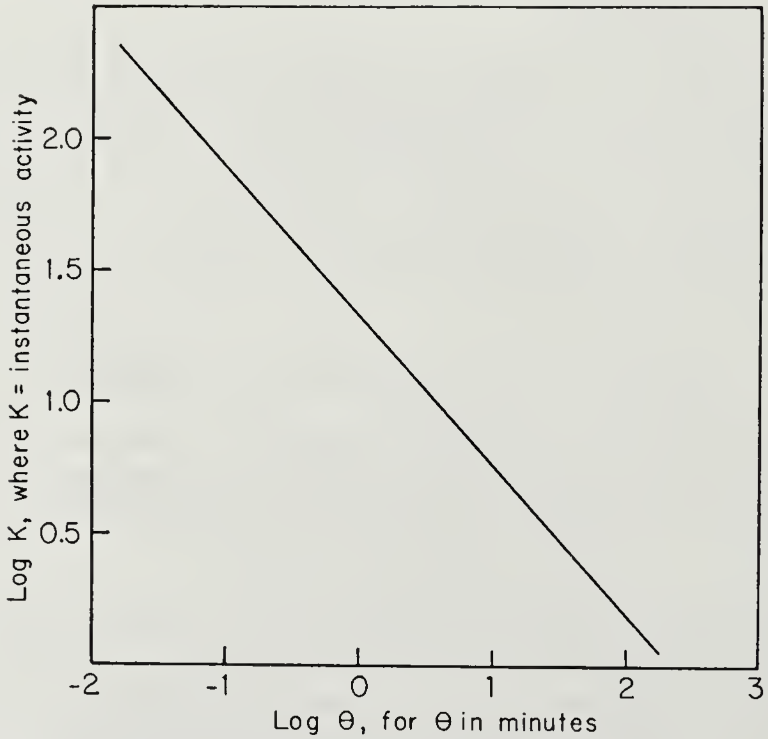


Figure 17. Instantaneous activity as a function of process period for cracking East Texas gas oil at 850°F. (After Blanding[8].)

There are circumstances in which the change of activity with time is very small, however. Thus, in the cracking of pure cumene[19, 89], and in the cracking of C_4 to C_7 paraffins[27], the declines of activity in a few hours were almost negligible. One is forced to the conclusion that each case must be considered individually, and that usually the determination of complete activity-time and coke-time curves is necessary for full knowledge.

Sometimes the effect of process period is so great that two catalysts do not show the same relative activities or product distributions when they are compared at different process periods. Because effective process periods are less than 15 minutes in most commercial cracking, and laboratory tests sometimes use periods of an hour or more, this effect poses a problem. Whitaker and Kinzer[123] have suggested that laboratory tests be made at two or more process periods. A plot of log conversion or log coke-on-catalyst against log of process period is approximately linear and may be extrapolated to the time corresponding to commercial operation.

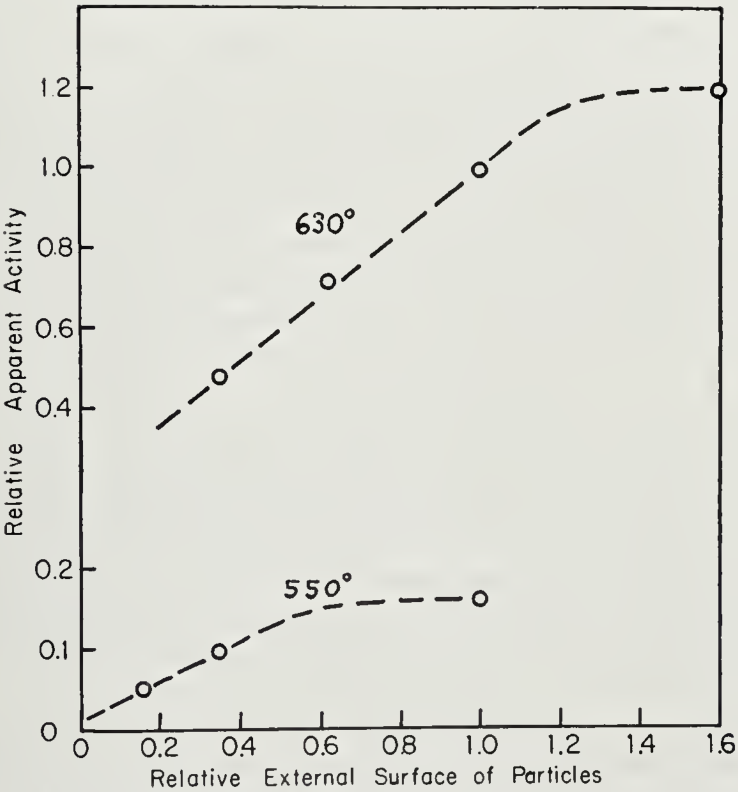


Figure 18. Variation of catalyst activity with particle size. (After Archibald, May and Greensfelder[4].)

Effect of Particle Size

Catalyst particle size may have an effect on the rate of cracking, for some of the reactions are so fast that diffusion can limit the rate. When this happens a true measure of the activity of interior surfaces is not obtained. This general subject has been well treated by Wheeler[121] and by Weisz and Prater[119]. Several examples of diffusion limitation in catalytic cracking are available.

Figure 18, constructed from the data of Archibald, May and Greensfelder[4], illustrates how the apparent activity of a catalyst increases as the average granule size is reduced to increase the relative external surface of the granules. In these experiments cracking of a West Texas gas oil was carried out at 550 and 630°C using an alumina-silica catalyst in the form of granules obtained by breaking pellets made by compressing a powdered material. A 20-minute process period was used in a small fixed bed reactor of special design, and activity was taken as proportional to the LHSV for 50 per cent reaction. As granules of smaller size were tested, the activity at first increased in direct proportion to the external surface of the granules, but at a certain size no further increase in activity occurred. The limiting size was smaller at the higher temperature, and was of the order of 1 mm diameter at 550°C and 0.5 mm diameter at 630°C. D. R. May, Saunders, Kropa, and Dixon[63] remarked that in the cracking of diarylethanes over clay in the presence of diluents at 525°C the cracking was proportional to the external surface area of the granules at high flow rates.

Still another example of an effect of particle size was set forth by Blue and colleagues[11] for the transfer of hydrogen from Decalin to butenes. This system has already been mentioned in the discussion on hydrogen transfer reactions. It was observed that reaction rates with various particle sizes were in approximate agreement with diffusion rates determined by measuring the rate at which radioactive butane was flushed out of a bed of the catalyst particles with a flow of inactive butane. The catalyst samples were TCC alumina-silica beads, whole and broken, and the hydrogen transfer was carried out at 340°C and about 6 LHSV. It was indicated that the particles were not fully effective unless below about 0.4 mm in diameter. With large particles the data could be fitted by assuming that an outer shell 0.2 mm thick represented the only portion of the catalyst completely available for reaction, and that successive inner 0.2 mm layers were each one-half as effective for reaction as the preceding outer layer.

At this point it may well be asked how important diffusion limitation is in ordinary laboratory cracking tests and in commercial cracking. Blue and colleagues have estimated that for a typical example of laboratory cracking, with 50 per cent conversion of a 220 molecular weight feed at 500°C and 4 LHSV, the influence of particle size is somewhat less than in the above example of hydrogen transfer. But this still leaves a significant dependence, and they expect a two-fold to six-fold increase in rate constant for a decrease in particle size from 4 mm diameter beads to 0.4 mm diameter beads. Wheeler[121] estimated less influence under typical catalytic cracking conditions, and stated that the internal surface of ⅛-inch diameter pellets was 80% effective for reaction. No doubt the glassy beads are less porous than the pellets. Nevertheless it is clear from these estimates as well as from the results of Archibald and co-workers that particle size can be quite important, especially at high temperatures. Particle size can affect the comparison of catalyst activities in research on new catalysts, the apparent kinetics and activation energies, and the product distributions, as Wheeler, and Weisz and Prater, have noted for the general case of porous catalysts.

Johnson, Kreger, and Erickson[57a] have shown the effects of particle diameter in the range 0.44 to 0.057 cm in the cracking of a gas oil at 482°C. The smaller particles were more active and more selective. The beads and crushed beads used by Johnson *et al.* were undoubtedly less porous than pellets made by compressing dried powders, as used in many laboratory cracking tests.

Kinetics in Fluid Systems

In a fluid catalyst reactor or with a moving bed the catalyst holding time (process period) is not directly measured, and the weight ratio of catalyst feed rate to oil feed rate is the known variable which governs average catalyst activity. This subject will be very briefly treated, mostly after the article by Shankland and Schmitkons[97] who base their considerations on an empirical equation for fixed bed cracking similar to Eq. (1). An average intensity of catalytic treatment of a hydrocarbon over a given process period is expressed as

$$I = kA(1/V_w)\theta^y \tag{11}$$

Here k is a constant determined by the operating temperature and pressure, A is a constant which defines the intrinsic catalyst activity, V_w is the weight hourly space velocity (weight of oil fed per hour per unit weight of catalyst), θ is the duration of the process period, and y is a constant, about -0.4 to -0.6 for the cracking of a gas oil over alumina-silica or a clay catalyst. The fraction converted, x, is approximately

$$x = JI/(JI + 1) \tag{12}$$

J is a factor which defines the ease of cracking of the feed. It will be noted that these equations are somewhat different from those of Voorhies (Eq. 1), but that an exponential decline of activity with time is still employed.

For a fluidized catalyst reactor, the average catalyst residence time, θ_f, may be substituted for the process period. Let W_c represent the weight of catalyst in the reaction zone; Z_c/hr the catalyst feed rate, weight per hour; C/O the catalyst to oil weight feed ratio, $C/O = (Z_c/\text{hr})/(W_0/\text{hr})$; and k' and A' constants as before. In this terminology $V_w = (W_0/\text{hr})/W_c$. Then

$$\theta_f = W_c/(Z_c/\text{hr}) = 1/V_w(C/O) \tag{13}$$

Substituting θ_f for θ in Eq. (11) it is readily shown that the average intensity of catalytic action in a fluid reactor is of the form

$$I = k'A'(C/O)^{-y}(V_w)^{-(1+y)} \tag{14}$$

Again, y is about -0.4 to -0.6. An equation of this type is useful in showing how the degree of cracking depends on C/O and V_w, but it must be viewed as an approximation. Although fluid and moving bed reactors have considerable differences, such an equation might be used for both (with different constants) as a first approach.

From an equation of the form of (14) an expression for the relative importance of C/O and V_w in determining conversion may be derived. Such an expression has often been called a severity factor. Thus, Shankland and Schmitkons[97], placing $y = -0.4$ in Eq. (14) define

$$\text{Severity factor} = (I/k'A')^{2.5} = (C/O)\,(V_w)^{-1.5} \tag{15}$$

For a given temperature, pressure, and catalyst, equal values of the severity factor should give equal intensities of cracking and thus equal conversions with a given feed, within the limits to which these equations are valid.

When effects of coke are considered in a fluid reactor it is necessary to consider that some particles of catalyst stay in the reactor much longer than others. Some of the mathematics of this situation have been given by Blanding[8] and by Crawford and Cunningham[20].

REGENERATION OF CATALYSTS

After use for average times of the order of 2 to 60 minutes, depending on conditions applied, cracking catalysts must be regenerated to remove coke and restore activity. Regeneration is invariably effected by burning in a controlled fashion with oxygen-containing gas. This is a very important operation, and as already stated has in large part determined the design of cracking plants. The major problem in regeneration is to burn off the coke without causing irreversible damage to the catalyst, and since a catalyst is regenerated thousands of times in the course of a normal lifetime, deactivation must be kept extremely small in any one regeneration. In spite of care there is a slow decline in prolonged use. The damage apparently comes about from exposure to too high a temperature, and also from the presence of steam in the reaction, flushing, and regeneration gases, even at lower temperatures. Regeneration must be carried out with adequate provision for removal of heat, and steam should be kept to a minimum. Inasmuch as 1 to 10 per cent by weight of the hydrocarbon feed remains as coke on the catalyst, the amount of heat to be removed is enormous. Furthermore, steam cannot be altogether avoided, for it is formed by combustion of the combined hydrogen in the coke; in addition, steam is by far the most convenient gas for flushing.

Despite the apparent difficulty of the regeneration problem, it has been solved practically in a number of ways. The truth is that cracking catalysts are outstandingly rugged and that with moderate care acceptable regeneration is obtained. Perhaps for this reason there have not been published many scientific studies of the regeneration reaction. Hagerbaumer and Lee[43] investigated the regeneration of TCC beads, Snuggs[99] and Johnson and Mayland[58] reported on fluidized catalyst, Dart, Savage, and Kirkbride[21] described results with a pelleted clay catalyst, and Pansing[83] correlated data from pilot and commercial fluid reactors. The following discussion is based on these five papers. Attention is focussed on the carbon content rather than on total coke because the carbon is easier to measure and also burns off more slowly than the hydrogen in the coke. It should be noted that although the terms burn and burning are commonly used, regeneretion of a cracking catalyst is not normally a combustion, but a slow chemical reaction proceeding at a nearly uniform temperature.

Variables that influence regeneration rate are:

(1) Temperature.
(2) Oxygen content of regeneration gas.
(3) Initial coke content of catalyst.
(4) Fraction of initial carbon that is yet unburned.
(5) Type of catalyst (composition, activity, impurities present).
(6) Mode of formation of coke (feed stock, cracking conditions).
(7) Carbon/hydrogen ratio of coke (aging of coke).
(8) Efficiency of contacting of gas and catalyst.
(9). Pressure.
(10) Steam partial pressure.

The most influential of these variables are temperature, oxygen content of gas, and amount of carbon on catalyst. Hagerbaumer and Lee expressed the carbon burning rate in pounds per hour per cubic foot of catalyst bed as

$$R = \mathrm{O}_m f_1(T) f_2(C_0) f_3(C/C_0)$$

Here O_m is the log mean oxygen concentration, and f_1, f_2, and f_3 are empirical functions of the temperature, the initial carbon content of the catalyst, and the fraction of unburned carbon, respectively. The use of the logarithmic mean implies a reaction first order in oxygen, and this is the order found by Dart and co-workers. The temperature function corresponds approximately to an Arrhenius function with activation energy of 35 kcal for the range 430 to 480°C according to Hagerbaumer and Lee, while Dart and co-workers give an activation energy of 26.6 kcal for the range 450 to 650°C. Pansing finds 35 kcal for an alumina-silica, and Johnson and Mayland give 41 kcal for a magnesia-silica. The functions f_2 and f_3 are not well defined. In the study of Dart and collaborators they are combined in a single function of the carbon content of the catalyst, and the burning rate is said to increase with the square of the carbon content up to about 2 per cent carbon on catalyst, while at higher carbon contents the rate is first order in the carbon. At very high carbon contents the order of the rate in carbon may be less than one.

An apparatus and technique for comparing regeneration rates of different powdered catalysts are described by Johnson and Mayland[58]. A catalyst containing 0.35 per cent by weight carbon that has been deposited in a standard manner is placed in a 2-inch diameter tube and is fluidized by a gas stream containing 2 per cent O_2 and 3 psia of steam. The time required at 1000°F to reduce the carbon content from 0.35 to 0.25 per cent is determined, and the standard burning rate is computed at 1000°F, 1 psia of O_2, 0.3 per cent C on catalyst, and 3 psia of H_2O vapor. In such tests, various clay, alumina-silica, and magnesia-silica catalysts had about the same burning rates. Aging in use or by steaming changed the rate somewhat, but not in proportion to surface area, as the data of Table 15 show.

TABLE 15. BURNING RATES AT STANDARD CONDITIONS OF JOHNSON AND MAYLAND

Catalyst	Area, m^2/g	Burning rate, lb C/ton cat./hr
Fresh alumina-silica	651	31
Same, used in plant	—	23–32
Fresh, steamed	278	25
Fresh, steamed	107	21
Fresh, heated in vacuum	228	24
Fresh, heated in vacuum	144	23

Johnson and Mayland demonstrated an important effect of steam partial pressure on the regeneration rate. Although steam alone causes a negligible rate of removal of carbon, in the presence of oxygen it considerably accelerates the rate. Increasing the steam partial pressure from zero to 6 psia causes a linear increase of the rate; see Figure 19. The total increase is by a factor of 3 to 4. Thus the most complete rate equation yet proposed is that of Johnson and Mayland:

$$\text{Rate} = k_1P_0(1 + k_2P_w)C^ne^{-E/RT}$$

where P_0 is oxygen pressure, P_w steam pressure, C the carbon content of the catalyst (deposited and aged in a specified way), and n is about 1.

The coke content of a commercial "spent" catalyst may lie in the range of 1 to 4 per cent by weight. Analysis of the coke will show a moderate hydrogen content, somewhere in the range of 2 to 10 per cent by weight of the coke. This corresponds to a hydrogen to carbon atomic ratio of between 0.3 and 1.3. The remainder of the coke consists of carbon, with small amounts of nitrogen and sulfur. The exact composition of coke depends on the feed and cracking conditions, and also on the thoroughness with which the catalyst has been stripped or flushed free of entrained or adsorbed volatile hydrocarbons. A well stripped coke does not have a hydrogen to carbon atomic ratio above 1.0, and evidently consists largely of highly condensed aromatic rings. In regeneration the hydrogen is burned relatively more rapidly than the carbon. Dart and collaborators show that when 20 per cent of the carbon has been burned about 65 per cent of the hydrogen has been burned. Thus the residual coke becomes poorer in hydrogen, and this correlates with the lower burning rate. In commercial practice catalysts are not burned clean, but are normally returned to the reactor when the carbon content reaches 0.3 to 0.7 per cent by weight.

In a fluidized catalyst regenerator the oxygen content of the efflux gas is normally 0.5 to 2 per cent; this presumably represents the gas throughout the regenerator. The temperature may range from 530 to 650°C, although it is rarely above 600°C. The carbon in the effluent gases is about equally divided between carbon dioxide and carbon monoxide; if anything, the dioxide is in excess. A high ratio of carbon monoxide to carbon dioxide is normally desired in these units because it diminishes the requirements for oxygen and for heat dissipation. Regeneration heat is absorbed by the relatively cold catalyst and inlet air for the most part, but some fluid regenerators have catalyst coolers.

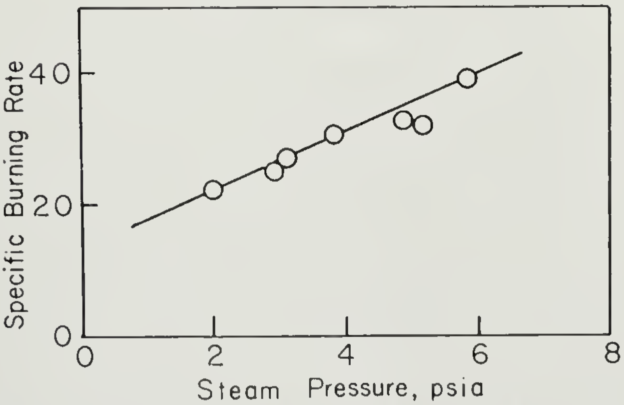


Figure 19. Effect of steam on regeneration rate of a used commercial alumina-silica. Specific burning rate = pounds carbon per ton of catalyst per hour per psia of O_2, at 1000°F and 0.3 per cent carbon on catalyst. (After Johnson and Mayland[58].)

In a moving bed regenerator the maximum temperature is around 620°C. In the Thermofor kiln from which the TCC process takes its name there may be ten consecutive regeneration zones, in each of which catalyst is contacted with air and with cooling coils. The oxygen content of the gas leaving the first zone may be 2.7 per cent, according to Hagerbaumer and Lee, and the outlet temperature about 510°C. This is the zone where most steam forms. In successive zones the exit oxygen content and the temperature are both increased, until the gas leaving the last zone may have an oxygen content of 11 to 14 per cent and the temperature may reach 620°C. The CO/CO_2 ratio in the TCC process is of the same order as that in the fluid process, but here a low ratio is ordinarily desired, and small amounts of chromium (about 0.1 %) have been added to newer samples of the bead catalyst to achieve this end and to accelerate the regeneration reaction. The newer Houdriflow and airlift TCC units achieve a higher catalyst flow rate and this simplifies regeneration because of the greater bulk and heat capacity of the circulated catalyst. For this reason these newer units may have only two consectuive regeneration zones in the kiln.

Metal contamination of cracking catalysts in use somewhat increases the regeneration rate.

Cracking of Petroleum Fractions

Methods of commercial cracking and one example of the products from a practical feed were presented early in this chapter. The present disussion will give a brief account of the influence of composition on the cracking of petroleum fractions and of the effects of operating variables.

Almost any petroleum fraction which is gaseous or liquid at the cracking temperature may be subjected to the action of cracking catalysts. Gasolines are sometimes so treated to diminish the olefin content and to lower the molecular weight. Kerosenes and light and heavy gas oils, boiling somewhere in the range 200 to 500°C are the usual materials cracked. Unvaporized petroleum residues are occasionally cracked by fluidized or moving bed techniques, but this is not particularly economic because of the high percentage of coke formed and the likelihood of contamination of the catalyst with metals dissolved in the residue.

A great deal has been learned through empirical studies and through the cracking of pure hydrocarbons about the most desirable feeds for cracking. One of the most remarkable features of the process, however, is that the gasoline produced is almost always of high and uniform octane number (80 to 84 F-2 or motor method and 90–95 F-1 or research), in spite of wide differences of feeds in the ease of cracking and the yield of gasoline. Oils to be cracked are usually selected from the standpoint of availability, gasoline yield, and coke forming tendency. Some understanding of the last two items can be reached from the knowledge of cracking reactions already presented, but before data for pure hydrocarbons can be employed it is necessary to know whether any special effects arise from the cracking of one hydrocarbon in the presence of another. Experiments have shown[115] that the most important effect of this type is the saturation of olefins, which is enhanced in the cracking of mixtures containing naphthenes of certain types, especially at low temperatures. The cracking reactions for an individual compound usually proceed at about the same rate in a mixture as with the separate compound when the same total hydrocarbon flow rate is employed. This was demonstrated in experiments at 500°C with mixtures of Decalin with either toluene, *n*-pentane, mesitylene, or 2-methylnaphthalene (if free from nitrogen bases). It was also demonstrated for a mixture of *n*-hexadecane and *n*-hexadecene. In experiments at 400°C the extents of cracking and product distributions were as expected for mixtures of *n*-hexadecane and Decalin, and of paraffin wax (a mixture of *n*-paraffins, about C_{20}-C_{28}) and abietanes (C_{18} naphthenes), except for a greater saturation of the gasoline fractions caused by hydrogen transfer from the naphthenes. With unusual compounds or very heavy coke formers no doubt effects of mixing on cracking rates will appear. For example, large amounts of styrene or phenanthrene, compounds causing high coke formation, caused moderate reduction of the cracking of *n*-hexadecane or Decalin[115].

Cracking of a highly paraffinic fraction will tend to give a great deal of gas rich in C_3 and C_4 compounds, and relatively low yields of gasoline and coke. A naphthenic feed, on the other hand, will produce less gas and more gasoline at the same conversion, and the gas will be richer in hydrogen, methane and C_2, although still predominantly C_3 and C_4 material. Petroleum fractions of high aromtic content may be expected generally to give intermediate gasoline yields, high coke formation, and a gas extremely high in hydrogen and methane[115]. A naphthenic gas oil is the ideal material for the production of gasoline. In fact a fairly good prediction of the amount of gasoline that will be obtained from the cracking of a petroleum fraction can be made on the basis of molecular weight and the amounts of paraffinic, naphthenic and aromatic carbon shown by analysis[115]. This prediction depends primarily on naphthene content and molecular weight. The effect of increasing molecular weight with the usual petroleum distillate fractions is to increase ease of cracking and the yield of gasoline, in line with findings with pure hydrocarbons.

The usual heavy oils subjected to cracking contain many hydrocarbons. When conditions are severe enough to crack the more refractory compounds, the products from the more easily cracked compounds are in part degraded to light gases and coke. This loss could be prevented by segregated cracking of separated portions, but a more practical way appears to be two-stage cracking in which products from the first stage are removed prior to the second stage[50]. Substantially lower coke and light gas yields result from this procedure, compared to those from single-stage cracking to the same conversion.

Table 16 presents gas compositions and product distributions from the laboratory cracking of three petroleum fractions of widely different composition over an alumina-silica catalyst at atmospheric pressure. The Tandjung (Borneo) distillate was highly paraffinic, the West Texas Gas oil was more naphthenic, and the kerosene extract was highly aromatic. The differences in gas compositions and products from these three stocks are in

TABLE 16. CATALYTIC CRACKING OF PETROLEUM STOCKS

Fixed-bed laboratory cracking over Al_2O_3–SiO_2 catalyst[45]

Stock	Tanjung Waxy Distillate	West Texas Gas Oil		Kerosene Aromatic Extract
LHSV	4.0	5.2	9.5	2.0
Process period, min	15	10	10	60
Temperature, °C	500	500	550	550
Conversion, % wt, no-loss basis[1]	66.1	55.2	54.5	35.7
Gaseous Products, % vol				
H_2	6.6	7.7	11.2	28.1
CH_4	11.4	14.1	16.5	34.7
C_2H_4	4.7	12.8	10.0	6.8
C_2H_6	4.4	7.7	7.3	6.8
C_3H_6	22.9	20.5	25.2	10.3
C_3H_8	8.7	7.7	7.0	5.2
i-C_4H_{10}	6.6	3.8	3.4	1.5
n-C_4H_{10}	13.6[2]	9.0	11.2	2.2
C_4H_8	19.1	16.7	8.1	4.4
Material Balance, % wt charge				
Gas	29.3	20.6	24.2	6.6
Gasoline	31.1	29.0	26.7	23.3
Bottoms	33.7	43.5	44.5	63.5
Coke	5.3	4.0	2.3	5.3
Loss	0.6	2.9	2.3	1.3
Coke, % wt converted product	8.0	7.4	4.5	15.6
Analyses and properties of cracking stocks				
Carbon Atom Percentages				
Aromatic	15	13		71
Naphthenic	5	33		8
Paraffinic	80	54		21
% wt Carbon	85.8	85.7		90.9
" Hydrogen	13.6	12.9		8.9
" Sulfur	0.06	1.36		—
" Nitrogen (Dumas)	0.2	0.1 (?)		—
Gravity, °API	41.9	31.4		15.9
Molecular weight	344	255		147

[1] 100-% wt Bottoms > 205°C, no-loss basis.

[2] Includes 1.7 mole % butadiene.

line with expectations from individual hydrocarbon results. At equal conversions and temperatures the effects would be even more pronounced, and the high coke formation from the aromatic material would be outstanding.

It is indeed clear that high boiling aromatic feeds are the least desirable from the standpoint of coke formation.

The operating conditions employed for the cracking of a given petroleum fraction or mixture affect the products markedly. For instance, it is possible to obtain a nearly saturated or a highly olefinic gasoline. The effects of conditions will not be discussed in detail here since they are found in many papers[5, 74, 96, 98]. The basic controlling variables are ordinarily considered to be catalyst, temperature, catalyst-to-oil ratio, catalyst holding time (or weight space velocity), pressure, and conversion. At first thought, conversion would be taken as a dependent variable, governed by conditions and the average amount of coke on the catalyst, but in considering effects of different catalysts or temperatures on product distribution it is much more satisfactory to compare results at constant conversion. This can be understood from the kinetics of systems involving either consecutive reactions or parallel reactions of different velocities.

In the cracking of a given feed with a given catalyst at about atmospheric pressure, temperature and conversion are taken as the principal correlating variables for product distribution, for other variables have lesser effects. Increasing conversion at constant temperature (as by lowering LHSV) has the following effects on products:

Increases light gases (C_1 and C_2)
Increases the ratio of gas to gasoline
Increases gasoline, which may pass through a maximum
Decreases olefinicity
Increases coke, and the ratio of coke to gasoline.

Increasing temperature at constant conversion has the following effects:

Increases light gases
Increases gas to gasoline ratio
Decreases gasoline
Increases olefinicity
Decreases coke

The effects of these changes on the octane number of the gasoline are not large. The octane number may increase by two or three units as temperature or conversion are increased over the workable range[74].

Related Catalytic Systems

Among the many substances which influence the rate of decomposition of hydrocarbons only the solid acidic oxides lead to the desirable operation and products associated with the term catalytic cracking. Other acidic catalysts, at lower temperatures, bring about the related reactions of olefin polymerization, alkylation of aromatics or paraffins, and isomerization of paraffins. The common basis for these conversions and catalytic cracking has been brought out by Greensfelder[32] and by Schmerling[95]. Here a few materials having somewhat or radically different catalytic action are mentioned.

Pure silica gel of high surface area has a mild accelerating effect on the decomposition of hydrocarbons, but the products are much like those from thermal cracking[37]. Pure alumina gel may have a somewhat higher activity[37], but activity depends markedly on impurities such as chloride[104]. Alumina has considerable dehydrogenation activity[37]. Reducible oxides such as iron oxide are quickly converted to metals by hydrocarbons at high temperatures, and the active metals so formed have a very destructive action, causing decomposition to carbon and hydrogen. Nickel displays marked activity for this destructive decomposition and also leads to methane formation.

Activated carbon causes rapid cracking. The decomposition of *n*-hexadecane over a steam activated cocoanut charcoal was from one to ten times as fast (basis equal volumes of catalyst) as over alumina-zirconia-silica, but the products were quite different, consisting largely of normal paraffins and olefins distributed rather evenly over the range C_1 to C_{13}, according to Greensfelder, Voge, and Good[37]. The absence of branched products was convincingly shown by Grosse[39]. From the composition of the products and the relative rates of cracking of other hydrocarbons containing different numbers of primary, secondary, and tertiary hydrogens, Greensfelder, Voge, and Good devised a simple theory to explain the action. It was postulated that the carbon reacts with the hydrocarbon to remove a hydrogen atom, and that the rates of removal of various types of hydrogens follow the same rules set forth by Kossiakoff and Rice[62] for the rates of formation of the corresponding radicals in thermal cracking. In the cracking over carbon it was supposed that the radical formed remains bound to the carbon surface and hence does not start vapor phase chain reactions which would lead to the usual thermal products. When the radical decomposes by the splitting of a beta bond it forms a normal, alpha olefin and a primary free radical, and the latter is assumed to be rapidly saturated or "quenched" by addition of a hydrogen atom from the supply held by the carbon surface. With these simple assumptions the rates and products for the cracking of five hexane isomers were explained, and the good agreement between experimental and calculated products from *n*-hexadecane set forth in Table 17 was obtained.

Hydrocracking may be defined as cracking in the presence of molecular hydrogen with an acidic catalyst containing a hydrogenating component. It bears many resemblances to catalytic cracking in the relative reactivities of various hydrocarbons, in the preferential formation of C_3 to C_6 material, in the isomerization which accompanies cracking, and in an isobutane/*n*-butane ratio exceeding equilibrium. Olefins are almost non-existent in the products because of the strong hydrogenating action. The catalyst, according to German usage, may be an acid-treated clay containing a small amount of molybdenum or tungsten as oxide or sulfide. A synthetic alumina-silica may be used in place of the acid-treated clay.

Aluminum chloride causes decomposition of higher hydrocarbons at about 280°C and its action appears to be closely related to that of conventional cracking catalysts. Indeed the early process of McAfee in which gas oils were converted to gasoline by heating in liquid phase with aluminum chloride is considered to have been the first catalytic cracking process.

TABLE 17. PRODUCTS FROM CRACKING *n*-HEXADECANE OVER ACTIVATED CARBON

Experimental cracking over Columbia Grade S activated carbon at 500°C, atmospheric pressure and 10 LHSV. Conversion 26.6%[37]. The table gives moles of product per 100 moles cracked.

	Calculated	Experimental
C_1	4	11
C_2	13	22
C_3	21	23
C_4	17	17
C_5	13	20
C_6	13	21
C_7	13	15
C_8	13	9
C_9	13	18
C_{10}	13	15
C_{11}	13	14
C_{12}	17	13
C_{13}	21	7
C_{14}	12	4
C_{15}	4	14
Total	200	223
H_2	0	26

McAfee's experiments were done about 1914[64]. The heavy oil and about 7.5 per cent aluminum chloride were heated in a large vessel at atmospheric pressure for a period of about 24 hours. Low boiling material was allowed to pass overhead, while higher boiling material was returned by means of a partial condenser. In the treatment of a reduced West Texas crude at 260 to 290°C, 33 per cent by weight of gasoline and 16 per cent coke were obtained. Recovery of the aluminum chloride was difficult in this process and it was not a commercial success.

Considerable further research has been done with aluminum chloride and bromide, but much remains to be learned of the reactions of hydrocarbons over these materials. Unlike cracking with alumina-silica, with aluminum chloride olefins and aromatics formed in cracking do not escape but are either saturated or remain in the lower phase to be converted to coke. The reactions definitely fit into the carbonium ion scheme. Isomerization accompanying cracking and extensive hydrogen transfer both occur, and very large amounts of isoparaffins are produced. Komarewsky and Warson[61] reported the cracking of gas oils boiling from about 220 to 400°C over aluminum chloride promoted with hydrogen chloride. The reaction was carried out in the liquid phase at a pressure of 13 atmospheres with a usual catalyst charge of 10 per cent by weight of the feed and a time of 15 hours. Conversions to gasoline and gas were about 70 per cent by weight, and the balance of 30 per cent remained with the aluminum chloride as coke. The liquid product, which boiled entirely below 150°C, was free of olefins and contained only small amounts of aromatics. Large amounts of isoparaffins, especially C_4 and C_5 were produced, and the gasoline had an octane number (F-2 or motor method) of 80. Potolovsky and Spektor[90] cracked *n*-hexadecane in the presence of aluminum chloride and HCl at 150 to 250°C. Products were mainly isoparaffins, especially isobutane, which was 88 to 96 per cent of the gas formed.

Boron fluoride added to a gas oil being cracked over alumina-silica increases the cracking, according to Paushkin and Lipatov[87], who reported more gasoline and more saturation of olefins in the presence of boron fluoride.

Conclusion

Catalytic cracking is a complex process, both because of the many reactions that occur and because of the numerous hydrocarbons that may be present in a practical feedstock. Nevertheless, the chemical events in in the process are fairly well known, and the carbonium ion theory explains most of them moderately well in a qualitative sense. One of its principal advantages is the concordance it establishes with many other acid-catalyzed hydrocarbon reactions.

Still, much remains to be learned. From the practical standpoint there is considerable room for better catalysts which will greatly reduce coke formation or permit the reactions to be made more specific for particular products. From the theoretical side much remains to be found out about the kinetics and mechanisms of the reactions. The theory is ambiguous on the mode of initiation of paraffin and naphthene cracking, and there is as yet little specific experimental information about many of the individual steps hypothesized in the chain of carbonium ion reactions. Quantitative aspects of the carbonium ion theory need to be developed. From the experimental side doubtless much could be added to the knowledge of the details of cracking reactions by studies with compounds containing radioactive carbon or the heavy isotope of carbon. Indeed, a start in this direction has been made by McMahon[65] who studied coke formation with radioactive paraffins; by Klimenok and co-workers[60] who found little or no exchange between radioactive methane or ethane and olefins; and by Andreyev and co-workers[2] who demonstrated secondary interaction by cracking *n*-hexane in the presence of radioactive ethylene.

There are other areas where fruitful research can be done on catalytic cracking. One is the kinetics of coke formation; another the nature of coke and its relationship to the decline of activity within a process period. The mechanisms of regeneration reactions need much study. Thus, catalytic cracking remains a challenging field for research as well as an extremely important industrial process.

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CHAPTER 6

CATALYTIC REFORMING OF PURE HYDROCARBONS AND PETROLEUM NAPHTHAS

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One of the most interesting and commercially important heterogeneous catalytic processes developed during the past fifteen years is the catalytic reforming of virgin and cracked naphthas to produce high octane gasolines and pure aromatic hydrocarbons. The initial research work carried out in this field was primarily directed toward the utilization of hydrogenation-dehydrogenation catalysts such as molybdenum and chromium oxides. The early experimental work, carried out at atmospheric pressure, had shown that these catalysts are active and fairly selective for the reforming reactions of hydrocarbons boiling in the naphtha range. Although these catalysts lost activity as the result of coke deposition, on regeneration in air they regained most of their original activity. It was also shown that these catalysts were potentially useful commercial catalyst systems because of their resistance to sulfur poisoning and their stability to frequent high temperature regeneration. The first commercial catalytic naphtha reforming unit, which went on stream in 1940, and the subsequent units built prior to 1950, employed a molybdena-alumina catalyst. Actual installed capacity by 1950 was less than 80,000 barrels per day, some of which was not used after World War II because of the lack of demand for high octane fuels, and the high cost of operating this process.

In the next few years, it became very obvious that petroleum catalytic scientists had been investigating the catalytic properties of the active metal hydrogenation-dehydrogenation catalysts as possible constituents of naphtha reforming catalysts. The late Professor V. I. Komarewsky[116] was one of the early workers in this field. These investigations led to the discovery of several new classes of hydrocarbon conversion catalysts which were more active and more selective than the metal oxide catalysts. These catalysts consisted of a metal such as platinum, palladium, nickel, etc., in combination with an acidic oxide such as silica-alumina or alumina. It was found that by carefully balancing the activity of each of the components, the resulting dual function catalyst was an excellent naphtha reforming catalyst. These researches led to the development of low investment cost fixed-bed reforming processes, employing platinum catalyst, which would operate continuously for long periods of time, under hydrogen pressures of the order of 500 psig before replacement of the catalyst was required. As a result of these developments, and the increasing demand for high octane motor fuels, a phenomenal expansion in catalytic reforming capacity has occurred during the last seven years. As of January 1, 1958, the installed catalytic reforming capacity in the United States was approximately 1.5 million barrels per day, of which 90 per cent was based on platinum containing catalysts, and the remainder used either an alumina supported molybdenum oxide or chromium oxide catalyst.

In the development of these new catalyst systems, a large amount of experimental work was carried out under simulated commercial reforming conditions, using pure hydrocarbons or mixtures of pure hydrocarbons, as the feed stocks. General availability of the mass spectrometer and other analytical tools permitted complete identification of most of the hydrocarbons in the products. In a number of cases, new dual-function catalyst systems for the catalytic reforming of naphtha were developed primarily from studies in which mixtures of pure hydrocarbons were used as the feed. As a result of these studies, a more complete understanding has been obtained of the role of each of the components in these catalysts, i.e., the hydrogenation-dehydrogenation component and the acidic oxide component, in the conversion of various types of hydrocarbons. These researches have led, not only to the development of commercial reforming catalysts, but also to the discovery of a number of new and unique catalyst systems for the selective isomerization of hydrocarbons.

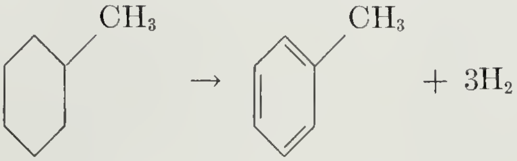
The first two parts of this chapter cover most of the literature available on the reactions of pure hydrocarbons in the presence of dual-function catalysts. The major portion of the literature reviewed in this chapter covers those researches in which the activity of these catalysts was investigated in the presence of hydrogen. The available information on the reactions of pure hydrocarbons in the presence of metal oxide catalysts is reviewed first. The reactions of pure hydrocarbons in the presence of metal-acidic catalysts are covered in the second part of this chapter. It should be pointed out that there is undoubtedly a much larger amount of pure hydrocarbon data which has not as yet been published because of secrecy restrictions. The last part of this chapter deals exclusively with the characteristics of the various commercial processes used in the United States and abroad for the catalytic reforming of naphthas.

Reforming Reactions of Pure Hydrocarbons with Metal Oxide Catalysts

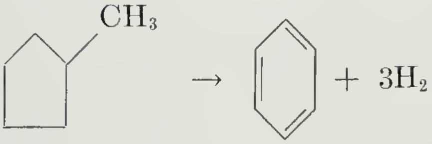
Catalytic reforming of petroleum naphthas comprises the following main hydrocarbon reactions:

Dehydrogenation Reactions

(1) Dehydrogenation of cyclohexanes to aromatics



(2) Dehydroisomerization of alkylcyclopentanes to aromatics

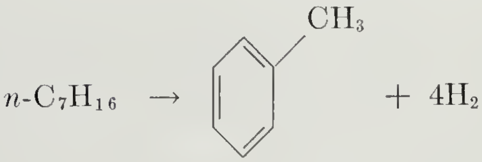


(3) Dehydrogenation of paraffins to olefins

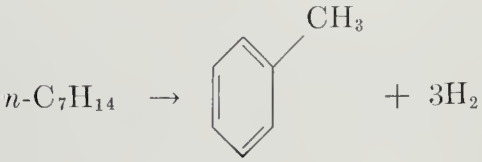
$$C_9H_{20} \rightarrow C_9H_{18} + H_2$$

(4) Dehydrocyclization of paraffins and olefins to aromatics

(a)



(b)



Isomerization Reactions

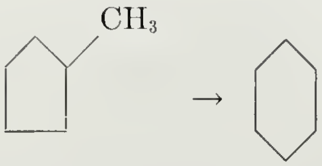
(1) Isomerization of *n*-paraffins to isoparaffins

n-heptane → 2-methylhexane

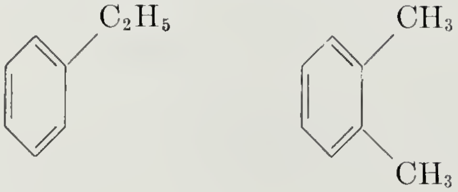
(2) Hydroisomerization of olefins to isoparaffins

heptene-1 + H_2 → 2-methylhexane

(3) Isomerization of alkylcyclopentanes to cyclohexanes



(4) Isomerization of substituted aromatics



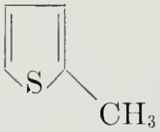
Hydrocracking Reactions

(1) Hydrocracking of paraffins

$$\text{(a)}\quad C_9H_{20} + H_2 \rightarrow C_5H_{12} + C_4H_{10}$$

$$\text{(b)}\quad C_9H_{20} + H_2 \rightarrow CH_4 + C_8H_{18}$$

(2) Hydrodesulfurization



$$+ 4H_2 \rightarrow C_5H_{12} + H_2S$$

These reactions occur to varying degree in all catalytic reforming processes. The extent to which each takes place depends upon the nature of the catalyst, the composition of the naphtha feed and the conditions of operation.

It has been shown[41, 124, 161] that the isomerization and hydrocracking reactions require the catalyst to have two separate and distinct functions—a hydrogenation-dehydrogenation function and an acidity function. These two functions may reside in different chemical components or they may reside in the same component. This is one of the distinctions which separates the metal-acidic oxide catalysts from the metal oxides. In the former, an active metal (e.g., platinum) serves as the catalytic site for hydrogenation, dehydrogenation, and metal catalyzed hydrocracking reactions. The acidic component (e.g., silica-alumina, chlorided alumina) provides the acid site for the isomerization, cracking and polymerization reactions of olefins. This fairly clear distinction between the two types of catalytic centers in the metal-acidic oxides cannot be so readily made with the Group VI oxide catalysts (e.g., chromia-alumina, molybdena-alumina) because here both types of catalytic centers are present in the transition metal oxide.

A second major difference between the metal-acidic oxide and the metal oxide reforming catalysts is in the level of dehydrogenation activity. The supported platinum metal catalysts are much more active for dehydrogenation of paraffins and of naphthenes than are the oxides of molybdenum and chromium, the two most active metal oxides. It is therefore necessary to operate the oxide catalysts at higher temperatures, lower throughput rates and lower partial pressures of hydrogen to obtain comparable yields of aromatics from paraffins and naphthenes. These operating conditions which are required for the less active oxide catalysts also favor the polymerization reactions leading to coke. Processes employing these catalysts therefore contain a regeneration cycle to burn off coke. The platinum-acidic oxide catalysts with their higher activity for dehydrogenation and for hydrogenation are used at higher partial pressures of hydrogen with considerably lower rate of coke formation and lower frequency for regeneration. The lower order of dehydrogenation activity of the oxide catalysts is also responsible for some of the major differences in their selectivity for the various hydrocarbon reforming reactions between the two classes of catalysts.

The metal oxide group of reforming catalysts are considered to be members of a broad family of dual-function catalysts—catalysts which contain a hydrogenation-dehydrogenation function and an acidity function. The selectivity for the various reactions in reforming can be interpreted on the basis of the activity levels of these two functions and the relation between them. This viewpoint of considering the oxides of the transition metals as bifunctional catalysts has been discussed by Clark[46]. In a summary of the general features of this class of catalysts, Clark places the bifunctional transition metal oxides between the transition metals and the solid oxide insulators. He associates the hydrogenation-dehydrogenation activity of the metal oxides with the metal ion sites, providing a common basis for this type of activity between the oxides of the metals and the more active metals themselves. This idea seems to be fairly widely accepted today.

Much of the published literature on reforming reactions of pure hydrocarbons with oxide catalysts deals with the dehydrocyclization reaction at atmospheric pressure. This part of the literature has been recently reviewed by Steiner[147].

Most of our attention in this section will be directed to the hydrocarbon reforming reactions which occur with the metal oxide catalysts under elevated pressures of hydrogen to try to give a clear picture of reactions at commercial reforming conditions.

Dehydrogenation Reactions

Dehydrogenation is the most important single reaction in the catalytic reforming of petroleum naphthas for two reasons. First, the dehydrogenation of naphthenes to aromatics is the chief octane upgrading reaction. Second, the dehydrogenation of paraffins and of cycloparaffins to the corresponding olefins provides reactive intermediates for subsequent isomerization, cyclization and acid-catalyzed hydrocracking reactions.

Dehydrogenation reactions are strongly influenced by temperature and by hydrogen partial pressure, the extent of reactions increasing as temperature increases and hydrogen partial pressure decreases. Equilibrium data are illustrated in Figure 1 for the conversion of cyclohexane to benzene and in Figures 2a and 2b for the conversion of methylcyclohexane to toluene[58].

Greensfelder, Archibald and Fuller[79] have compared the activity of chromia-alumina and molybdena-alumina catalysts for dehydrogenating methylcyclohexane at atmospheric pressure without hydrogen addition and at 20 atmospheres with hydrogen addition. Their results, presented in Table 1 and Figures 3 and 4, show that the behavior of these catalysts is very dependent on hydrogen partial pressure.

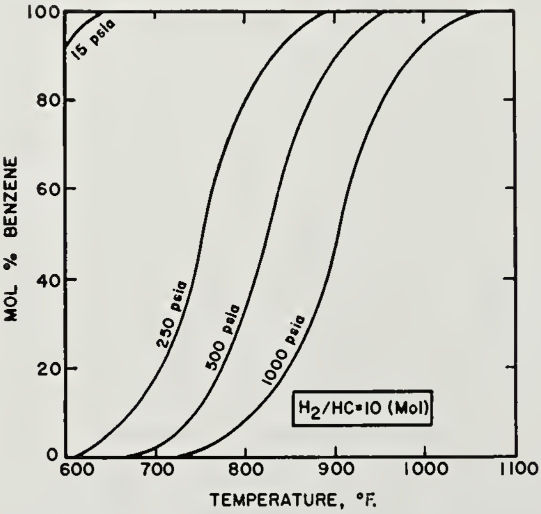


Fig. 1. Equilibrium distribution for the system cyclohexane-benzene-hydrogen

At atmospheric pressure (Figure 3), the chromia-alumina catalysts require an induction period of 2 to 4 hours before reaching their maximum stabilized activity level. Although these catalysts were usually reduced in hydrogen before charging the liquid feed, the activation occurring during the initial on-stream period may be due to further reduction of chromium oxides. The much higher activity of chromia on γ-Al_2O_3 (containing oxides of cerium and potassium) compared to chromia on α-$Al_2O_3 \cdot H_2O$ has been attributed to the preferential form of the γ-Al_2O_3[17].

At these same conditions molybdena on α-$Al_2O_3 \cdot H_2O$ has very good initial activity but deactivates rapidly with time on stream. This rapid deactivation at atmospheric pressure without hydrogen addition is undoubtedly due to coke deposition on the catalyst surface. At similar operating conditions using *n*-heptane as a feed and molybdena on activated alumina catalysts, Russell and Stokes[142] obtained coke deposits of 4 grams per 100 cc catalyst in a 1.5 hour test period. These conditions of very low partial pressure of hydrogen favor coke formation on dual-function catalysts. At 20 atmospheres pressure, with hydrogen added (Figure 4), the chromia-alumina catalyst has low dehydrogenation activity while molybdena-alumina has a very high sustained activity. Thus, at this higher pressure the intrinsic activity of chromia-alumina is too low to cause extensive dehydrogenation while the intrinsic activity of molybdena-alumina is high enough to overcome the mass action effect of the increased hydrogen pressure. The stability of the molybdena catalyst here is attributed to the use of an increased hydrogen partial pressure sufficient to limit coke formation.

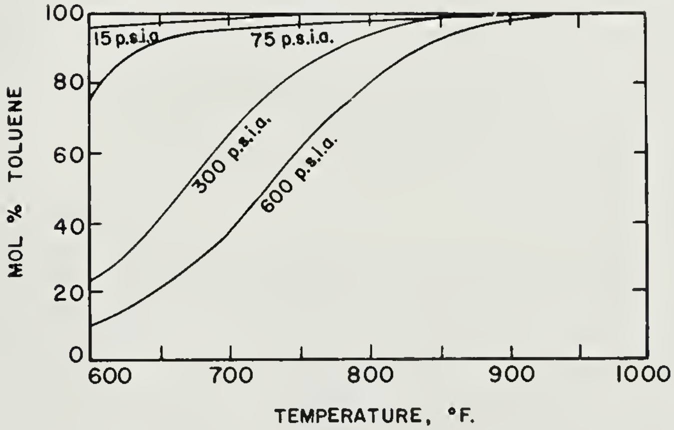


Figure 2a. Equilibrium distribution for the system methylcyclohexane-toluene-hydrogen in the absence of added hydrogen.

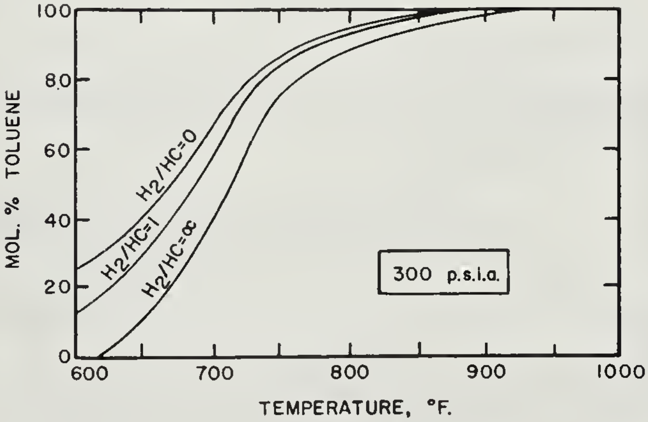


Figure 2b. Effect of added hydrogen on the equilibrium distribution for the system methylcyclohexane-toluene-hydrogen.

Rudershausen and Watson[140] have studied a number of the variables affecting the activity of a coprecipitated molybdena-alumina catalyst for dehydrogenating cyclohexane in a differential flow reactor over the pressure range 10 to 100 psig. Decline in catalyst activity with time on stream at different values of total reactor pressure and hydrogen to hydrocarbon ratio is shown in Figure 5. The activity of the catalyst at 100 psig is about three times higher than it is at 10 psig, for periods up to 90 minutes, at the same temperature and liquid space velocity, in line with the increased contact time at the higher pressure. At 100 psig, the catalyst maintains higher activity at a hydrogen to hydrocarbon mole ratio of 4:1, compared to 1.4:1, probably because of lower coke deposition.

TABLE 1. DEHYDROGENATION OF METHYLCYCLOHEXANE[79]

Effect of H_2 Pressure on Chromia and Molybdena Catalysts

Catalysts: Mo/Al = 21 wt. % MoO_3 on α-$Al_2O_3 \cdot H_2O$
Cr/Al^1 = Cr_2O_3 (ca. 16 wt. %) + CeO_2 (*ca.* 0.9 wt. %) + K_2O (*ca.* 1.4 wt. %) on γ-Al_2O_3
Cr/Al^2 = 20 wt. % Cr_2O_3 on α-$Al_2O_3 \cdot H_2O$
Temperature: 490°C

Catalyst	Pressure (atm.)	H_2/HC (mole)	LHSV (v/v/hr)	Contact Time (sec)	Liquid Product (0–15 hr)		
					Aromatics (mole %)	Yield (vol. %)	Yield (% of theor.)
Mo/Al	1	0	0.36	22	74.5	76	83
Cr/Al^1	1	0	0.36	22	98.7	78	88
Cr/Al^2	1	0	0.36	22	69.2	80	87
Mo/Al	20	5[a]	0.24	113	94.5	71	80
Cr/Al^1	20	5[a]	0.24	113	12.9	92	94

[a] 2.5 H_2 + 2.5 natural gas.

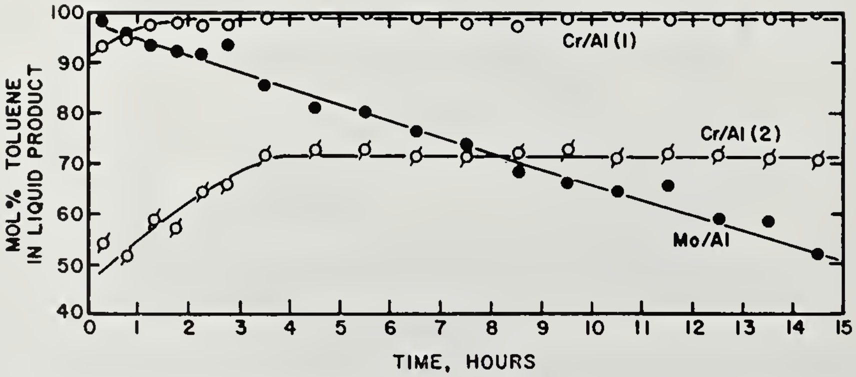


Figure 3. Comparison of chromia and molybdena catalysts for dehydrogenating methylcyclohexane at atmospheric pressure. Catalyst compositions and process conditions listed in Table 1.

The loss of activity with time on stream under a given set of conditions is related to coke formation, as illustrated in Figure 6. Here activity factor is plotted both against process time and carbon on catalyst, and is seen to decrease in the same manner with each variable. At a given reactor pressure, coke formation is decreased by increasing the hydrogen to hydrocarbon ratio, as shown in Figure 7. The extent of this decrease is directly propor-

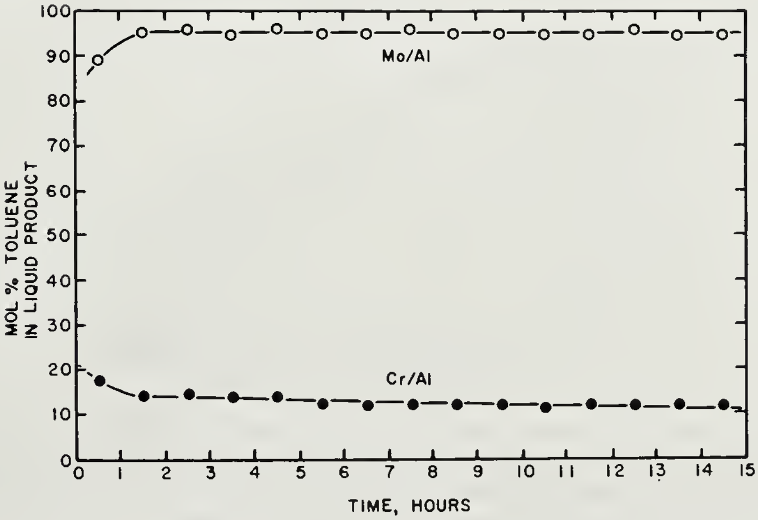


Figure 4. Comparison of chromia and molybdena catalysts for dehydrogenating methylcyclohexane at 20 atm. Catalyst compositions and process conditions listed in Table 1.

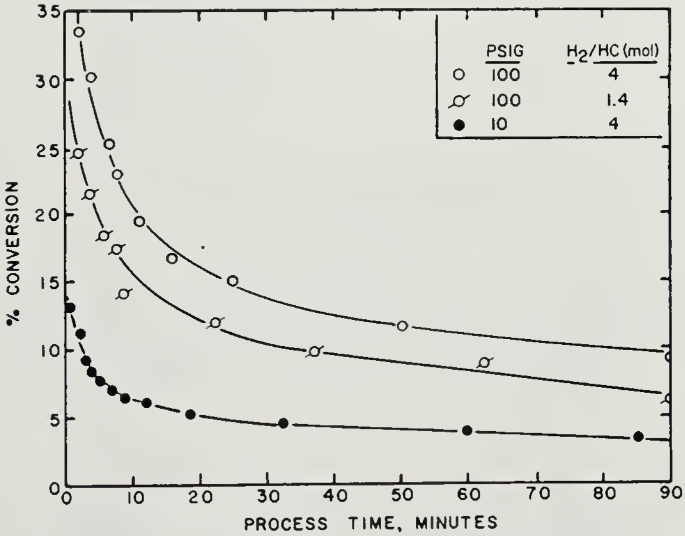


Figure 5. Effect of pressure, hydrogen dilution and process time on the conversion of cyclohexane with molybdena-alumina. *Catalyst:* Coprecipitated molybdena-alumina (10 wt. % MoO_3). *Conditions:* 940°F, $WHSV^{-1} = 10.4$ hr/g/g after pretreating for 15 min. in H_2 stream at 1000°F.

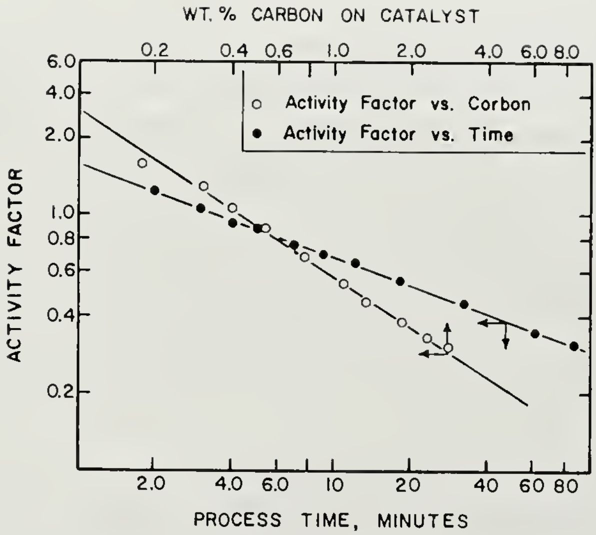


Figure 6. Effect of process time and coke deposition on the activity of molybdena-alumina for conversion of cyclohexane. *Catalyst:* Coprecipitated molybdena-alumina (10 wt. % MoO_3). *Conditions:* 940°F, 10 psig, $WHSV^{-1} = 10.4$ hr/g/g, $H_2/HC = 4$ (mole) after pretreating for 15 min. in H_2 stream at 1000°F.

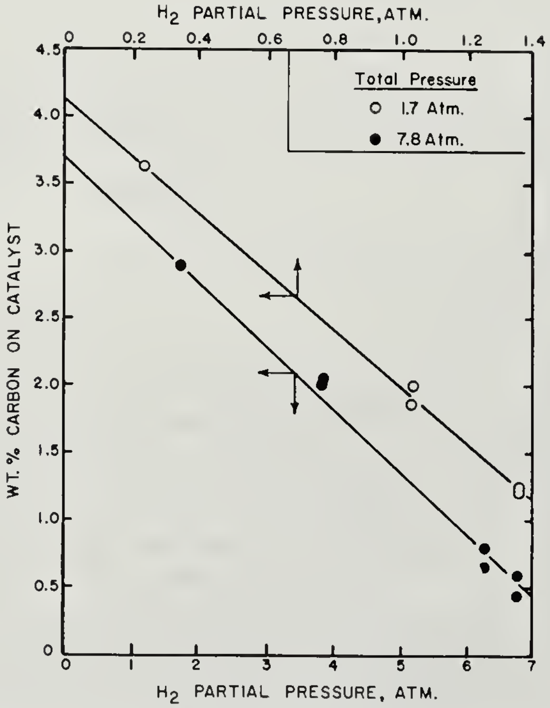


Figure 7. Effect of hydrogen partial pressure on coke deposition in the conversion of cyclohexane with molybdena-alumina. *Cataylst:* Coprecipitated molybdena-alumina (10 wt. % MoO_3). *Conditions:* 940°F, $WHSV^{-1} = 10.4$ hr/g/g, 15 min. runs after pretreating for 15 min. in H_2 stream at 1000°F.

tional to the resulting increase in hydrogen partial pressure and occurs as a result of increased hydrogenation of unsaturated coke precursors.

The reactions of cyclohexane in a synthetic blend with *n*-heptane using molybdena-alumina and chromia-alumina catalysts have been studied at hydrogen pressures typical of those used in commercial reforming, with complete analysis of all reaction products[55]. Comparative evaluations of a cogelled chromia-alumina, a coprecipitated molybdena-alumina, and a molybdena impregnated on gel alumina—three principal types of oxide reforming catalysts—are illustrated in Figures 8a–c. The conversion of cyclohexane as a function of temperature is plotted in the upper curve of Figure 8a. Both of the molybdena catalysts are considerably more active than chromia-alumina. For example, at hydrogen partial pressures of 100 psia, 850°F, and liquid feed rates of 1 v/v/hr the mole per cent cyclohexane converted was 99 per cent for molybdena on gel alumina and 93 per cent for coprecipitated molybdena-alumina, compared to 35 per cent for chro-

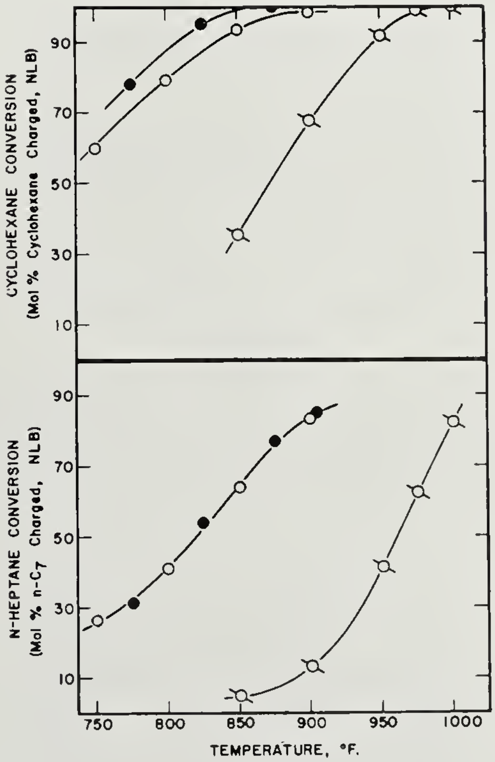


Figure 8a. Comparison of chromia-alumina and molybdena-alumina catalysts. Reforming activity with a *n*-heptane, cyclohexane blend (50:50 mole %). *Catalyst:* ● Molybdena impregnated on gel alumina (10 wt. % MoO_3); ○ Coprecipitated molybdena-alumina (10 wt. % MoO_3); ⊘ Cogelled chromia-alumina (32 wt. % Cr_2O_3). *Conditions:* 100 psig, $H_2/HC = 6$ (mole), LHSV = 1 v/v/hr.

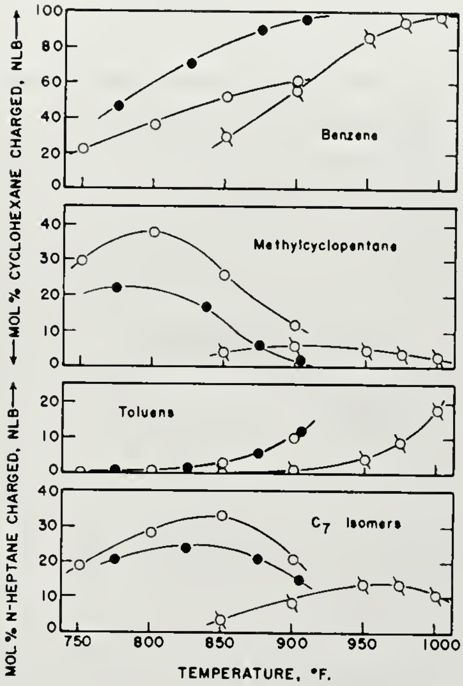


Figure 8b. Comparison of chromia-alumina and molybdena-alumina catalysts. Product yields from reforming a n-heptane, cyclohexane blend (50:50 mole %). *Catalysts:* ● Molybdena impregnated on gel alumina (10 wt. % MoO_3); ○ Coprecipitated molybdena-alumina (10 wt. % MoO_3); ⊘ Cogelled chromia-alumina (32 wt. % Cr_2O_3). *Conditions:* 100 psig, $H_2/HC = 6$ (mole), LHSV = 1 v/v/hr.

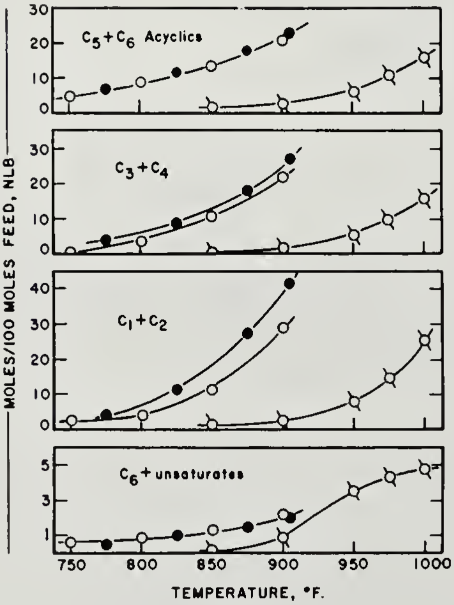


Figure 8c. Comparison of chromia-alumina and molybdena-alumina catalysts. Product yields from reforming a n-heptane, cyclohexane blend (50:50 mole %). *Catalysts:* ● Molybdena impregnated on gel alumina (10 wt. % MoO_3); ○ Coprecipitated molybdena-alumina (10 wt. % MoO_3); ⊘ Cogelled chromia-alumina (32 wt. % Cr_2O_3). *Conditions:* 100 psig, $H_2/HC = 6$ (mole), LHSV = 1 v/v/hr.

mia-alumina. At these process conditions, the principal cyclohexane conversion products are benzene and methylcyclopentane. The distribution of these products varies with catalyst and with temperature, as shown in the two top curves of Figure 8b. The two molybdena-alumina catalysts are more active than chromia-alumina for both the dehydrogenation of cyclohexane to benzene and the isomerization of cyclohexane to methylcyclopentane. The higher benzene yields obtained with molybdena on gel alumina compared to coprecipitated molybdena-alumina is only partly due to increased activity. The remainder is due to increased selectivity for dehydrogenation, with less isomerization at the lower temperatures and less hydrocracking at the higher temperatures. Both molybdena on gel alumina and chromia-alumina produce benzene yields approaching 100 per cent at complete conversion of the cyclohexane, despite the considerable difference in activity between these catalysts. The coprecipitated molybdena-alumina is much less selective for dehydrogenation to benzene because of increased hydrocracking at high conversion levels.

Isomerization Reactions

Isomerization reactions play a significant role in the catalytic reforming of petroleum naphthas. The two most important of these are (1) the conversion of paraffins to the higher octane number isoparaffins and (2) the dehydroisomerization of alkylcyclopentanes to aromatics by a sequence of reactions involving isomerization of a 5-member ring to a 6-member ring followed by dehydrogenation to the aromatic.

The extent to which isomerization can increase the octane number of paraffins is illustrated by the data in Figure 9[58]. These values illustrate how the octane number increases with increased chain branching and with a decrease in molecular weight. However, the limits imposed by thermodynamics on the isomer distribution places a relatively low ceiling on the octane number which can be obtained by isomerization alone, as shown by the values in Figure 9a[104]. Nevertheless, the increase in octane number accompanying isomerization, together with the fact that paraffin isomerization involves small volumetric changes, makes this reaction a contributor to the over-all octane yield.

Isomerization and Dehydroisomerization of Naphthenes. The importance of naphthene isomerization lies in the fact that most of the substituted cyclopentanes have lower blending octane numbers than the corresponding aromatics to which they can be converted by dehydroisomerization. This is illustrated by the data in Table 2. Since naphthenic reformer feed stocks contain appreciable quantities of alkylcyclopentanes[69] selective dehydroisomerization becomes an important property of any reforming catalyst.

Conversion of alkylcyclopentanes to aromatics requires that the cyclo-C_5 ring first be isomerized to a cyclo-C_6 ring followed by dehydrogenation. The first example of this two-step reaction sequence in a single pass was reported by Greensfelder and Fuller[80] for the direct conversion of methylcyclopentane to benzene using a molybdena-alumina catalyst at reforming conditions. In a later publication[79] these results were compared with a chromia-alumina catalyst. The results of Table 3 show that molybdena-alumina is an effective catalyst for this reaction at reforming conditions while chromia-alumina containing cerium and potassium oxides is not. At 10 atmospheres pressure, 490°C, 0.16 v/v/hr LHSV and 3 mole ratio of hydrogen to hydrocarbon, molybdena-alumina produced 76 vol. per cent of liquid product during a 10-hour flow period with a decrease in aromatic content from 76 to 33 wt. per cent over the process periods 1 to 2 and 7 to 10 hours, respec-

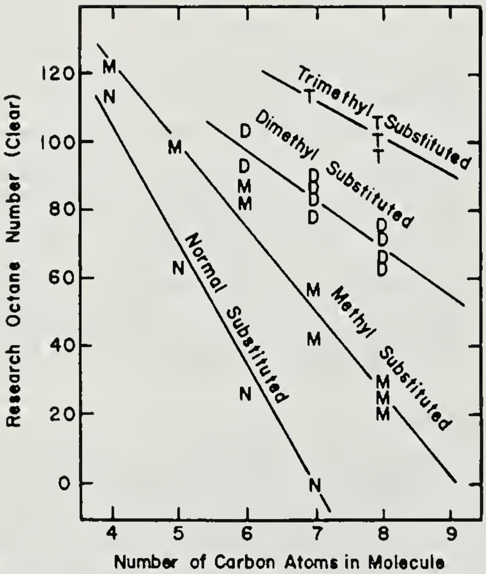


Figure 9. Octane quality of paraffinic hydrocarbons. Ratings above 100 are blending values from 20% blends in 60 octane reference fuel.

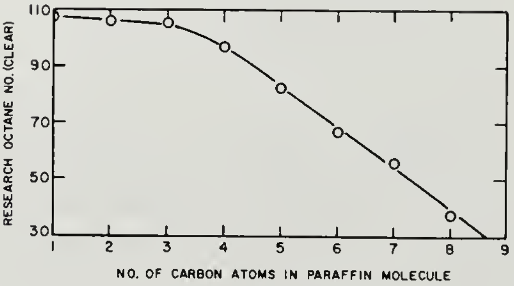


Figure 9a. Research octane number of 900°F. Equilibrium paraffin isomer mixture.

TABLE 2. OCTANE NUMBERS OF PURE HYDROCARBONS[16]

Paraffins:	Blending Research Octane No. (Clear)*
Paraffins:	
n-Butane	113
Isobutane	122
n-Pentane	62
2-Methylpentane	99
2,2-Dimethylpropane	100
n-Hexane	19
2-Methylpentane	83
3-Methylpentane	86
2,2-Dimethylbutane	89
2,3-Dimethylbutane	96
n-Heptane	0
2-Methylhexane	41
3-Methylhexane	56
3-Ethylpentane	64
2,2-Dimethylpentane	89
2,3-Dimethylpentane	87
2,4-Dimethylpentane	77
3,3-Dimethylpentane	83
2,2,3-Trimethylbutane	113
n-Octane	−19
n-Nonane	−17
Naphthenes:	
Methylcyclopentane	107
Ethylcyclopentane	75
1,1-Dimethylcyclopentane	96
1,3-Dimethylcyclopentane (*cis*)	98
1,3-Dimethylcyclopentane (*trans*)	91
1,1,3-Trimethylcyclopentane	94
Cyclohexane	110
Methylcyclohexane	104
Ethylcyclohexane	43
1,1-Dimethylcyclohexane	95
1,2-Dimethylcyclohexane (*cis* or *trans*)	85
1,3-Dimethylcyclohexane (*cis*)	67
1,4-Dimethylcyclohexane (*trans*)	85
1,4-Dimethylcyclohexane (*cis*)	68
1,4-Dimethylcyclohexane (*trans*)	64
1,1,3-Trimethylcyclohexane	85
1,3,5-Trimethylcyclohexane (*cis*)	60
Isopropylcyclohexane	62
Aromatics:	
Benzene	99
Toluene	124
1,2-Dimethylbenzene	120
1,3-Dimethylbenzene	145
1,4-Dimethylbenzene	146

TABLE 2. (*Continued*)

Parafins	Blending Research Octane No. (Clear)*
Aromatics:	
Ethylbenzene	124
n-Propylbenzene	127
Isopropylbenzene	132
1-Methyl-2-ethylbenzene	125
1-Methyl-3-ethylbenzene	162
1-Methyl-4-ethylbenzene	155
1,2,3-Trimethylbenzene	118
1,2,4-Trimethylbenzene	148
1,3,5-Trimethylbenzene	171

* Calculated value of pure hydrocarbon from research method rating of clear mixture of 20% hydrocarbon and 80% primary reference fuel (60% isooctane + 40% *n*-heptane).

tively. The decrease in activity with time on stream is attributed to coke formation. At the same total pressure lower conversions were obtained at shorter contact times. Lower conversions were also obtained at 20 atmospheres and at 1 atmosphere pressure. In the absence of added hydrogen, the catalyst deactivated rapidly because of coke formation.

In a study of the dehydrogenation of methylcyclopentane over a chromia-alumina catalyst at high temperatures and at atmospheric pressure Heinemann[100] found that some dehydroisomerization occurred. At 1150°F, with hydrogen added in the ratio of 3 moles per mole of hydrocarbon and 1 LHSV, 12.1 per cent conversion to benzene was obtained at a total conversion of 48.7 per cent. Better selectivity (10.4 per cent benzene at a total conversion of 29.7 per cent) was obtained at 1050°F by adding 1 per cent of benzene to the charge because of a reduction in cracking activity. At

TABLE 3. DEHYDROISOMERIZATION OF METHYLCYCLOPENTANE WITH CHROMIA AND MOLYBDENA CATALYSTS[79]

Catalysts: Mo/Al = 19–21 wt. % MoO_3 on α-$Al_2O_3 \cdot H_2O$
Cr/Al = 15.8 wt. % Cr_2O_3 + 0.85 wt. % CeO_2 + 1.39 wt. % K_2O on γ-Al_2O_3
Temperature: 490°C

Catalyst	Pressure (atm.)	H_2/HC (mole)	LHSV (v/v/hr)	Contact Time (sec.)	Yield (vol. %)	% Aromatics in Product at Process Time (hr)
Mo/Al	10	3	0.16	100	76	76(1–2), 44(3–6), 33(7–10)
“	20	5	0.26	100	79	39(1), 25(4), 22(6), 17(10)
“	10	10	0.12	50	68	64(1), 45(3), 33(7), 30(12)
“	1	3	0.09	30	21	85(1–5), 9(6–12)
Cr/Al	10	3	0.16	100	91	<1(1–6)

these process conditions the principal reaction products were monoolefins with smaller amounts of diolefins, gas, and coke.

Comparison of the properties of molybdena-alumina and chromia-alumina catalysts for the isomerization and dehydrogenation of a naphthene at partial pressures of hydrogen similar to those used commerically is illustrated by the reactions of cyclohexane in Figures 8a–c, referred to previously[55]. At 100 psig with a 6 mole ratio of hydrogen to hydrocarbon, molybdena on gel alumina and coprecipitated molybdena-alumina are considerably more active for the isomerization of cyclohexane than chromia alumina (Figure 8b). Methylcyclopentane yields at 800°F were 38 per cent with coprecipitated molybdena-alumina, 21 per cent with molybdena on gel alumina and, by extrapolation, essentially zero with chromia-alumina.

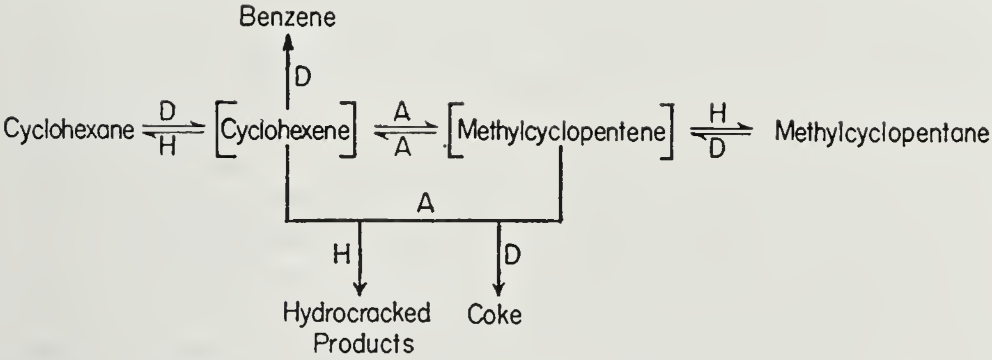


Figure 10. Reaction scheme for reforming naphthenes over dual-function catalysts. H-D = hydrogenation-dehydrogenation sites. A = Acid sites.

As the conversion of cyclohexane increases with temperature (Figure 8a) the yields of methylcyclopentane pass through a maximum and then decrease owing to the competing reactions of dehydrogenation and hydrocracking (Figure 8b). With chromia-alumina the maximum yield of methylcyclopentane was 6 mole per cent at 900°F. At complete conversion of the cyclohexane the benzene yields approach 100 per cent with molybdena on gel alumina and chromia-alumina, showing little evidence of hydrocracking the ring hydrocarbons under these conditions. Considerable hydrocracking occurs with coprecipitated molybdena-alumina at high conversion levels and thereby reduces the ultimate yields of benzene. The greater activity of the coprecipitated molybdena-alumina catalyst for isomerization at low conversion levels and for hydrocracking at high conversions reflects a relatively high degree of catalyst acidity.

The distribution of products obtained in the conversion of cyclohexane with these oxide catalysts can be interpreted according to the reaction scheme illustrated in Figure 10. This model is adapted from one first proposed by Mills *et al.* for reforming over dual-function catalysts[124]. It assumes two types of catalytic sites with transferral of olefin intermediates between them. Here *D* and *H* represent dehydrogenation-hydrogenation sites associated with the properties of the transition metal ion and *A* represents acid catalyst sites associated in some way not clearly defined with the properties of the oxides[46]. The severity of conditions required for hydrocarbon conversion (a measure of total catalyst activity) depends on the absolute activities of these sites. But the extent of the different possible reactions (degree of selectivity) depends more on the relation between these activities. For example, chromia-alumina has a lower activity than molybdena-alumina for dehydrogenation, isomerization and dehydroisomerization of naphthenes. However, its selectivity for dehydrogenating cyclo-C_6 naphthenes to aromatics at higher temperatures is excellent. That is, high yields of aromatics can be obtained with only small losses due to hydrocracking. The interpretation of these results, in terms of the reaction scheme shown in Figure 10, is that in chromia-alumina the activity of the *D-H* sites is relatively low (high temperature requirement) but that the ratio of activities of the *D-H* sites to *A* sites is relatively high. Because of this relationship between the activities of the two types of sites chromia-alumina has good selectivity for dehydrogenation reactions but poor selectivity for the acid-catalyzed reactions of isomerization and hydrocracking.

Molybdena-alumina catalysts have higher activity than chromia-alumina for dehydrogenation, isomerization and dehydroisomerization of naphthenes. They also have higher selectivity for isomerization and dehydroisomerization. The interpretation here is that the activity of both the *D-H* sites and the *A* sites of molybdena-alumina is higher than in chromia-alumina. The coprecipitated molydena-alumina catalyst has a much higher selectivity than molybdena on gel alumina for the isomerization of cyclohexane to benzene (Figure 8b). It also has greater hydrocracking activity at high conversion levels, resulting in lower yields of benzene. These results are interpreted to reflect a lower ratio of activity of *D-H* sites to *A* sites in the coprecipitated catalyst than in the impregnated catalyst. In the competition of the two types of sites for the intermediate olefin the *A* sites are more successful and more reaction occurs by acid catalysis.

This effect is further illustrated for the conversion of cyclohexane where the concentration of acid centers is systematically increased by adding silica to a series of molybdena-alumina catalysts. Catalyst evaluation results under reforming conditions are listed in Table 4[55]. At the same conversion of cyclohexane (95 to 98 per cent) and the same temperature (825°F) the yield of methylcyclopentane increases from 18 to 45 per cent and the yield of benzene decreases from 70 to 37 per cent as silica is added up to 25 wt. per cent. This change in product distribution is believed to result solely from the change introduced by the added silica-alumina acid function. For each catalyst the yield of benzene increases with temperature but the increase in acid-catalyzed hydrocracking resulting from silica addition affects these yields adversely. At 900°F, the yield of benzene decreases from 98 to 56 per cent and the combined yield of benzene plus methylcyclopentane decreases from 100 to 66 per cent as silica is added to 25 per cent. Practically all of the converted cyclohexane which does not appear in the product as these two components is hydrocracked. The isomerization of paraffins and the selectivity for cracking into large fragments, as opposed to demethanation, are also increased by increasing the concentration of acid centers. Another effect of the increased acidity is an increase in coke formation, an expected result of the reaction scheme illustrated in Figure 10.

TABLE 4. EFFECT OF SILICA ON MOLYBDENA-ALUMINA-SILICA CATALYSTS[65]

Feed: 50 ml % n-heptane + 50 ml % cyclohexane

Conditions[a]: 100 psig. $H_2/HC = 6$ (mol), LHSV = 1 v/v/hr

Evaluation Results	Wt.% SiO_2[b]			
	0	5	10	25
C_7 isomer yield[c] at 825°F	24	32	39	46
Toluene yield[c] at 825°F	1	1	1	1
Toluene yield at 900°F	10	11	10	10
Methylcyclopentane yield[d]	18	22	40	45
Benzene yield[d] at 825°F	70	61	38	37
Benzene yield at 900°F	98	89	62	56
Mole ratio $C_3 + C_4/C_1 + C_2$ at 80% n-C_7 conversion	0.65	0.85	1.45	1.90
$\left(\frac{\text{Methylcyclopentane + benzene}}{\text{Cyclohexane converted}}\right)$[d] at 900°F	1.0	0.94	0.77	0.66
Wt. % coke on catalyst[e]	0.2	0.4	1.1	1.5

[a] Pretreated 16 hr. in H_2 stream at 950°F, 1 atm.

[b] Catalysts prepared by wet ball-milling Al_2O_3 hydrogel with SiO_2 hydrogel; 10 wt. % MoO_3 added to calcined support by impregnation method.

[c] Basis—mole % n-heptane charged.

[d] Basis—mole % cyclohexane charged.

[e] After 6 hr on stream at increasing severity. Last hour at 95% conversion of feed.

The distinction between the hydrogenation-dehydrogenation function and the acid function cannot be defined as clearly in the oxide system of catalysts as in systems containing a reduced metal. The reason is that in the oxides both types of catalytic functions reside in the same molecular component. Further, the levels of dehydrogenation activity in the metal oxides are much lower than in the platinum reforming catalysts, as will be shown. For these reasons, it has not yet been possible to measure uniquely the activity of each function independent of the other. Nevertheless, we feel that the relative order of activity of these functions can be usefully estimated from the results of reaction studies with pure hydrocarbons in the manner illustrated.

Isomerization of Paraffins. The isomerization of *n*-paraffins over chromia-alumina and molybdena-alumina was first studied in detail under hydroforming conditions by Greensfelder, Archibald and Fuller[79]. Their results, summarized in Table 5, clearly show that molybdena-alumina is much more active for the isomerization of paraffins than is chromia-alumina.

TABLE 5. PARAFFIN ISOMERIZATION WITH CHROMIA AND MOLYBDENA CATALYSTS UNDER HYDROFORMING CONDITIONS[79]

Catalysts: Mo/Al = 21 wt. % MoO_3 on α-$Al_2O_3 \cdot H_2O$
Cr/Al = 15.8 wt. % Cr_2O_3 + 0.85 wt. % CeO_2 + 1.39 wt. % K_2O on γ-Al_2O_3
Conditions: 490°C, 10 atmospheres pressure, 3 mole ratio of H_2/HC, 100 sec. contact time

Catalyst	Feed	LHSV (v/v/hr)	% Isomers in Product at Process Time (hr)	Equilibrium
Mo/Al	*n*-butane	0.15	17 at 1–4 hr; 15 at 13–16 hr	37% isomers
Cr/Al			2 " " "; 3 " " "	
Mo/Al	*n*-pentane	0.16	53 at 1–3 hr; 41 at 10–12 hr	74% isomers
Cr/Al			8 " " "; 6 " " "	
Mo/Al	*n*-heptane	0.20	49.5 clear O.N. dearom. prod.[a]	58 clear O.N.
Cr/Al			10 clear O.N. dearom. prod.[b]	

[a] Contains 10% butanes (i/n = 4/6), 3% pentanes, 75% heptanes
[b] Contains 3% butanes, 0.3% pentanes, 90% heptanes

At 490°C, hydrogen to hydrocarbon mole ratio of 3, total pressure of 10 atmospheres and 0.15 v/v/hr LHSV, the molybdena catalyst produced an isomer yield about seven times higher than the chromia catalyst from either *n*-butane or *n*-pentane.

The isomerization of *n*-pentane in the presence of molybdena-alumina catalysts under hydrogen pressures has been studied in detail by Clark, Matuszak, Carter and Cromeans[47]. They showed that the activity and selectivity of molybdena-alumina catalysts for the isomerization of *n*-pentane under hydrogen pressure was very much dependent on the mole ratio of hydrogen to pentane, especially at ratios considerably lower than generally used in hydroforming. This effect is illustrated in Figure 11 using a molybdena-alumina-silica catalyst. At 860°F, 500 psig and 1.3 v/v/hr LHSV, the isomerization selectivity with *n*-pentane increased from 68 per cent with no added hydrogen to a maximum of 95 per cent at a hydrogen to pentane mole ratio of 0.5, and then decreased sharply to below 70 per cent at ratios greater than 0.8. The selectivity maximum was obtained at conversion levels of 40 to 55 wt. per cent, with a corresponding decrease in hydrocracking of the pentanes to C_4 and lighter hydrocarbons. The selectivity maximum in a very narrow band around 0.5 mole ratio of hydrogen to pentane was attributed to a critical hydrogen chemisorption on the catalyst. Too low a dilution with hydrogen produces more unsaturates and excessive coking and results in lower activity and selectivity. Higher dilution with hydrogen decreases the partial pressure of the pentane and so decreases the conversion. The lower isomerization selectivity at hydrogen to pentane mole ratios above the critical range of 0.3 to 0.8 was unexpected.

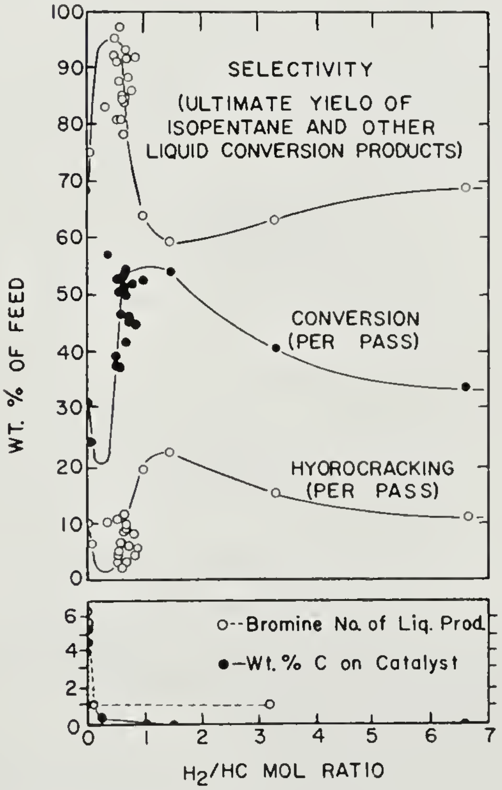


Figure 11. Effect of hydrogen to hydrocarbon ratio on *n*-pentane isomerization with molybdena-alumina-silica. *Catalyst (wt. %)*: 6.4% MoO_3, 4.6% SiO_2, 89% Al_2O_3. *Conditions:* 500 psig, 860°F, LHSV = 1.3 v/v/hr, Run time = 2.5–4 hr.

Operating pressure also affects the activity and selectivity of this catalyst for isomerizing *n*-pentane, as shown in Figure 12. At 830°F, 1.3 v/v/hr liquid space velocity, and 0.7 mole ratio of hydrogen to pentane, the conversion of the pentane increased from 29 wt. per cent at 125 psig to a maximum of 39 wt. per cent at 250 to 500 psig. Further increase in pressure up to 900 psig decreased conversion progressively down to 30 wt. per cent. Selectivity for isopentane increased linearly over this region of 125 to 900 psig from 91 to 96 per cent, with simultaneous decrease in coking and hydrocracking.

Not enough information has been published to tell how general this "low-hydrogen isomerization" is with respect to both hydrocarbon reactant and to catalyst. These investigators indicate that n-pentane shows the effect especially well. A number of other molybdena catalysts were investigated at low mole ratios of hydrogen to pentane. These were studied to help explain the role of catalyst composition in the pentane isomerization reaction. Isomerization was carried out at 500 psig, 820 to 860°F, 1.2–1.4 v/v/hr LHSV, and 0.5 to 0.9 mole ratio of hydrogen to pentane with the results shown in Table 6.

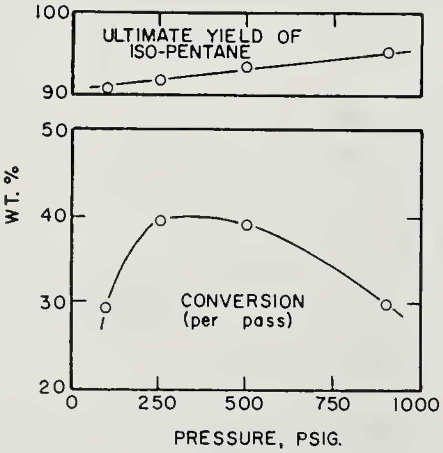


Figure 12. Effect of pressure on n-pentane isomerization with molybdena-alumina-silica. *Catalyst (wt. %)*: 6.4% MoO_3, 4.6% SiO_2, 89% Al_2O_3. *Conditions:* 830°F, LHSV = 1.3 v/v/hr, H_2/HC = 0.7 (mole).

Unsupported molybdenum oxide has poor activity and poor selectivity for isomerization. Molybdena supported on activated charcoal was even less active. This comparison is cited to show that merely dispersing molybdena on an inert support is not sufficient to catalyze the reaction effectively. Alumina alone was similarly not active nor did it give a selective reaction. As has been shown, molybdena impregnated on alumina gives a very active and selective catalyst, suggesting either that molybdena is more effectively dispersed on alumina and/or that molybdena complexes with alumina in a way not yet understood. The addition of small amounts of silica (about 5 wt. per cent) increases both the activity and the selectivity for the pentane isomerization reaction. This is expected on the basis that silica creates silica-alumina acid centers and these effectively promote the

TABLE 6. LOW HYDROGEN ISOMERIZATION OF *n*-PENTANE WITH MOLYBDENA CATALYSTS[47]

Catalyst Type	MoO_3[a]	Al_2O_3	Mo/Al[c]	Mo/C	Mo/Al/Si[b]	Mo/Al/F	Mo/Al/Si	Mo/Al/Si[a]	Pt/Mo/Al/Si	Mo/Al/Si
Composition, wt. %										
Molybdena	100	0	9	15.0	6.4	10	20	20	20	24.2
Alumina	0	100	91	0	89.0	88	75	75	75	72.0
Silica	0	0	0	0	4.6	0	5	5	4	3.8
Charcoal	0	0	0	85.0	0	0	0	0	0	0
Flourine	0	0	0	0	0	2	0	0	0	0
Platinum	0	0	0	0	0	0	0	0	1	0
Test conditions, (500 psig, 4 hr)										
Temperature, °F	860	860	860	860	860	860	860	820	820	820
LHSV (v/v/hr)	1.3	1.3	1.2	1.4	1.4	1.3	1.3	1.3	1.32	1.38
H_2/HC (mole)	0.90	0.78	0.75	0.75	0.51	0.86	0.76	0.75	0.73	0.66
Product distribution, (wt. % feed)										
Methane	9.2	1.5	0.7	1.3	0.5	1.8	0.6	0.2	0.3	0.4
Ethane	1.3	0.6	1.1	0.7	1.0	2.5	0.9	0.2	0.2	0.5
Propane	2.2	0.9	1.4	1.9	1.4	5.8	1.4	0.9	0.7	0.8
Butanes	2.5	0.8	1.8	0.6	1.8	6.8	2.7	1.0	0.9	1.3
Isopentane	2.0	2.4	34.2	4.2	45.3	41.9	49.6	45.2	42.3	49.3
n-pentane	81.0	93.4	59.9	91.3	50.0	40.5	43.8	50.1	50.1	45.5
Other liquids[d]	1.8	0.4	0.9	—	—	0.7	1.0	2.4	2.5	2.2
Total conversion, wt. %	19.0	6.6	40.1	8.7	50.0	59.5	56.2	49.9	46.9	54.5
Liquid yield per pass, wt. %	84.8	96.2	95.0	95.5	95.2	83.1	94.4	97.7	97.9	97.0
Hydrocarbon recovery, wt. %	—	—	—	—	94.0	—	—	100.5	99	96.2
Ultimate yield, wt. %										
Liquid products	20	42	87.6	48	90.6	71.6	90.0	95.4	95.5	94.5
Isopentane	11	36	85.3	48	90.6	70.6	88.2	90.6	90.2	90.2
Carbon, wt. % of catalyst	—	—	—	—	—	—	—	0.12	0.03	0.17
” , wt. % of feed	—	—	—	—	0.1	—	—	0.04	0.01	0.12

[a] Regenerated once
[b] Regenerated 36 times
[c] Coprecipitated
[d] Cyclopentane (⅔) + Neohexane (⅓) — tentative indication by I.R. analysis

Table 7. Isomerization of *n*-Hexane with Tungsten Oxide and Molybdenum Oxide Catalysts[38]

Conditions: 350 psig, $H_2/HC = 4$ (mole), LHSV = 1.0 v/v/hr

Temperature, °F	601	649	700	757	599	710	804	923	601	702	802	905
Total recovery, wt. % charge	95.3	95.9	95.1	91.0	100.7	95.8	101.4	94.8	92.1	93.0	96.2	97.6
Catalyst	6.3 Wt. % WO_3 on Silica-Alumina				14.9 Wt. % MoO_3 on Silica-Alumina				14.9 Wt. % MoO_3 on Alumina			
Product Distribution (Mole % Charge-NLB)												
Methane	1.1	0.5	1.1	0.5			2.1	15.6	1.6			2.1
Ethane			0.6	0.6			2.0	14.0	1.4			2.6
Propane		0.4	1.4	9.0	1.6	2.0	21.5	90.8	1.6	0.6	1.0	2.0
Isobutane			0.1	0.9		0.4	1.2	3.1	1.0			0.3
n-Butane	0.4		0.6	0.4	1.0		0.9	3.0	1.3			1.2
Isopentane	0.5	0.5	0.6	1.2			1.0	3.7				0.5
n-Pentane	0.5	0.2	0.7	0.8			1.6	2.4				1.4
2,2-Dimethylbutane						1.7	2.5	2.0				
2,3-Dimethylbutane			1.4	1.1		2.7	5.6	2.5				
2-Methylpentane	1.6	4.2	10.8	18.8	1.9	10.5	27.9	12.6	0.1	0.6	0.5	7.8
3-Methylpentane	2.1	2.5	7.6	11.2	1.6	5.9	16.0	8.1	0.5	0.5	1.0	6.2
n-Hexane	95.3	92.7	77.8	61.4	95.3	77.4	32.3	11.6	94.8	98.6	98.1	80.8
Conv. *n*-Hexane (mole % charge)	4.7	7.3	22.2	38.6	4.7	22.6	67.7	88.4	5.2	1.4	1.9	19.2
C_6 Isomer yield (mole % charge)	3.7	6.7	19.8	31.1	3.5	20.8	52.0	25.2	0.6	1.1	1.5	14.0
Selectivity factor	0.79	0.92	0.89	0.81	0.75	0.92	0.77	0.28	0.12	0.79	0.79	0.73
Wt. % C on catalyst				0.18				0.42				0.08

acid-catalyzed isomerization reaction by the mechanism illustrated in Figure 10. In the same way, the addition of 2 per cent fluoride to molybdena-alumina increases catalyst activity but, at these conditions, decreases the isopentane yield because of excessive hydrocracking, a side reaction also catalyzed by acid centers. The addition of 1 wt. per cent platinum to molybdena-alumina-silica produced less coke deposit but did not increase either the activity or the selectivity of the catalyst for pentane isomerization. The lower coke formation resulting from plantium addition is expected since platinum has excellent hydrogenation activity and will effectively catalyze the hydrogenation of unsaturated coke precursors. The present day nonregenerative platinum reforming processes make use of this property. The failure of platinum to promote the isomerization reaction suggests that in the sequence of reactions required to produce isopentane from n-pentane, the rate limiting step is the intermediate acid catalyzed isomerization of n-pentene to isopentene as will be more fully discussed later. The fact that acid promoters like silica and fluoride increase the isomerization activity of molybdena-alumina bears this out.

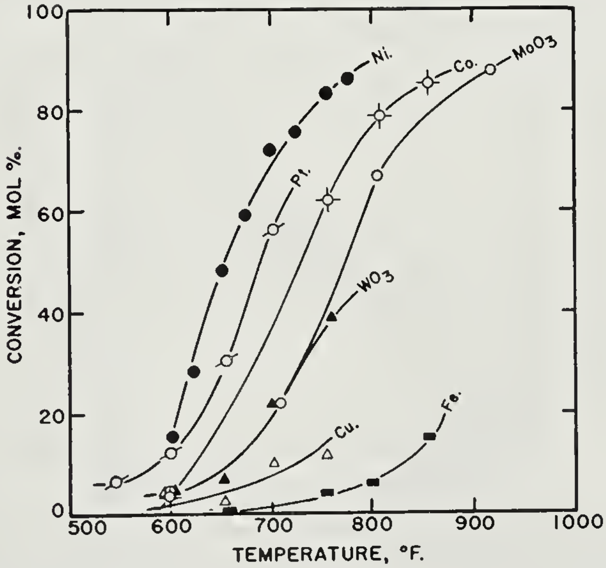


Figure 13. Conversion of n-hexane with metals and metal oxides supported on silica-alumina. *Catalysts (wt.%)*, Supported on 420 m^2/g SiO_2-Al_2O_3 (13% Al_2O_3): ● = 5% Ni; ⊘ = 0.5% Pt; ⌖ 5% Co; ○ = 14.9% MoO_3 ; ▲ = 6.3% WO_3 ; △ = 5% Cu; ▬ = 5% Fe. *Conditions:* 350 psig, H_2/HC = 4 (mole), LHSV = 1 v/v/hr.

Ciapetta and Hunter[38] have studied the isomerization of n-hexane at reforming conditions using supported catalysts containing transition metals and oxides. Their results are shown in Table 7 and in Figures 13 and 14. At 350 psig, 4 mole ratio of hydrogen to n-hexane and a liquid space velocity of 1 v/v/hr they found that molybdena-silica-alumina was considerably more active and more selective than molybdena-alumina, owing to the increased acidity contributed by the silica-alumina. Tungsten oxide-silica-alumina compared favorably with molybdena-silica-alumina except for an indication of lower selectivity at conversion levels above 30 per cent. Catalysts containing nickel, platinum or cobalt supported on silica-alumina were both more active and more selective than any of the oxide catalysts. Copper-silica-alumina and iron-silica-alumina, however, had much poorer isomerization properties than the oxides. Since all of these compositions contained the same high activity silica-alumina it is reasonable to assume, as a first approximation, that the order of activity of the acid function is the same for all of them. The main differences in isomerization properties must then be related to the differences in the activities of the dehydrogenation component.

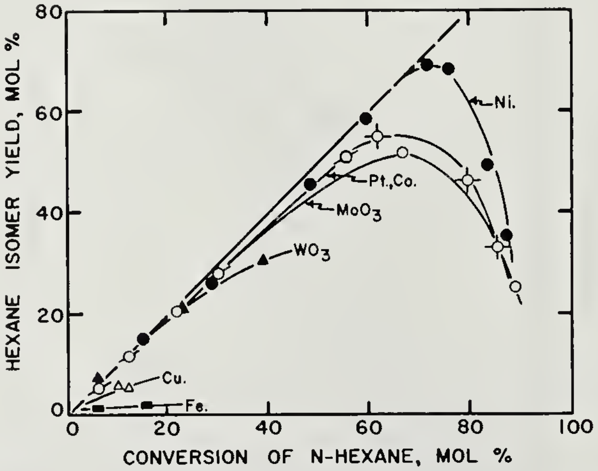


Figure 14. Hexane isomer yields with metals and metal oxides supported on silica-alumina. *Catalysts* (*wt.* %) supported on 420 m²/g. SiO_2-Al_2O_3 (13% Al_2O_3): ● = 5% Ni; ⌀ = 0.5% Pt; ¤ = 5% Co; ○ = 14.9% MoO_3 ; ▲ = 6.3% WO_3 ; △ = 5% Cu; ▬ = 5% Fe. *Conditions:* 350 psig, H_2/HC = 4 (mole), LHSV = 1 v/v/hr.

In another investigation[55] chromium oxide, molybdenum oxide and platinum were studied as the dehydrogenation components of catalyst systems containing silica-aluminas of varying composition. These catalysts were evaluated with an equi-molar blend of *n*-heptane and cyclohexane at 100 psig, 6 mole ratio of hydrogen to hydrocarbon, 1 v/v/hr space velocity and at different temperatures. The results showed that for any of these dehydrogenation components, the activity and selectivity of the catalyst for the isomerization of *n*-heptane could be varied between fairly wide limits by changing the activity of the acid component. However, for each of the dehydrogenation components, there appeared to be an upper limit which could not be exceeded at these conditions of operation. Thus, compositions containing chromium oxide as the sole dehydrogenation component gave maximum yields of isoheptane no higher than 25 mole per cent at 60 per cent conversion (values based on *n*-heptane charged) at temperatures no lower than 950°F. With molybdenum oxide as the dehydrogenation component the maximum isomer yield was increased to 45 mole per cent at 60 per cent conversion, at temperatures down to 800°F. Among the most active and selective catalysts were platinum-silica-aluminas which gave isoheptane yields of 59 mole per cent at 60 per cent conversion at 700°F. In this study the support composition was varied in order to optimize the isomerization properties of the catalyst for each of the dehydrogenation components. The major differences in these three catalyst systems must, therefore, be related again to the activity of the dehydrogenation component.

TABLE 8. H_2-D_2 EXCHANGE ACTIVITY ON METAL OXIDE-SILICA-ALUMINA CATALYSTS[46]

Catalysts: 4 wt. % metal oxide impregnated on support, pretreated in H_2 at 500°C

Metal Oxide	Rate Constant Sec^{-1} at 80°C
MoO_3	100
CrO_3	15
NiO	12[a]
ZnO	1.02
FeO	0.64
WO_3	0.3[b]
UO_3	0.06[b]

[a] Catalyst reduced in H_2 at 300°C
[b] Rate constant measured at 200°C

To interpret these results on the isomerization of *n*-hexane and of *n*-heptane with these different dual-function catalysts it would be desirable to have an independent measure of the activity of each catalytic function without interference from the other. No single method has been applied to measure the acidity function in all of these different systems. Two methods have been used, however, to determine the activity of the dehydrogenation function. One is the reaction between H_2 and D_2 to form HD, the other is the conversion of cyclohexane to benzene.

Clark[46] has used the H_2-D_2 exchange reaction as a generalized measure of hydrogenation-dehydrogenation activity for some transition metal oxides supported on silica-alumina, with the results shown in Table 8, for catalysts pretreated in hydrogen at 500°C. The much higher exchange activity of molybdena-silica-alumina compared to chromia-silica-alumina is in line with the isomerization results on molybdena and chromia catalysts previously discussed. If exchange activity is to correlate with isomerization activity, dehydrogenation components with exchange values much lower than chromia would not be very effective. Iron oxide falls into this category and zinc and uranium oxides would be expected to fit similarly. The attempted correlation between the two sets of results fails, however, with nickel and with tungsten oxide on silica-alumina. As dehydrogenation components in combination with silica-aluminas nickel is much more effective for isomerization than molybdena and tungsten oxide is similarly more effective than chromia. Their exchange activities, on the catalysts reported, however, are lower.

A better correlation between dehydrogenation activity and isomerization properties was obtained when this functional property was measured as the rate of converting cyclohexane to benzene in a differential flow reactor under reforming conditions[55]*. This method is a modification of one previously described[162]. Dehydrogenation activity measurements were made on a number of catalysts containing supported transition metals and oxides as dehydrogenation components, with the results given in Table 9. Chromia-

TABLE 9. DEHYDROGENATION ACTIVITY VALUES OF SOME SUPPORTED METAL AND OXIDE CATALYSTS[55]

Catalyst (wt. %)	Dehydrogenation Activity Index[a] (μmoles benzene/g. catalyst/sec.)
34% Cr_2O_3 cogelled with Al_2O_3	0.5
10% MoO_3 coppt'd. with Al_2O_3	3
5% Ni on Al_2O_3 or SiO_2–Al_2O_3	13
5% Co on Al_2O_3	13
0.5% Ir on Al_2O_3	190
1% Pd on Al_2O_3	200
5% Ni on SiO_2	320
1% Rh on Al_2O_3	890
0.5% Pt on Al_2O_3 or SiO_2-Al_2O_3	1400–4000

[a] Determined with cyclohexane in a differential flow reactor at 800°F, 100 psig $H_2/HC = 6$ (mole), after 30 min. pretreatment in flowing H_2 at the same conditions.

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* Dehydrogenation activity is measured at benzene concentrations between 1 to 5 mole per cent at 100 psig, 6 mole ratio of hydrogen to hydrocarbon and 800°F. Catalyst, 100 to 150 mesh, is diluted with powdered "Vycor" to a volume of 0.5 cc, then pretreated in the reactor for 0.5 hour at run conditions. Pure grade cyclohexane, percolated over silica gel, is charged with added hydrogen downflow through the catalyst bed. Samples are taken at time intervals up to 2 hours to test equilibration. Runs are made at two or more space velocities to define a linear relation between benzene concentration and reciprocal space velocity extending to the origin. The slope of this line is taken as the index of dehydrogenation activity, defined as μ moles benzene/g catalyst/sec. Typical liquid space velocities required to give 3 mole per cent benzene in the liquid product at these conditions varied from 5 v/v/hr with chromia catalysts to 35,000 with platinum catalysts.

alumina has one-sixth the activity of molybdena-alumina, in agreement with the order of activities determined by H_2-D_2 exchange. The supported metal catalysts have activities ranging up to several orders of magnitude higher than the oxides. To develop a correlation between the activity of the dehydrogenation function of a dual-function catalyst and its isomerization properties we shall apply these dehydrogenation values, as a first approximation, to the *n*-hexane and *n*-heptane isomerization data obtained with similar catalyst systems.

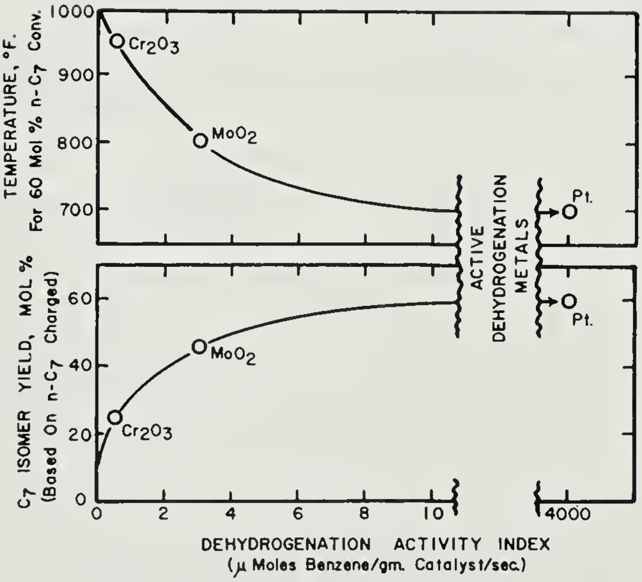


Figure 15. Relation between the dehydrogenation activity of dual-function catalysts and their isomerization properties. Isomerization results at 60 mole% conversion of *n*-heptane in a 50:50 blend with cyclohexane at feed rate of 1 v/v/hr, 100 psig and $H_2/HC = 6$ (mole). Dehydrogenation activity determined with cyclohexane at 800°F, 100 psig and $H_2/HC = 6$ (mole).

Figure 15 shows the relationship between the dehydrogenation activity, so applied, and the maximum activity and selectivity obtained with catalysts containing chromia, molybdena and platinum supported on silica-aluminas for isomerizing *n*-heptane at the conditions stated. Isomerization efficiency increases with dehydrogenation activity in the following order: Cr_2O_3-SiO_2-Al_2O_3 < MoO_3-SiO_2-Al_2O_3 < Pt-SiO_2-Al_2O_3. The *n*-hexane isomerization results at other conditions show that silica-alumina supported nickel, platinum and cobalt are superior to molybdena, the most active oxide reported in this series.

From all of these results, certain conclusions regarding the functional requirements for a good isomerization catalyst can now be drawn based on these tests. For any given acid component of a dual-function catalyst system, isomerization activity and selectivity will increase with increasing activity of the dehydrogenation function up to some limiting value. This value has not been critically determined and it may even vary with the nature of the acid component and with reaction conditions. But for silica-alumina compositions, this limiting value for the dehydrogenation activity appears to lie between 3 (molybdena) and 1400 (platinum) when determined by the procedure outlined. The good isomerization results using nickel and cobalt suggest that it may be as low as 13.

The concept of a limiting value for the activity of the dehydrogenation function suggests that this is the value required to give an equilibrium concentration of reactive olefin intermediate in the isomerization reaction[162]. Further increase in dehydrogenation activity then has no effect on isomerization as shown by the fact that platinum-silica-alumina is neither more active nor more selective than nickel-silica-alumina for the isomerization of *n*-hexane. Below this limiting value, however, the dehydrogenation activity of the catalyst may be too low to provide reactive olefin intermediate in sufficient concentration for acid components of high activity and, therefore, controls the isomerization reaction.

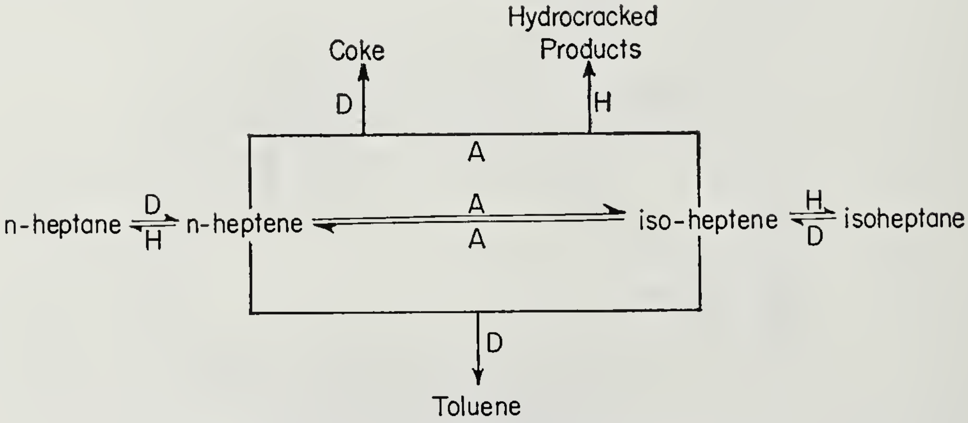


Figure 16. Reaction scheme for reforming paraffins over dual-function catalysts. H-D = Hydrogenation-dehydrogenation sites. A = Acid sites.

These concepts support the sequence of reactions postulated[41, 124, 161] for the isomerization of paraffins with dual-function catalysts. This reaction scheme, extended to include the reactions of hydrocracking, dehydrocyclization and coking is illustrated in Figure 16 with *n*-heptane.

According to this scheme, the rate of isomerization depends upon the activity of both catalytic functions. Either one may be rate, and therefore, activity and selectivity controlling. The available evidence suggests that with catalysts containing metals sufficiently active for dehydrogenation to exceed a certain limiting value, such as cobalt, nickel, rhodium, palladium, iridium and platinum, the over-all reaction rate is limited by the activity of the acid component for isomerizing the intermediate olefin. When the activity for dehydrogenation falls below this limiting value, either functional activity of the catalyst may be rate controlling. Thus, the lower activities and lower selectivities of isomerization catalysts containing oxides of chromium, molybdenum and tungsten as well as low activity metals like copper and iron are attributed to a level of dehydrogenation activity intrinsically too low. The effect of increasing the concentration of silica-alumina acid centers in a series of molybdena-alumina-silica catalysts is shown by the data in Table 4. With the addition of silica in concentrations up to 25 wt. per cent, the acid promoted reactions of isomerization, selective cracking and coke formation increase, consistent with the reaction model of Figure 16.

Promoted Chromia Catalysts. Evaluation results with a series of chromia catalysts are presented in Table 10, using a feed of *n*-heptane and cyclohexane at 100 psig, 6 mole ratio of hydrogen to dehydrocarbon and 1 v/v/hr liquid space velocity[55]. Pure chromium oxide gel, prepared from chromic acid and isopropyl alcohol, has acidic properties as shown by its ability to convert *n*-heptane to isoheptanes in 11 mole per cent yield at 900°F. A chromia-silica cogel, made by reacting chromic acid with ethylorthosilicate in alcohol is somewhat more selective for isomerization. The improvement contributed by silica may be due either to an enhanced chromium oxide surface or to a chemical interaction between the cogelled oxides to produce additional acid centers. A typical chromia-alumina reforming catalyst made by cogelation has lower activity than either fresh chromia gel or chromia-silica gel, but higher selectivity for isomerization due to a reduction in cracking activity. The presence of alumina in commercial catalysts of this type is dictated mainly by the requirement for long life. Impregnation of cogelled chromia-alumina with potassium oxide decreases catalyst activity for isomerization and cracking. The dehydrogenation results with cyclohexane showed no decrease in the activity of the dehydrogenation function of this catalyst. The decrease in the acid-catalyzed reactions of isomerization and cracking is, therefore, interpreted as resulting solely from an exchange of basic potassium ions for acid centers. Voltz and Weller[154] have reported that potassium oxide decreases the relative acidity of chromia-alumina, determined by quinoline adsorption, and also decreases its activity for the acid-catalyzed isomerization of pentene-1 at 300°C and atmospheric pressure. However, in their system potassium also decreased hydrogenation-dehydrogenation activity, as determined both by ethylene hydrogenation at -78°C and by cyclohexane dehydrogenation at 538°C and atmospheric pressure. Comparative results showing the effect of potassium oxide on chromia-alumina catalysts are summarized in Table 11,

TABLE 10. COMPARISON OF CHROMIA CATALYSTS[55]

Feed: 50 mole % n-heptane + 50 mole % cyclohexane

Conditions[a]: 100 psig, H_2/HC = 6 (mole), LHSV = 1 v/v/hr

Catalyst Composition (Wt. %)	Avg. Cat. Temp. (°F)	n-Heptane Converted	C_7 Isomer Yield	Toluene Yield	Cyclohexane Converted	Methylcyclopentane Yield	Benzene Yield	Feed Cracked to C_1–C_6 Acyclics
		(mole % n-heptane charged, NLB)			(mole % cyclohexane charged, NLB)			(mole % NLB)
Cr_2O_3 Gel[b]	900	59	11	2	100	2	98	18
55% Cr_2O_3-SiO_2 cogel[c]	900	58	15	3	100	3	97	16
10% Cr_2O_3 on H-40 Al_2O_3[d]	950	55	21	6	88	10	65	14
32% Cr_2O_3-Al_2O_3 cogel[e]	950	41	14	5	92	5	87	9
+ 1.8% K_2O[f]	950	24	7	5	90	3	87	2
+ 2% NiO[f]	950	69	12	7	100	2	98	19
+ 0.02% Pt[g, h]	950	46	14	7	100	4	98	7
+ 5% Si/Al[g, i]	950	48	23	6	83	10	61	11
+ 0.03% Pt + 5% Si/Al[g, j]	900	56	27	6	100	3	97	4

[a] Preheated 16 hr in H_2 stream at 950°F and 1 atm.

[b] Prepared from chromic acid and isopropyl alcohol, reduced slowly in H_2.

[c] Prepared from chromic acid and ethylorthosilicate in alcohol, reduced slowly in H_2.

[d] Alcoa H-40 Al_2O_3 contains 5% SiO_2.

[e] U. S. Patent 2,773,839.

[f] Added by impregnating the nitrate and calcining to the oxide.

[g] Added by wet ball-milling Cr_2O_3-Al_2O_3 hydrogel with added component in powder form.

[h] Added as 0.6% Pt/Al_2O_3.

[i] Added as 90% SiO_2-10% Al_2O_3, 430 m^2/g.

[j] Added as 0.6% Pt on 90% SiO_2—10% Al_2O_3, 430 m^2/g.

TABLE 11. EFFECT OF POTASSIUM OXIDE ON CHROMIA-ALUMINA CATALYSTS

Dehydrogenation of Methylcyclohexane at 490°C, 0.36 LHSV and 1 atm.

Catalyst (wt. %)[17]	(mole % toluene in liquid at process time)		
	1 hr	5 hr	20 hr
16% Cr_2O_3 on γ-Al_2O_3	98	98	93
1.4% K_2O + 0.9% CeO_2 added	96	98	98

Dehydrogenation, Isomerization, Hydrogenation Reactions and Catalyst Acidity

Catalyst (wt. %)[154]	Dehydrogenation of Cyclohexane at 538°C 1 LHSV, 1 atm. (vol. % benzene in liq.)	Isomerization of Pentene-1 at 300°C 1 LHSV, 1 atm. (vol. % pentene-2 in liq.)	Hydrogenation of Ethylene at −78°C	Relative Acidity (meq. quinoline adsorbed/g)
20% Cr_2O_3 on Al_2O_3	19.3	62.8	active	0.078
1.5% K_2O added	(8.2)	15.7	inactive	0.041

Reforming Cyclohexane-n-Heptane (50:50 mole %) at 950°F, 100 psig, $H_2/HC = 6$, LHSV = 1

Catalyst (wt. %)[55]	Cyclohexane Converted	Benzene Yield	Methylcyclopentane Yield	*n*-Heptane Converted	C_7 Isomer Yield	Toluene Yield	Dehydrocyclization Selectivity %	Cracking to C_1–C_6 Acyclic (mole % feed)
	(mole % cyclohexane charged)			(mole % *n*-Heptane charged)				
32% Cr_2O_3-Al_2O_3 cogel	92	87	5	41	14	5	12	9
1.8% K_2O added	90	87	3	24	7	5	21	2

including the results obtained by Archibald and Greensfelder[17] with potassium and cerium oxides on chromia-alumina.

The addition of nickel to chromia-alumina increases dehydrogenation activity but does not increase isomerization selectivity. Isomerization yields are actually lowered somewhat because of an increase in cracking activity. Similar results are obtained when small amounts of platinum (0.017 wt. per cent) are added. Dehydrogenation activity was increased but isomerization yield was not affected. These results suggest that with chromia-alumina the rate limiting step in the isomerization reaction is the acid-catalyzed isomerization of the olefin intermediate, not the rate of producing the initial olefin nor the rate of hydrogenating the iso-olefin. If the olefin isomerizing step is rate limiting with chromia-alumina, isomerization activity and selectivity should be increased by increasing the concentration of acid centers. Two examples demonstrating this effect are listed in the data of Table 10. In one case, 5 wt. per cent of a high activity silica-alumina cracking catalyst was added by ball milling the powder with a chromia-alumina hydrogel. In the other, chromia was impregnated onto an alumina-silica support. Both catalysts showed improved isomerization properties.

It would be expected that other acidic materials might similarly promote the isomerization activity of chromia catalysts although none has been reported in the technical literature to our knowledge. There is a limit, however, to the extent that isomerization can be increased by increasing catalyst acidity alone, for any given set of operating conditions. This limit, as discussed earlier, is determined by the dehydrogenation activity of the catalyst. An increase in the activity of this function can then raise the level of isomerization activity obtainable. This is illustrated by the simultaneous addition of platinum and silica-alumina promoters to chromia-alumina. The higher dehydrogenation activity contributed by the platinum does not in itself increase the isomeriztion activity of chromia-alumina since the olefin producing step is not rate limiting. However, it may increase the supply of reactive olefin intermediate, and this can be used advantageously if the acidity function is also increased. The resulting chromia catalyst with both functions promoted is more active for isomerization than one containing only an acidity promoter.

Effect of Preparation Variables on Properties of Molybdena-Alumina Catalysts. The properties of molybdena-alumina catalysts have been found to vary greatly with preparation procedure. Webb, Smith and Earhardt have compared catalysts prepared by impregnation methods with those made by coprecipitation[156]. Impregnated catalysts were prepared from alumina trihydrate (Baeyer process Gibbsite), alumina monohydrate (Boehmite, obtained from the trihydrate by calcining at 600°F), and gamma-alumina (obtained by calcining the trihydrate at 1300°F). The effects of peptizing the alumina with acetic acid before impregnation and of adding silica containing diluents were also studied with these aluminas. The coprecipitated form was made by adding ammonia or ammonium carbonate to a mixture of ammonium molybdate in aluminum chloride. Catalyst evaluation data are shown in Figures 17 and 18. The following conclusions were drawn by the authors:

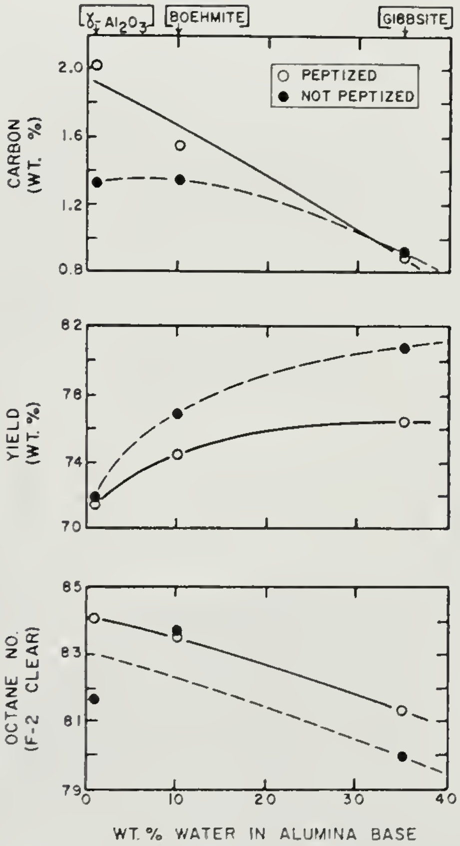


Figure 17. Effects of alumina type and peptization on the properties of impregnated molybdena-alumina catalysts. Reforming Mid-Continent naphtha at 100 psig, $H_2/HC = 6$ (mole) and block temperature = 932°F.

(1) The reforming activity of impregnated molybdena-alumina catalysts depends upon the water of hydration of the alumina at the time of impregnation, the highest activity being associated with the lowest water content.

(2) The reforming activity of impregnated catalyst is increased by peptizing the alumina before impregnation.

(3) Dilution with a silica component increases the thermal stability of impregnated catalysts.

(4) Coprecipitated catalysts are activated on heating over the tempera-

ture range of 1100 to 1470°F and have a much greater stability than any of the impregnated catalysts studied.

X-ray diffraction analysis showed that all of these catalysts, impregnated as well as coprecipitated, have the gamma-alumina structure after calcining at 1112°F. The main difference found for the two preparation procedures was the crystallite size of the alumina. It is this factor which appears to govern catalyst stability. The more stable precipitated catalysts have crystallite sizes as little as one-tenth that of the impregnated catalysts. Silica functions as a stabilizer by retarding crystal growth. Russell and Stokes have also shown that silica effectively stabilizes the activity of impregnated molybdena-alumina catalysts heated to high temperatures[142].

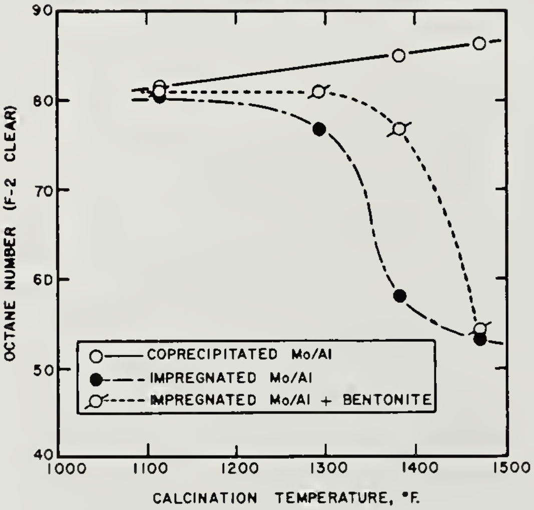


Figure 18. Effect of preparation method and silica addition on thermal stability of molybdena-alumina catalysts. Reforming Mid-Continent naphtha at 100 psig, $H_2/HC = 6$ (mole) and block temperature = 932°F.

The effects of preparation variables on the properties of molybdena-alumina catalysts have also been evaluated by studying the reforming reactions of pure hydrocarbons. The reactions of n-heptane over molybdena-aluminas at atmospheric pressure were investigated by Russell and Stokes[141, 142]. At these conditions the principal reactions are dehydrocyclization to toluene, cracking and coke formation. Evaluation of molybdena-alumina catalysts under reforming conditions with a mixed feed of n-heptane and cyclohexane provides more detailed information on the individual hydrocarbon reactions[55]. Results are presented in Table 12 for three different catalyst preparations—molybdena impregnated on gel alumina, molybdena impregnated on eta-alumina, and a coprecipitated molybdena-alumina. Marked differences are observed in their response to heat treatment in the region of 1000 to 1400°F and in their activity, especially for the acid catalyzed reactions of isomerization and cracking.

TABLE 12. COMPARISON OF MOLYBDENA-ALUMINA CATALYSTS[55]

Feed: 50 mole % *n*-heptane + 50 mole % cyclohexane

Conditions[a]*:* 850°F, 100 psig, H_2/HC = 6 (mole), LHSV = 1 v/v/hr

Catalyst[b]	Calcination Temp.[c] (°F)	*n*-Heptane Converted	C_7 Isomers Yield	Toluene Yield	Cyclohexane Converted	Methylcyclopentane Yield	Benzene Yield	Feed Cracked to C_1–C_6 Acyclics
		(mole % *n*-Heptane charged, NLB)			(mole % cyclohexane charged, NLB)			(mole %, NLB)
MoO_3 on Gel Al_2O_3[d]	1000	65	23	3	98	14	81	20
	1400	20	10	1	73	4	67	7
MoO_3 on η Al_2O_3[e]	1000	74	32	5	90	31	45	24
	1400	77	32	5	93	30	45	27
Coprecipitated MoO_3-Al_2O_3[f]	1000	34	20	1	64	23	35	9
	1400	81	32	6	98	19	58	31

[a] Pretreated 16 hr in H_2 stream at 950°F and 1 atm.

[b] Nominal composition 10 wt. % MoO_3

[c] Catalysts calcined 16 hr in air

[d] Filtrol Al_2O_3 gel

[e] Prepared from β-$Al_2O_3 \cdot 3H_2O$

[f] Coprecipitated at pH = 7.5 from ammonium molybdate and aluminum nitrate

Molybdena on gel alumina loses considerable activity for all of the reactions of *n*-heptane and cyclohexane when the temperature of calcination is raised from 1000 to 1400°F. Webb *et al*'.s impregnated catalysts deactivated similarly[156] as shown in Figure 18, as did those reported by Russell and Stokes[142] using activated alumina supports. When eta-alumina (prepared from $\beta \cdot Al_2O_3 \cdot 3H_2O$) is used as a support material, however, the resulting catalyst is seen to have excellent thermal stability. The results of Table 12 show no loss in activity for any of the reactions over the calcination region 1000 to 1400°F. Another major difference found with molybdena on eta-alumina is an increased activity for isomerization and cracking reactions. This is interpreted to reflect increased catalyst acidity since there is no evidence for any increase in dehydrogenation activity. The lower yields of benzene actually obtained with this catalyst result not from any decrease in activity for cyclohexane conversion, but rather to a product distribution shift in favor of the competing reactions of isomerization and cracking as illustrated by the reaction model in Figure 10. Still a third type of molybdena-alumina is one prepared by coprecipitation. After calcining at 1000°F, this catalyst has relatively low reforming activity. Considerable activation results in heating to 1400°F, as has been reported by Webb *et al.*[156] and by Russell and Stokes[142]. The heat activated coprecipitated molybdena-alumina has reforming activity very similar to molybdena impregnated on eta-alumina. The hydrocarbon evaluation results indicate comparable acidic properties for these two catalysts, and at a higher acidity level than in molybdena on gel alumina. A recent abstract on the study of the acidity of different forms of alumina and their activity for olefin isomerization has been reported[134]. Alumina prepared from aluminum isopropoxide and calcined at temperatures up to 1300°F exhibited strong acidic properties.

These results suggest that the properties of molybdena-alumina catalysts are governed primarily by the crystallographic form of alumina and only secondarily by the method used to add the molybdena. The activation which occurs on heating the coprecipitated material to 1400°F, accompanied by a decrease in surface area from 213 to 110 m^2/g, may be due to the development of a preferred crystallographic form of alumina or of a molybdena-alumina complex. X-ray diffraction patterns showed, however, only a crystal growth of gamma-alumina, with the appearance of a new phase, tentatively identified as delta-alumina, at 1400°F. The similar reforming properties of coprecipitated molybdena-alumina heated to 1400°F and of molybdena impregnated on eta-alumina heated in the temperature region of 1000 to 1400°F suggests similar catalyst structures. X-ray diffraction studies have not yet, however, confirmed this.

Sodium oxide reduces the acidity of aluminas[134] and has a detrimental effect on the stability of molybdena-alumina reforming catalysts. McGrath and Hill[121] have reported that the first commercial catalyst of this type had a short life because of the presence of several tenths per cent sodium. Catalyst life was considerably extended by reducing its sodium content.

Dehydrocyclization Reactions

The catalytic conversion of paraffins and olefins to aromatics over oxide catalysts at atmospheric pressure has been summarized in detail by Steiner[147]. Some feature of the reaction and its utility in catalytic reforming have been discussed by Haensel[93]. The use of dehydrocyclization in the syntheses of aromatic compounds has been reviewed by Hansch[94].

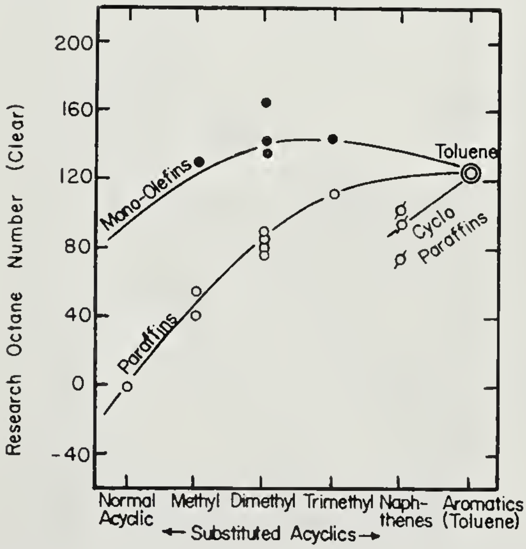


Figure 19. Octane quality of C_7 hydrocarbons. Ratings above 100 are blending values from 20% blends in 60 octane reference fuel.

The importance of dehydrocyclization in catalytic reforming processes is due to the very high blending octane numbers of the resulting aromatics. This is illustrated by the data in Table 2 and in Figures 19 and 20. These are considerably higher than the octane values which can be produced by isomerization of paraffins, particularly those of high molecular weight. Even though dehydrocyclization involves appreciable volume contraction because of the increased density of the aromatic liquid product, as compared with isomerization, the aromatization reaction assumes increasing importance as a contributor of high octane blending components as octane requirements rise.

Thermodynamic considerations show that dehydrocyclization like dehydrogenation is favored by high temperature, low partial pressure of hydrogen and increasing carbon number of reactant. The effects of temperature, pressure and hydrogen dilution on the equilibrium distribution of the two systems *n*-hexane-benzene-hydrogen and *n*-heptane-toluene-hydrogen are illustrated in Figures 21 and 22. It is apparent that the dehydrocyclization of *n*-heptane is greatly favored over that of *n*-hexane. For example, at 950°F, 500 psig and 10 mole ratio of hydrogen to hydrocarbon, the concentration of toluene in equilibrium with *n*-heptane is 74 mole per cent, compared to 17 mole per cent benzene in equilibrium with *n*-hexane. Pressure also has a very pronounced effect. At 800°F and 6 mole ratio of hydrogen to hydrocarbon, the concentration of toluene in equilibrium with *n*-heptane is 4 mole per cent at 500 psig, 32 per cent at 250 psig and 93 per cent at 100 psig. Varying hydrogen dilution in the range of normal processing has a relatively small effect on the equilibrium distribution as is evident from the figures. The temperature coefficient of the distribution is high as shown by the fact that 30 to 35°F rise in temperature will double the dehydrocyclization of *n*-heptane from 25 to 50 mole per cent in the pressure range of 100 to 500 psi. The reaction is strongly endothermic with $\Delta H = 60.34$ kcal/mole at 800°K[58].

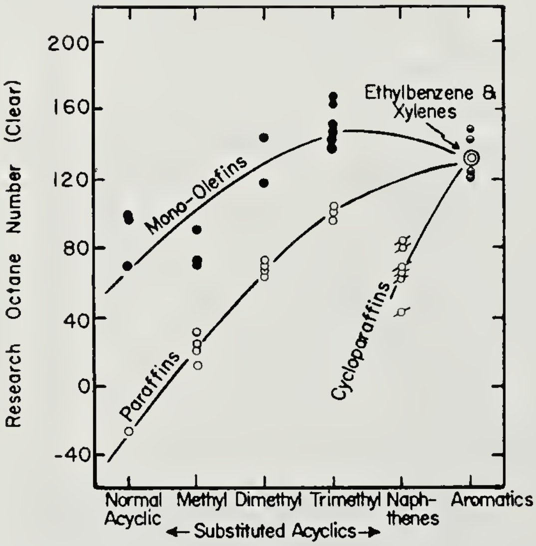


Figure 20. Octane quality of C_8 hydrocarbons. Ratings above 100 are blending values from 20% blends in 60 octane reference fuel.

Because the formation of high octane aromatics by dehydrogenation of naphthenes and by dehydrocyclization of paraffins is so strongly dependent on temperature, hydrogen partial pressure, and contact time, differences in catalyst activity can be largely overcome by adjusting operating severity. Thus, metal oxide reforming catalysts with lower intrinsic activity for dehydrogenation and dehydrocyclization than the platinum reforming catalysts are generally used at higher temperatures, lower partial pressures of hydrogen and lower throughput rates to obtain high aromatic yields.

Hettinger *et al.*[104] have compared the dehydrocyclization activity of chromia-alumina and molybdena-alumina with various active metals supported on alumina using *n*-heptane at 200 psig, 925°F, 5 mole ratio of hydrogen to hydrocarbon and weight hourly space velocities of 2 to 10. Their results, illustrated in Figure 23, show that the oxide catalysts have much lower dehydrocyclization activity than the active metals supported on alumina. At the lowest throughput rate, 2 WHSV, the conversions of *n*-hep-

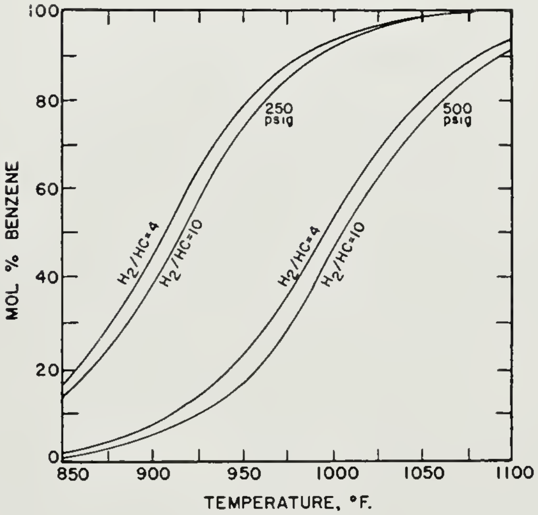


Figure 21. Equilibrium distribution for the system *n*-hexane-benzene hydrogen.

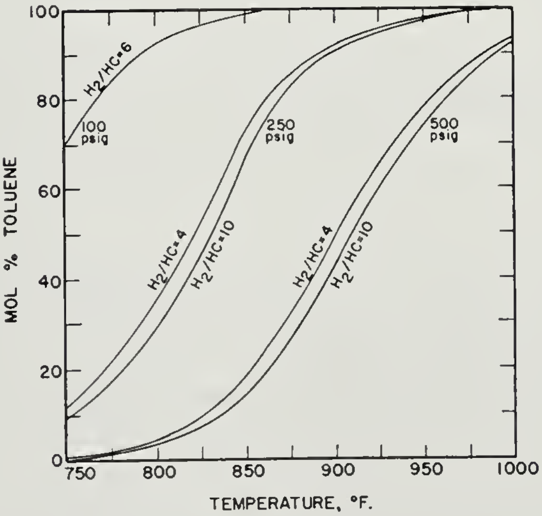


Figure 22. Equilibrium distribution for the system *n*-heptane-toluene-hydrogen.

tane to aromatics + naphthenes, read from their figure, are 1 mole per cent for chromia-alumina, 9 per cent for molybdena-alumina, and 41 per cent for platinum-alumina. These conditions are clearly not favorable for producing extensive dehydrocyclization with the lower activity oxide catalysts.

The classical work on the conversion of paraffins to aromatics was largely carried out at atmospheric pressure, temperatures about 500°C, and space velocities in the range of 0.1 to 1.0 v/v/hr with no hydrogen added. At these conditions chromium oxide gel, chromia-alumina and molybdena-alumina catalysts give aromatic yields in the range of 50 to 60 wt. per cent based on feed. These yields are higher than those which were obtained with supported metal catalysts in the early investigations of the dehydrocyclization reaction. These facts seem to be the basis for a still widely held impression that the Group VI metal oxides in general, and chromium and molybdenum oxides in particular, are unique dehydrocyclization catalysts. Present information indicates, however, that the dehydrocyclization activity of any catalyst system is related to its activity for dehydrogenation and that operating conditions, particularly hydrogen partial pressure, are a determining factor. The activity of a catalyst for dehydrocyclization and its relation to dehydrogenation activity can be and often is obscured by the deactivating effect of coke formation, especially with the more acidic catalysts. It was not until dehydrocyclization was studied under elevated pressures of hydrogen with complete analysis of all reaction products that the importance of reaction conditions to catalyst performance was fully realized.

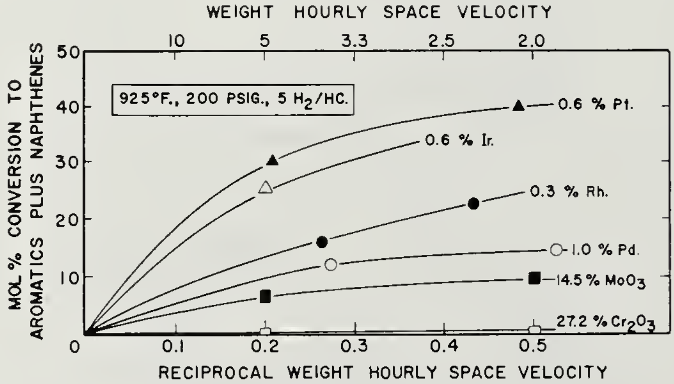


Figure 23. Dehydrocyclization activity of various metals and metal oxides supported on alumina using a *n*-heptane feed.

Greensfelder, Archibald and Fuller[79] showed that the dehydrocyclization activity of chromia-alumina and molybdena-alumina is, like dehydrogenation activity, markedly affected by hydrogen pressure. Their results, given in Table 13 and Figure 24, show initial toluene concentrations in the liquid product of 70 to 80 mole per cent from both catalysts at 1 atmosphere pressure, 490°C, and 0.36 v/v/hr LHSV. The more acidic molybdena catalyst deactivates very rapidly at these conditions owing to coke formation. After four hours on stream the toluene concentration decreased to 25 mole per cent, compared to 83 mole per cent with the chromia catalyst. In a similar study of molybdena-alumina catalysts, Russell and Stokes[141] obtained coke yields of 24 wt. per cent based on *n*-heptane feed after only 1.5 hours on stream at 490°C and 0.23 v/v/hr LHSV. At their conditions the other reaction products were 55 wt. per cent toluene (69 vol. per cent of the liquid product) 2 wt. per cent olefin and 21 wt. per cent gas, based on feed.

TALBE 13. DEHYDROCYCLIZATION OF *n*-HEPTANE[79]

Effect of H_2 Pressure on Chromia and Molybdena Catalysts

Catalysts: Mo/Al (1) = 21 wt. % MoO_3 on γ-Al_2O_3
Mo/Al (2) = 21 wt. % MoO_3 on α-$Al_2O_3 \cdot H_2O$
Cr/Al = Cr_2O_3 (*ca.* 15 wt. %) + CeO_2 (*ca.* 0.8 wt. %) + K_2O (*ca.* 1.4 wt. %) on γ-Al_2O_3

Temperature: 490°C

Catalyst	Pressure (atm.)	H_2/HC (mole)	LHSV (v/v/hr)	Contact Time (sec)	Liquid Product (0–15 hr.)		
					Aromatics (mole %)	Yield (vol. %)	Yield (% of theor.)
Mo/Al(1)	1	0	0.36	25	22.6	89	95
Cr/Al	1	0	0.36	25	73.6	67	84
Mo/Al(2)	20	5[a]	0.24	127	26.0	65	69
Cr/Al	20	5[a]	0.23	135	<1	87	87

[a] 2.5 H_2 + 2.5 natural gas

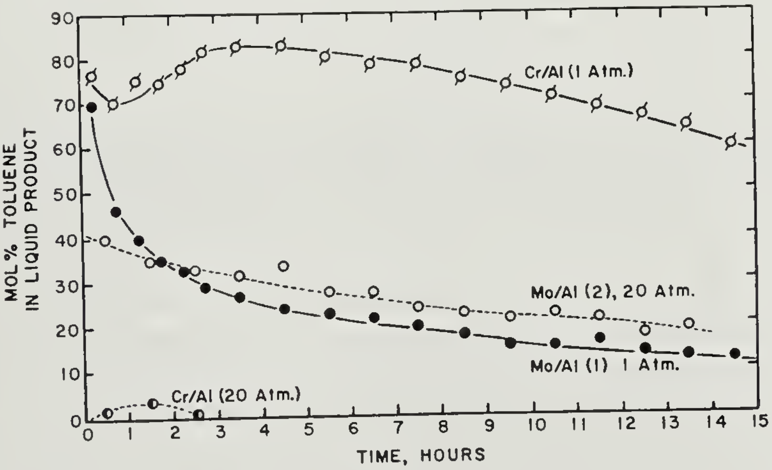


Figure 24. Dehydrocyclization of *n*-heptane. Effect of hydrogen pressure on chromia and molybdena catalysts. Catalyst compositions and process conditions listed in Table 13.

Increasing the pressure to 20 atmospheres with a simulated hydrogen containing recycle gas reverses the behavior of molybdena and chromia catalysts. With molybdena-alumina, the toluene concentration is reduced to an initial value of 41 mole per cent but stability is greatly improved because the increase in hydrogenation under hydrogen pressure effectively reduces coke build-up on the catalyst. At these conditions the chromia catalyst is virtually inactive.

Comparisons of chromia-alumina and molybdena-alumina for reforming of commercial naphthas at different partial pressure of hydrogen have been reported by Hughes, Stine and Darling[108]. They found that in reforming to a given octane level with a cogelled chromia-alumina catalyst coke yield decreased and liquid yield increased with increasing partial pressure of hydrogen and that the effects were very pronounced over the region 0 to 120 psi. Since hydrogen addition reduces the extent of dehydrogenation and dehydrocyclization, it is necessary to increase operating severity to maintain octane level. Even so, the length of on-stream period before regeneration was required was greatly extended by the use of hydrogen.

Hydrogen addition also has a marked effect on the performance of a chromia-alumina catalyst at atmospheric pressure. Donnell, Schneider and Stevenson[57] reformed a C_6-C_7 paraffinic fraction at near atmospheric pressures with and without hydrogen addition. At about the same octane level, the use of hydrogen decreased the coke yield from 7.5 to 1.4 wt. per cent and increased the $C_5 +$ liquid yield from 72 to 82 vol. per cent, all figures based on feed. Dehydrocyclization and dehydrogenation are the major reforming reactions at these conditions.

Promoted Oxides and Other Catalyst Systems. Studies of promoted chromia and molybdena catalysts and of other oxide systems for dehydrocyclization at atmospheric pressure have been reported by a number of investigators[31, 66, 78, 94, 102, 115, 147, 150]. Quantitative evaluation of catalysts for dehydrocyclization activity and selectivity is complicated by the fact that in many of these studies results are based only on the composition of the liquid product, not on total aromatic yield. Without this knowledge one cannot tell whether a given liquid product is high in aromatics because of extensive dehydrocyclization (high aromatic yield) or because of extensive cracking of the non-aromatic fraction (low aromatic yield). Most of the results show, however, that in the oxide class of catalysts used for aromatizing *n*-heptane at atmospheric pressure, chromia-alumina is more active, more selective, and more stable than molybdena-alumina, and that the oxides of vanadium[31], cerium[31], zirconium[66], thorium[31], neodymium[115], and samarium[115] have lower activity.

The best catalyst reported in the literature for converting *n*-paraffins to aromatics at atmospheric pressure seems to be the promoted chromia-alumina developed by Archibald and Greensfelder[17]. This catalyst contains

15.5 wt. per cent Cr_2O_3 supported on gamma-alumina and promoted by 1.34 wt. per cent K_2O and 0.82 wt. per cent CeO_2. Figure 25 shows that the promoters increase integrated space time yield of aromatics by maintaining catalyst activity, not by increasing intrinsic activity. The 40 per cent decrease in coke on the promoted catalyst after 15 hours on stream is believed to be responsible for its higher time-average activity. This is attributed to a selective poisoning of acid centers which causes a decrease in cracking reactions as well as the reactions which lead to coke formation. Thus, chromium oxide catalysts for dehydrogenating butanes make less coke and have greatly increased running cycles when promoted by sodium oxide similar to the results just described[46]. Although improved liquid yields were not reported for the potassium-cerium promoted catalyst a simultaneous decrease in acid-catalyzed cracking reactions might be expected. In the hydrogenation of isobutylene dimer at 390°C, 700 psig, $H_2/HC = 2$ and 1 v/v/hr LHSV, addition of sodium oxide to chromium oxide gel reduced the cracking of the feed from 12 to 15 to 2 per cent at approximately the same level of hydrogenation activity (99.5 *vs.* 98.5 per cent saturation of the C_8 product, respectively)[46].

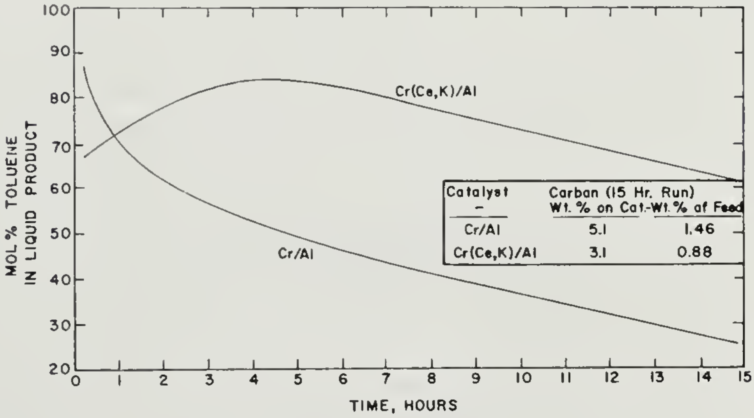


Figure 25. Effect of potassium and cerium oxides on chromia-alumina catalysts for dehydrocyclizing *n*-heptane. *Catalysts (wt. %):* Cr/Al = 15.5% Cr_2O_3 on γ-Al_2O_3; Cr(Ce, K)/Al = 15.5% Cr_2O_3, 0.82% CeO_2, 13.4% K_2O on γ-Al_2O_3. *Conditions:* 490°C, atmospheric pressure, LHSV = 0.36 v/v/hr after 1 hr. pretreatment in hydrogen at run conditions.

Among other components studied by Archibald and Greensfelder in combination with chromium on γ-Al_2O_3, lithium oxide reduced activity for dehydrocyclizing *n*-heptane, sodium oxide was either a weak depressor or a weak promoter, depending on concentration, and cesium oxide was slightly more effective than potassium oxide. Platinum had no apparent effect on this particular system.

The effect of various components on the dehydrocyclization properties of chromia catalysts is illustrated by the results in Table 10, obtained with an equi-molar feed of *n*-heptane and cyclohexane at 1 v/v/hr liquid space velocity under hydrogen pressures of 100 psi[55]. Extensive conversion is required at these conditions to obtain toluene yields of the order of 5 mole per cent based on the heptane charged. An active chromium oxide gel gave only 2 per cent toluene at 59 per cent heptane conversion at 900°F, 11 per cent isoheptanes were produced and most of the remainder was cracked to lighter hydrocarbons. A chromia-silica cogel gave similar results. Chromia-alumina cogel was less active but more selective for dehydrocyclization. At 950°F, 5 per cent toluene was obtained at 41 per cent conversion. The temperature coefficient of the reaction is high, however, and at 1000°F, 18 per cent toluene was obtained at 81 per cent conversion (Figure 8b). Dehydrocyclization selectivity is increased by selectively repressing cracking activity as the results with potassium oxide impregnated on chromia-alumina show. With this catalyst, at the same average temperature, 5 per cent toluene was obtained at 24 per cent conversion, an increase in dehydrocyclization selectivity (moles toluene/100 moles *n*-heptane converted) from 12 to 21 per cent. Dehydrocyclization selectivity is also increased by selectively increasing dehydrogenation activity, as shown by the results with chromia-alumina promoted with 0.018 wt. per cent platinum. At 950°F, this catalyst gave 7 per cent toluene at 46 per cent conversion. Small amounts of added nickel also promote dehydrogenation and dehydrocyclization activities. However, the simultaneous increase in cracking offsets this advantage and does not improve dehydrocyclization selectivity. Acidic promoters alone (e.g., silica-alumina) seem to have little effect on dehydrocyclization properties of chromia-alumina, but in combination with a dehydrogenation promoter (platinum + silica-alumina) dehydrocyclization activity is considerably improved. At 900°F this doubly promoted catalyst gave 6 per cent toluene at 56 per cent conversion.

In general, at these conditions, molybdena catalysts are more active but less selective for dehydrocyclization than chromia catalysts because more of the feed is converted by the acid-catalyzed reactions of isomerization and cracking. For example, for a 10 per cent toluene yield, molybdena-alumina required 83 per cent heptane conversion at 900°F, compared to 65 per cent conversion at 978°F with chromia-alumina (Figures 8a, 8b). Molybdena on gel alumina and a coprecipitated molybdena-alumina have comparable activity and selectivity for dehydrocyclization, despite relatively large differences in activity for the acid catalyzed reactions of isomerization and cracking (Figure 8b). The addition of silica to molybdena-alumina also increases activity for acid-catalyzed reactions without any apparent effect on dehydrocyclization (Table 4).

It is well established that the dehydrocyclization of paraffins proceeds through an olefin intermediate. The evidence for this has been reviewed by Steiner[147] in a comprehensive summary of the dehydrocyclization reaction with oxide catalysts at atmospheric pressure and lower. This evidence is supported by the results obtained with both oxide and metal catalysts at reforming conditions. Figure 26A, from the work of Hughes, Stine and Darling[108], shows the effect of contact time on the yields of olefins and aromatics in reforming a commercial naphtha with chromia-alumina catalyst at a constant partial pressure of hydrogen of 75 psi and 1020°F. At low contact time the olefin yield is high and the aromatic yield low. With increasing contact time aromatic yield increases as olefin yield decreases.

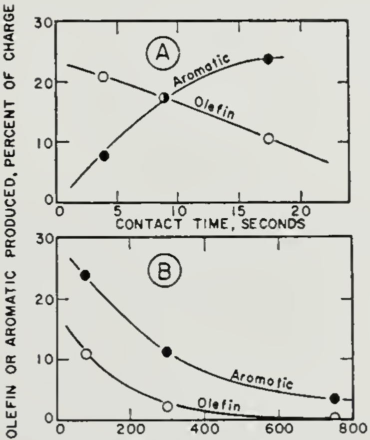


Figure 26. Effect of contact time and hydrogen pressure in reforming a Mid-Continent naphtha using chromia-alumina. A = Constant 75 psi H_2 pressure at 1020°F. B = Constant 18 sec. contact time at 1020°F.

These results support the postulate that olefins are intermediates in the sequence of reactions producing aromatics from paraffins. With increasing hydrogen pressure at constant contact time and temperature, lower yields of olefins and aromatics are obtained, as shown in Figure 26B. The effect of increasing hydrogen pressure on reducing the extent of dehydrocyclization is a general one. It follows both from thermodynamic considerations and from the fact that the competing reaction of hydrocracking also increases with hydrogen pressure[56, 104]. Since dehydrogenation has been established as the first step in the dehydrocyclization of a paraffin, dehydrogenation activity must be a functional catalyst property of primary importance. The higher dehydrocyclization activity obtained by Hettinger *et al.*[104] with active metals supported on alumina compared to the oxides (Figure 23) is in line with the higher activity of the metal catalysts for dehydrogenation (Table 9). The relative importance of the acid function in these dehydrocyclization catalyst systems has not been so well established. The aromatization of isoparaffins with less than six carbon atoms in a straight chain must involve an isomerization step in the reaction sequence. Isomerization must also be necessary for converting *n*-octane to *meta*- and *para*-xylene with a chromia-alumina catalyst as reported by Herrington and Rideal[103] and for converting *n*-paraffin to polyalkylbenzenes with a platinum-alumina-halogen catalyst as reported by Donaldson, Pasik and Haensel[56]. These isomerization reactions over bifunctional catalysts are believed to proceed via acid catalyzed rearrangement of olefin intermediates through a carbonium ion mechanism[28, 41, 56]. The present results reviewed on the dehydrocyclization of *n*-heptane with oxide catalyst systems do not, however, contribute very much to an understanding of the function of acidity in aromatizing this hydrocarbon. The results on potassium promoted chromia-alumina at 100 psi pressure, with decreased activity for acid catalyzed reactions of isomerization and cracking, show no change in activity for converting *n*-heptane to toluene (Table 10); the selectivity increase is due to a decrease in these side reactions. At atmospheric pressure the increased time-average yield of toluene with the cerium-potassium promoted catalyst is attributed to an increased activity maintenance resulting from reduced coke deposition, not to an increase in intrinsic activity (Figure 25). The results with the doubly promoted chromia-alumina catalyst (platinum + silica-alumina) compared to those containing only single promoters (Table 10) suggest, however, a cooperative mechanism of both the dehydrogenation and the acid functions. A good correlation between dehydrocyclization activity and the activity of these individual catalyst functions remains to be developed.

REFORMING REACTIONS OF PURE HYDROCARBONS WITH METAL-ACIDIC OXIDE CATALYSTS

Isomerization of Alkanes

n-Pentane. The isomerization of *n*-pentane was investigated by Ciapetta and Hunter[39] in the presence of a high area (S.A = 420 m^2/g) silica-alumina catalyst containing 5 per cent by weight of nickel. The reaction conditions and experimental results are shown in Table 14. The conversion of *n*-pentane as a function of temperature is shown in Figure 27. At a pressure of 24.8 atmospheres, the conversion of *n*-pentane commences at approximately 340°C and increases to 65 mole per cent at 407°C. Complete analysis of the products showed that isopentane was the major constituent. The selectivity factor (moles isopentane/mole *n*-pentane converted) increases with conversion and reaches a value of 0.86 at a *n*-pentane conversion of 49 mole per cent. The maximum yield of isomer, as shown in Figure

28, is obtained between 55 and 60 per cent conversion of *n*-pentane. At higher conversions, methane, propane, and butanes are formed as a result of hydrocracking of the pentanes. The higher yields of *n*-butane than isobutane show that the *n*-pentane is more easily hydrocracked than isopentane.

Table 14. Isomerization of *n*-Pentane[39]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. *H_2/HC:* 4 (Mole)

Run No.	270	271	272	273	274
Temperature, °C	343	371	382	393	497
Total recovery, wt. % charge	85.5	84.8	99.7	105.0	93.4
Product Distribution Moles/100 Moles of Charge (no-loss basis)					
Methane	0.4	3.1	5.4	15.7	24.7
Ethane			0.5	1.9	3.4
Propane	2.3	1.5	2.3	5.4	7.9
Isobutane	0.6	2.5	1.4	3.0	1.9
n-Butane	0.1	1.9	4.1	9.3	13.2
Isopentane	5.4	31.3	41.8	43.4	41.1
n-Pentane	92.3	63.1	51.1	39.4	35.3
Conv. *n*-pentane, mole % charge	7.7	36.9	48.9	60.6	64.6
Yield isopentane, mole % charge	5.4	31.3	41.8	43.4	41.1
Selectivity factor	0.70	0.85	0.86	0.72	0.64

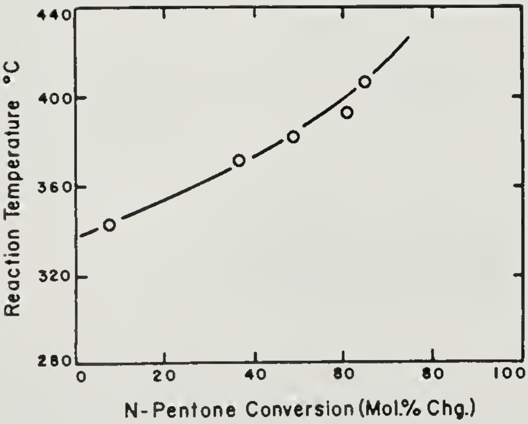


Figure 27. Isomerization of *n*-pentane. Effect of temperature on conversion of *n*-pentane.

Haensel and Donaldson[91] investigated the conversion of *n*-pentane in the presence of a platinum catalyst. Issued U. S. patents[86, 87] indicate that this catalyst consists of small amounts (0.1 to 1 wt. per cent) of platinum supported on a halogen activated alumina base. The reaction conditions and results are given in Table 15. At a *n*-pentane conversion of 39.9 mole per cent, this catalyst shows a high selectivity for the isomerization of *n*-pentane to isopentane; over 96 per cent of the *n*-pentane converted appears in the products as isopentane. Comparison of the data in Tables 14 and 15 shows that the platinum containing catalyst is less active than the nickel-silica-alumina catalyst. The platinum catalyst requires a temperature of 432°C compared to 375°C for 40 per cent conversion of *n*-pentane.

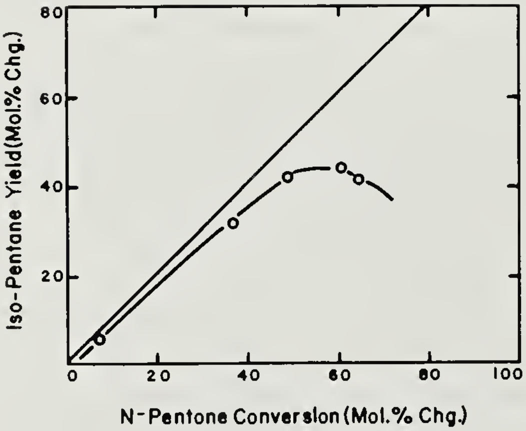


Figure 28. Isomerization of *n*-pentane. Isopentane yield *vs*. conversion *n*-pentane.

Table 15. Isomerization of *n*-Pentane[91]

Pressure: 950 psig. *LHSV:* 1.0 v/v/hr
H_2/HC: 2.9 (mole)

Temperature, °C	432
Total recovery, wt. % charge	97.8
Isobutane, mole % charge	0.7
n-butane	0.9
Isopentane	38.3
n-Pentane	60.1
Conv. *n*-Pentane, mole % charge	39.9
Yield isopentane, mole % charge	38.3
Selectivity factor	0.96

Hexanes. The isomerization of *n*-hexane has been extensively investigated by Ciapetta and Hunter[38] using various metal-acidic oxide catalysts. The results using a 5 per cent nickel-silica-alumina catalyst are given in Tables 16 and 17. Data for three different batches of this catalyst are included in the table to show the reproducibility of the procedure used to prepare the catalyst. As shown in Figure 29 the conversion of *n*-hexane

Table 16. Isomerization of n-Hexane[38]

Effect of Reaction Temperature

Pressure: 24.8 atm. *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	416	417	418	419	420	421	422	423	577	558
Temperature, °C.	328	355	385	412	327	357	386	413	314	342
Total recovery, wt. % charge	92.6	90.4	89.4	93.7	93.1	93.4	92.4	92.6	97.1	96.2
Catalyst	SA-5N (VII)								SA-5N (VII-E)	
Product Distribution Moles/100 Moles of Charge (no-loss basis)										
Methane				44.5				27.9	0.5	1.6
Ethane				4.0				2.0		
Propane	1.2	1.6	4.3	19.1	1.0	1.0	4.3	18.6		0.4
Isobutane			0.9	4.0			0.4	3.3		0.4
n-Butane			0.6	5.9			1.0	3.4		
Isopentane			3.7	16.3		0.1	2.0	12.5		
n-Pentane		0.1	1.9	11.5		0.1	1.4	7.8	0.4	1.8
2,2-Dimethylbutane	0.5	3.6	5.1	2.1		2.2	4.8	3.6		0.5
2,3-Dimethylbutane	1.1	5.0	5.6	3.2	0.2	4.3	4.7	4.1		3.3
2-Methylpentane	15.0	29.6	34.1	18.7	17.8	31.6	36.1	24.0	7.1	21.2
3-Methylpentane	10.8	19.6	23.0	12.9	11.3	21.6	24.4	15.5	6.0	19.3
n-Hexane	71.8	41.2	23.2	12.7	70.0	39.2	23.0	15.5	86.5	53.4
Conv. *n*-Hexane, mole % charge	28.2	58.8	76.8	87.3	30.0	60.8	77.0	84.5	13.5	46.6
C_6 isomer yield, mole % charge	27.4	57.8	67.8	36.9	29.3	59.7	70.0	47.2	13.1	44.3
Selectivity factor	0.97	0.98	0.88	0.42	0.98	0.98	0.91	0.56	0.97	0.95
Wt. % C on catalyst				0.05				0.14		

TABLE 17. ISOMERIZATION OF *n*-HEXANE[38]

Effect of Reaction Temperature

Pressure: 24.8 atm. *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	489	490	491	492	482	483	484	485
Temperature, °C	316	343	370	400	331	360	388	411
Total recovery, wt. % charge	98.9	96.9	95.5	96.1	98.1	93.8	96.6	94.6
Catalyst	SA-5N (VII-D)							

Product Distribution Moles/100 Moles of Charge (no-loss basis)

Methane	0.5	0.5	3.2	36.6	1.1	1.6	9.7	46.7
Ethane	0.3	1.1		2.9	0.6	0.6	0.9	6.6
Propane	0.8	2.0	1.2	10.0	2.0	1.2	5.9	15.8
Isobutane			0.4	2.7	0.9	0.4	1.0	3.6
n-butane		0.4	0.3	3.7	0.4	0.4	0.4	7.3
Isopentane			1.3	12.5		0.4	5.5	14.3
n-Pentane	0.2	0.2	2.0	9.1	0.4	1.0	2.5	10.3
2,2-Dimethylbutane	0.6	1.3	5.3	4.7	2.8	6.2	5.9	3.3
2,3-Dimethylbutane	0.5	1.5	4.5	4.5	3.3	7.1	6.4	4.5
2-Methylpentane	8.3	25.8	33.9	23.0	14.2	27.4	30.4	17.1
3-Methylpentane	5.2	17.3	24.3	16.9	10.9	21.3	23.0	14.5
n-Hexane	84.6	52.2	27.4	16.1	66.2	35.4	21.7	13.0
Conv. *n*-hexane, mole % charge	15.4	47.8	72.6	83.9	33.8	64.6	78.3	87.0
C_6 isomer yield, mole % charge	14.6	45.9	68.0	49.1	31.2	62.0	65.7	39.4
Selectivity factor	0.95	0.96	0.94	0.59	0.93	0.96	0.84	0.45
Wt. % C on catalyst				0.05				0.04

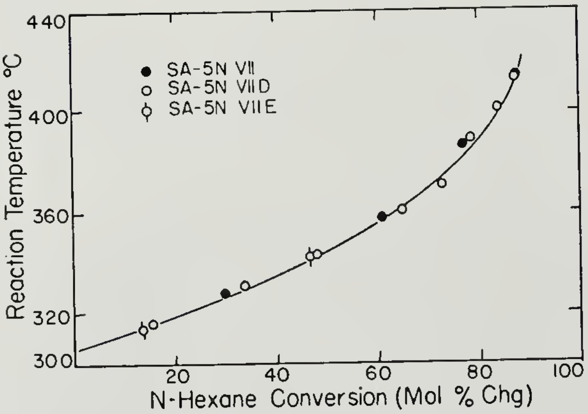


Figure 29. Isomerization of *n*-hexane. Effect of temperature on conversion of *n*-hexane.

begins at approximately 305 to 310°C and reaches a value of 85 per cent at 410 to 415°C. Analysis of the products showed that isohexanes were the major constituents.

The yields of isohexanes as a function of the *n*-hexane conversion are plotted in Figure 30. The 45° line in the figure represents quantitative formation of isohexanes from the *n*-hexane converted. The data show that the yield of isohexanes increases with conversion of *n*-hexane, and reaches a maximum value at approximately 70 to 75 per cent conversion. At higher conversions of *n*-hexane, the isomer yield decreases sharply owing to extensive hydrocracking to lower molecular weight products. The high selectivity of the nickel-silica-alumina catalyst for the isomerization of *n*-hexane, at conversions below 70 per cent, is shown graphically in Figure 31.

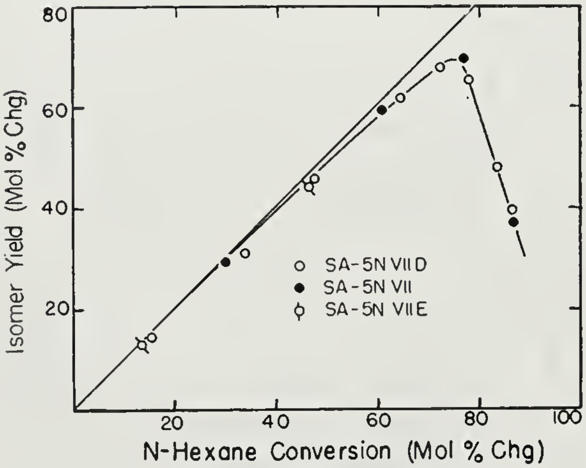


Figure 30. Isomerization of *n*-hexane. Hexane isomer yield *vs.* conversion of *n*-hexane.

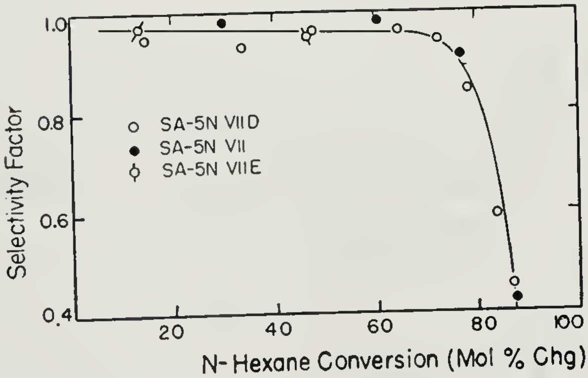


Figure 31. Isomerization of *n*-hexane. Hexane isomer selectivity *vs.* conversion of *n*-hexane.

All the hexane isomers are obtained in the presence of the nickel-silica-alumina catalyst. The data show that the methylpentanes are present in the highest concentration. The yields of isomers, as well as the change in yield as a function of the n-hexane conversion, are plotted in Figures 32 and 33. The yields of 2- and 3-methylpentanes reach maximum values of 36 per cent and 25 per cent, respectively, at a n-hexane conversion of 75 per cent. The maximum yields of the dimethylbutanes are less than 10 per cent.

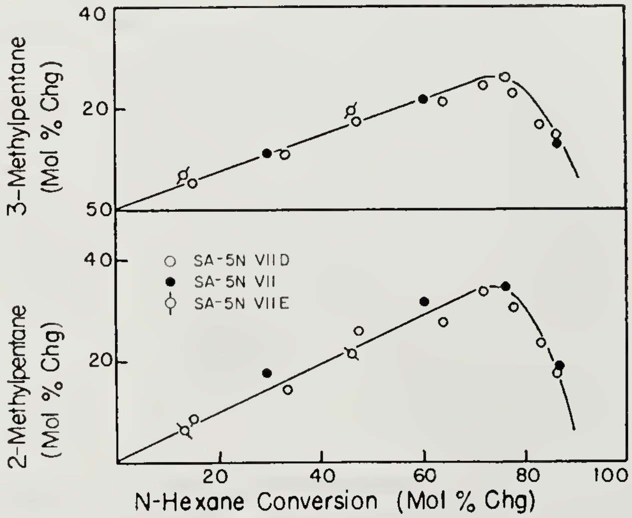


Figure 32. Isomerization of n-hexane. Yields of 2-methylpentane and 3-methylpentane *vs.* conversion of n-hexane.

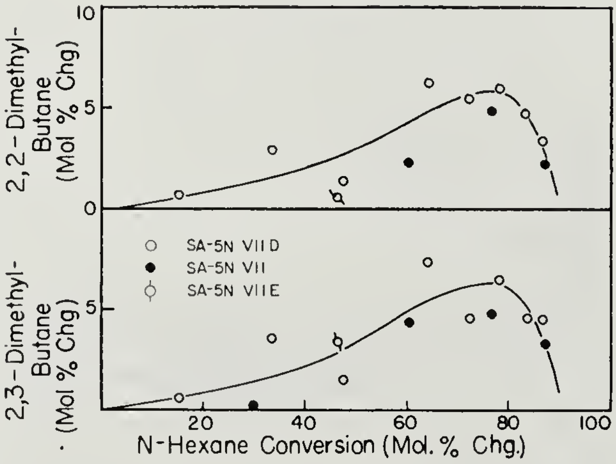


Figure 33. Isomerization of n-hexane. Yields of 2,3-dimethylbutane and 2,2-dimethylbutane *vs.* conversion of n-hexane.

Figures 34 and 35 show the yields of lower molecular weight alkanes, formed by hydrocracking, as a function of the n-hexane conversion. As expected, the amounts of methane, ethane, propane, butanes and pentanes, are very small until the conversion of *n*-hexane increases above 75 per cent.

Other metals of Group VIII of the Periodic System which have a high

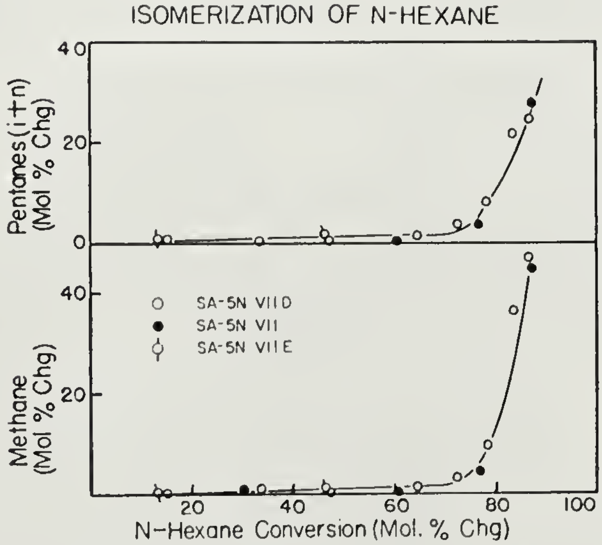


Figure 34. Isomerization of *n*-hexane. Yields of methane and pentanes *vs.* conversion of *n*-hexane.

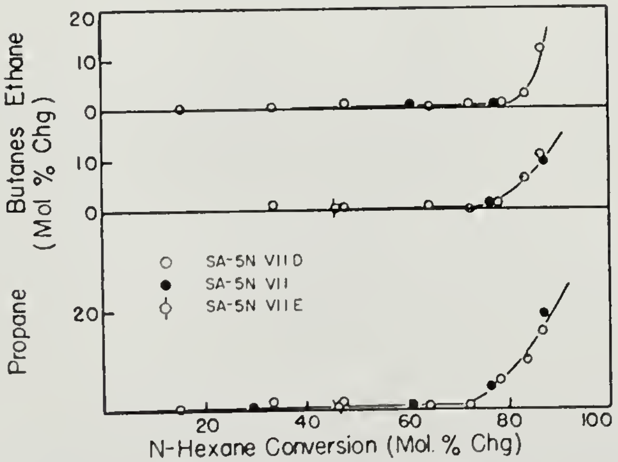


Figure 35. Isomerization of *n*-hexane. Yields of propane, butanes and ethane *vs.* conversion of *n*-hexane.

hydrogenation-dehydrogenation activity can be substituted for nickel. The results obtained using a high area silica-alumina catalyst with 5 wt. per cent cobalt and 0.5 wt. per cent platinum are shown in Tables 18 and 19 and Figures 36 and 37. The conversion of *n*-hexane as a function of temperature and the isomer yields are compared with those obtained with a standard nickel-silica-alumina catalyst. These catalysts also possess a high activity and selectivity for the isomerization of n-hexane to isohexanes. It is interesting to note that the catalyst containing 0.5 wt. per cent platinum is more active for the isomerization of n-hexane than one containing 5 wt. per cent cobalt, and almost as active as the standard 5 per cent nickel catalyst. A much smaller concentration of platinum is required because of its higher hydrogenation-dehydrogenation activity. Table 19 and Figures 36 and 37 also show the results obtained with a silica-alumina catalyst containing 5 wt. per cent iron. As a result of its poorer hydrogenation-dehydrogenation properties, this catalyst is much less active for the conversion of n-hexane. Even at a temperature of 458°C, the iron catalyst gives a n-hexane conversion of only 2.2 mole per cent. The major product formed is propane.

TABLE 18. ISOMERIZATOIN OF n-HEXANE[38]

Pressure: 24.8 atm. *LHSV:* 1.0 v/v/hr
H_2/HC: 4 (mole)

Run No.	681	682	683	684	710	711	712	713
Temperature, °C	287	316	346	373	314	344	372	401
Total recovery, wt. % charge	97.9	96.5	99.3	98.5	89.2	93.0	94.3	90.5
Catalyst	SA-0.5 Pt. (II)				SA-5 Cu (I)			
Metal	Platinum				Copper			
Product Distribution (Mole % Charge—NLB)								
Methane	1.1			0.5	2.2	0.5	9.7	
Ethane	0.6		0.3	1.1			0.6	0.6
Propane	1.8	0.8	0.8	1.8	1.0	0.4	2.5	2.5
Isobutane				0.4	0.4		0.1	2.4
n-Butane	0.4	0.4	1.2	0.9		0.1	0.3	0.6
Isopentane			0.4	2.3			0.6	2.0
n-Pentane	0.2		0.2	0.4			0.7	1.6
2,2-Dimethylbutane	0.2		0.6					
2,3-Dimethylbutane	1.2	3.0	2.8	4.0				
2-Methylpentane	3.6	6.1	13.2	29.2	0.9	1.4	3.1	3.6
3-Methylpentane	0.4	2.8	11.3	18.6	1.6	0.8	2.6	1.5
n-hexane	92.4	87.4	70.0	43.5	96.5	97.4	89.6	87.2
Conv. n-hexane, mole % charge	7.6	12.6	30.0	56.5	3.5	2.6	10.4	12.8
C_6 isomer yield, mole % charge	5.4	11.9	27.9	51.8	2.5	2.2	5.7	5.1
Selectivity factor	0.71	0.95	0.93	0.92	0.71	0.85	0.54	0.40
Wt. % C on catalyst				0.19				0.08

The conversion of n-hexane in the presence of a silica-alumina catalyst containing 5 wt. per cent copper is also shown in Table 18 and Figures 36 and 37. This catalyst is more active than the iron catalyst; a *n*-hexane conversion of 12.8 mole per cent is obtained at 401°C. At this conversion the isohexane yield is low, 5.1 mole per cent, and hydrocracking to form pentanes, butanes, propane, and methane is a prominent reaction.

TABLE 19. ISOMERIZATION OF *n*-HEXANE[38]

Pressure: 24.8 atm. *LHSV:* 1.0 v/v/hr
H_2/HC: 4 (mole)

Run No.	339	342	343	344	346	348	349	350
Temperature, °C	314	402	432	458	348	403	427	458
Total recovery, wt. % charge	91.2	92.8	96.3	94.2	94.8	96.8	91.8	96.0
Catalyst	SA-5 Co (III)				SA-5 Fe (II)			
Metal	Cobalt				Iron			
Product Distribution (Mole % Charge—NBL)								
Methane		5.4	27.9	37.6			0.5	1.1
Ethane		0.6	2.9	5.7			0.6	1.7
Propane	0.6	4.9	18.9	37.7	0.6	1.8	4.1	14.8
Isobutane		0.8	1.8	3.7		0.2	0.7	2.7
n-Butane		0.4	3.8	7.9		0.2	0.6	1.8
Isopentane		2.0	8.7	10.6		0.2	0.6	1.3
n-Pentane		1.6	5.8	7.2	0.1	0.4	0.6	0.6
2,2-Dimethylbutane		2.1	2.1	1.0				
2,3-Dimethylbutane		5.1	5.1	3.5				
2-Methylpentane	1.3	28.6	22.9	16.4	0.3	1.0	1.0	1.0
3-Methylpentane	0.8	19.8	16.9	12.4	0.8	1.3	0.9	1.2
n-Hexane	97.9	37.2	20.8	14.8	98.7	96.0	93.9	84.6
Conv. *N*-Hexane, mole % charge	2.1	62.8	79.2	85.2	1.3	4.0	6.1	15.4
C_6 isomer yield, mole % charge	2.1	55.6	47.0	33.3	1.1	2.3	1.9	2.2
Selectivity factor	1.00	0.89	0.59	0.39	0.85	0.58	0.31	0.14

The isohexanes can be isomerized as readily and as selectively as *n*-hexane in the presence of metal-acidic oxide catalysts. The experimental results for 2-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane, using a nickel-silica-alumina catalyst[39], are shown in Table 20. The conversion of each of these isomers as a function of the reaction temperature is shown in Figure 38. Below a conversion of approximately 50 mole per cent, 2-methylpentane is more reactive than *n*-hexane. The presence of a tertiary carbon atom activates the hexane molecule. However, the presence of two adjacent tertiary carbon atoms, as found in 2,3-dimethylbutane, does not enhance the reactivity of the molecule. Approximately the same reaction temperatures were required for equal conversions of 2,3-dimethylbutane and *n*-hexane. The results obtained using 2,2-dimethylbutane show that

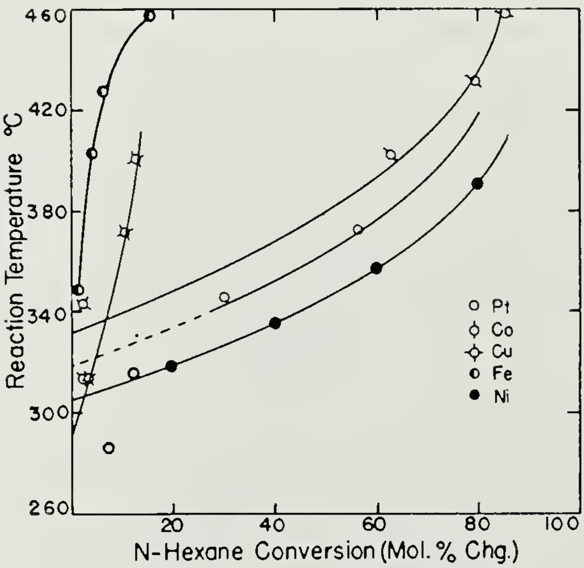


Figure 36. Isomerization of *n*-hexane. *N*-hexane conversion *vs.* temperature in presence of metal-silica-alumina catalysts.

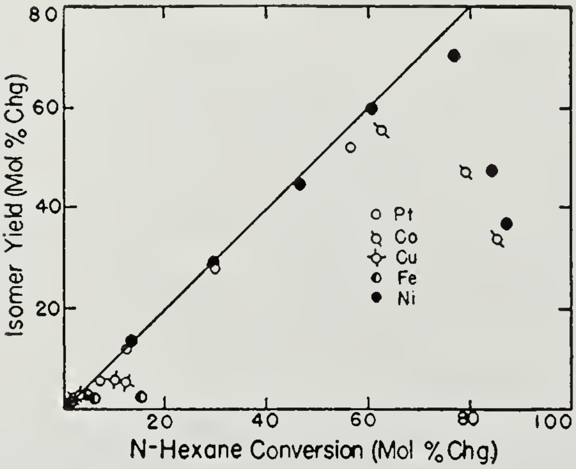


Figure 37. Isomerization of *n*-hexane. Hexane isomer yield *vs.* conversion of *n*-hexane in presence of metal-silica-alumina catalysts.

the presence of a quaternary carbon atom stabilizes the molecule. Approximately 30°C higher temperature is required to obtain the same conversion of 2,2-dimethylbutane as used for *n*-hexane.

The yield of isomers from the three isohexanes is plotted as a function of the conversion of the feed in Figure 39. The data show that the 5 per

Table 20. Isomerization of Hexane Isomers[39]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. *H_2/HC:* 4 (mole)

Run No.	328	776	777	778	779	659	660	661	662	655	656	657	658
Temperature, °C	287	302	329	357	385	288	314	343	371	287	316	344	372
Total recovery, wt. % charge	97.4	98.0	98.1	100.2	97.8	94.4	95.3	95.1	96.8	92.1	95.0	96.1	96.8
Hexane	2-Methylpentane					2,3-Dimethylbutane				2,2-Dimethylbutane			
Product Distribution Moles/100 Moles of Charge (no-loss basis)													
Methane	0.5	0.4	0.4	0.4	2.1				1.1				
Ethane	—	0.4	0.4	0.4	0.4								
Propane	0.6	0.4	—	0.4	0.8	0.4	0.4	0.4	0.4			0.4	0.4
Isobutane		0.4	1.3	0.4	1.2								
n-Butane	—	—	—	—	—						1.3	0.4	
Isopentane	0.1	—	—	—	1.3	0.4	0.1	0.8	1.8				0.5
n-Pentane	—	—	—	—	1.6					0.5	0.5		0.8
2,2-Dimethylbutane	—	1.5	1.5	6.1	5.9	3.2	6.7	10.1	11.7	98.6	93.7	85.2	63.5
2,3-Dimethylbutane	0.7	3.8	4.8	7.5	6.9	96.1	86.4	64.2	32.0	1.0	4.9	7.5	10.3
2-Methylpentane	87.8	73.9	57.8	39.7	34.1		2.8	11.2	23.2			3.2	10.1
3-Methylpentane	10.9	15.6	25.8	25.7	24.7		1.6	7.8	14.7				6.2
n-Hexane	—	4.1	9.0	20.0	24.1		2.2	5.7	15.9			3.7	8.3
Conv. of hexane, mole % charge	12.2	22.0	39.0	58.1	64.0	3.9	13.6	35.8	68.0	1.4	6.3	14.8	36.5
C_6 isomer yield, mole % charge	11.6	20.9	37.9	57.1	59.6	3.2	13.3	34.8	65.5	1.0	4.9	14.4	34.9
Selectivity factor	0.95	0.95	0.97	0.95	0.93	0.82	0.98	0.97	0.96	0.72	0.78	0.98	0.96
Wt. % C on catalyst					0.03				0.05				0.21

cent nickel-silica-alumina catalyst is a very selective isomerization catalyst for these hydrocarbons even at conversions as high as 70 mole per cent.

The experimental equilibrium distribution of the hexane isomers obtained in the isomerization of *n*-hexane at reaction temperatures of 387 and 412°C, and 2-methylpentane at 412°C are shown in Table 21. The calculated thermodynamic equilibrium distribution of the hexane isomers, using the data of Rossini and co-workers[139], are also shown. The calculated and experi-

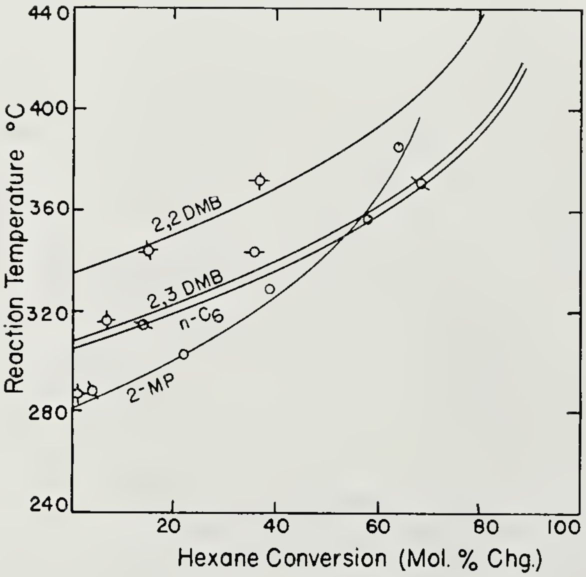


Figure 38. Isomerization of hexane isomers. Effect of temperature on conversion of hexane isomers.

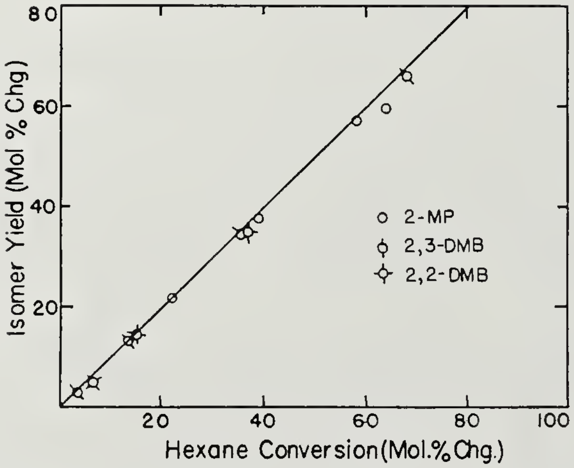


Figure 39. Isomerization of hexane isomers. Hexane isomer yields *vs.* conversion of hexanes.

mental data are in fair agreement for n-hexane and 2,3-dimethylbutane, but large discrepancies are shown for the methylpentanes and 2,2-dimethylbutane. These same discrepancies were observed by Evering and D'Ouville[65], and Koch and Richter[113], who investigated the isomerization of the hexanes in the presence of aluminum chloride. The large discrepancy between the experimental and calculated values for 2,2-dimethylbutane suggest that a kinetic factor limits the isomerization of the methylpentanes to this more highly branched isomer.

Heptanes. The isomerization of heptanes in the presence of metal-acidic oxide catalyst has been studied by several investigators. Haensel and Donaldson[91] investigated the conversion of n-heptane, in the presence of a platinum catalyst. Their experimental data are given in Table 22. At a temperature of 459°C, the conversion of n-heptane amounted to 87.5 mole per cent. The products show that 59 mole per cent of the converted n-heptane was isomerized to isoheptanes. The remainder of the converted n-heptane was hydrocracked to form primarily propane and butanes. The lower molecular weight hydrocarbons found in the products show that hydrocracking occurs by all three of the following reactions:

TABLE 21. EQUILIBRIUM CONCENTRATIONS FOR ISOMERIC HEXANES[39]

Temperature, °C	387			412	
Feed	n-hexane	2-methylpentane†	Calc.*	n-hexane	Calc.*
2,2-Dimethylbutane	6.0	6.2	25.2	6.0	23.5
2,3-Dimethylbutane	6.2	7.2	10.0	7.5	10.0
2-Methylpentane	36.8	35.6	27.6	36.0	28.6
3-Methylpentane	26.2	25.8	15.8	26.1	16.6
n-Hexane	24.7	25.2	21.4	27.1	22.3

* Ref. 139
† Temperature—385°C

$$(1)\quad C_7 \rightarrow C_1 + C_6$$

$$(2)\quad C_7 \rightarrow C_2 + C_5$$

$$(3)\quad C_7 \rightarrow C_4 + C_3$$

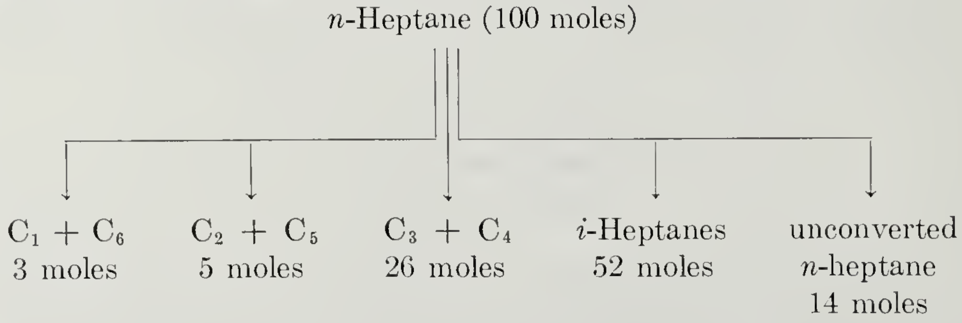
The preponderance of propane and butanes found in the products shows that reaction (3) which involves more central cracking of the molecule is the favored path of hydrocracking in the presence of this catalyst. The larger amounts of isobutane compared to n-butane indicate that isomerization of the intermediate olefin (n-heptene) to isoheptenes precedes hydro-

TABLE 22. ISOMERIZATION OF *n*-HEPTANE[91]

Pressure: 500 psig *LHSV:* 2.0 v/v/hr
H_2/HC: 3.3 (mole)

Temperature, °C	459
Total recovery, wt. % charge	100
Product Distribution (Mole/100 Mole Charge)	
Methane	3.1
Ethane	5.2
Propane	25.1
Isobutane	18.5
n-Butane	8.2
Isopentane	3.8
n-Pentane	2.3
Hexanes	3.0
2,2,3-Trimethylbutane	1.4
2,2-Dimethylpentane	1.6
3,3-Dimethylpentane	1.8
2,4-Dimethylpentane	1.6
2,3-Dimethylpentane	6.0
2-Methylhexane	19.0
3-Methylhexane	20.4
n-Heptane	12.5
Bottoms	1.6
Conversion, mole % charge	87.5
Isoheptanes, mole % charge	51.8
Selectivity factor	0.59

cracking under the conditions investigated. The almost equivalent molar concentrations of methane and hexanes, ethane and pentanes, and propane and butanes suggest that the three hydrocracking reactions occur independently of each other. Starting with 100 moles of *n*-heptane the reaction, under these conditions, takes place in the following manner:



The isomerization of *n*-heptane, 2,3- and 2,4-dimethylpentanes, and 2,2,3-trimethylbutane was investigated by Ciapetta and Hunter[39] in the presence of a high area silica-alumina catalyst containing 5 wt. per cent nickel. The experimental data are summarized in Tables 23 and 24. Figure 40 shows the conversion of the heptanes as a function of the reaction temperature. The total isomer yields from each of the heptanes is plotted in Figure 41 as a function of the conversion of the feed.

TABLE 23. ISOMERIZATION OF HEPTANE ISOMERS[39]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. H_2/HC: 4 (mole)

Run No.	322	323	324	325	252	253	254
Temperature, °C	288	315	332	353	270	291	316
Total recovery, wt. % charge	97.5	97.2	98.7	97.5	95.5	98.8	98.7
Heptane	*n*-Heptane				2,3-Dimethylpentane		
Product Distribution Moles/100 Moles of Charge (no-loss basis)							
Methane			1.3	4.4			
Ethane					0.7	0.7	0.7
Propane	1.1	1.6	2.5	9.3	1.6	3.4	5.3
Isobutane		0.5	0.7	7.6		1.8	4.4
n-Butane			0.2	1.4	0.3		0.2
Isopentane			0.1	0.4			
n-Pentane			0.1	0.3			
Hexanes			0.6	3.8	0.1		0.1
2,2,3-Trimethylbutane							
2,2-Dimethylpentane					1.3	5.5	7.3*
2,3-Dimethylpentane					87.0	70.0	45.6
2,4-Dimethylpentane		3.4	6.6	4.8	6.0	9.5	14.2
3,3-Dimethylpentane					1.3	2.9	5.6
2-Methylhexane	1.4	6.4	17.8	23.3	0.3	3.6	8.9
3-Methylhexane	4.0	9.1	32.4	39.1	2.6	5.7	13.3
n-Heptane	94.1	81.2	40.7	18.9			
Conv. of heptane, mole % charge	5.9	18.8	59.3	81.1	13.0	30.0	54.4
C_7 isomer yield, mole % charge	5.4	18.9	56.8	67.2	11.5	27.2	49.3
Selectivity factor	0.92	1.0	0.96	0.83	0.89	0.91	0.91
Wt. % C on catalyst				0.12			0.15

* Approximately 1% 2,2,3-Trimethylbutane by infrared analysis.

The data plotted in Figure 40 show that this catalyst is very active for the conversion of the heptanes. Initial isomerization of *n*-heptane occurs at a temperature below 300°C. The presence of tertiary carbon atoms in the heptane molecule greatly increases its reactivity. Thus, 2,3-dimethylpentane requires approximately 15°C lower temperature than *n*-heptane for the same conversion. The 2,4-dimethylpentane is even more reactive and gives the same conversion at a 35°C lower temperature. However, the presence of a quaternary carbon atom adjacent to a tertiary carbon atom, as in 2,2,3-trimethylbutane, deactivates the molecules. To obtain the same conversion a higher temperature (≈25°C) is required than for *n*-heptane. Good, Voge and Greensfelder[75] found a similar effect in the catalytic cracking of pure hydrocarbons in the presence of a zirconia-silica-alumina catalyst.

Table 24. Isomerization of Heptane Isomers[39]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. *H_2/HC:* 4 (mole)

Run No.	313	314	315	316	408	409	410	411
Temperature, °C	256	286	313	343	304	320	338	354
Total recovery, wt. % charge	92.5	96.7	97.5	97.6	94.2	99.9	95.1	93.6
Heptane	2,4-Dimethylpentane				2,2,3-Trimethylbutane			
Product Distribution Moles/100 Moles of Charge (no-loss basis)								
Methane		0.6	1.2	20.0	0.6	0.6	0.6	
Ethane				0.7	0.7	1.3	1.7	1.3
Propane		1.4	4.1	17.7			0.2	5.9
Isobutane			3.8	15.8		0.3	1.6	5.7
n-Butane			0.9	2.2	0.2		0.3	0.2
Isopentane				1.0		0.1	0.1	0.2
n-Pentane				1.8		0.1		
Hexanes			0.8	14.3		0.1	0.3	0.2
2,2,3-Trimethylbutane	1.3	7.5	13.0	5.5	88.8	81.9	76.6	62.2
2,2-Dimethylpentane					4.7	8.5	6.4	5.9
2,3-Dimethylpentane	11.3	19.7	22.7	9.2	3.1	4.7	3.8	4.4
2,4-Dimethylpentane	85.5	59.0	24.9	6.9	2.9	3.9	4.4	4.3
3,3-Dimethylpentane	0.3	2.7	8.2	4.5				
3-Ethylpentane		0.1	0.8	1.0				
2-Methylhexane	0.9	3.9	11.3	14.5			1.9	5.3
3-Methylhexane	0.7	6.5	12.0	15.9			5.5	11.1
n-Heptane			1.9	6.6				
Conv. of heptane, mole % charge	14.5	41.0	75.1	93.1	11.2	18.1	23.4	37.8
C_7 isomer yield, mole % charge	14.5	40.4	69.9	57.2	10.7	17.1	22.0	31.0
Selectivity factor	1.00	0.98	0.93	0.61	0.96	0.95	0.94	0.82
Wt. % C on catalyst				0.11				0.08

The high selectivity of the nickel-silica-alumina catalyst for the isomerization of heptanes, even at conversions of 60 to 80 per cent, is evident from the data shown in Tables 23 and 24 and Figure 41. At a *n*-heptane conversion of 59.3 per cent (Run 324), 96 per cent of the converted *n*-heptane appears in the product as isoheptanes. Similarly in the case of 2,4-dimethylpentane, at a conversion of 75.1 per cent (Run 315), 93 per cent of the converted heptane feed is isomerized to other heptanes. These results show that metal-acidic-oxide catalysts are vastly superior to the more familiar Friedal-Crafts catalysts such as aluminum chloride[34, 109, 114] for the isomerization of heptanes.

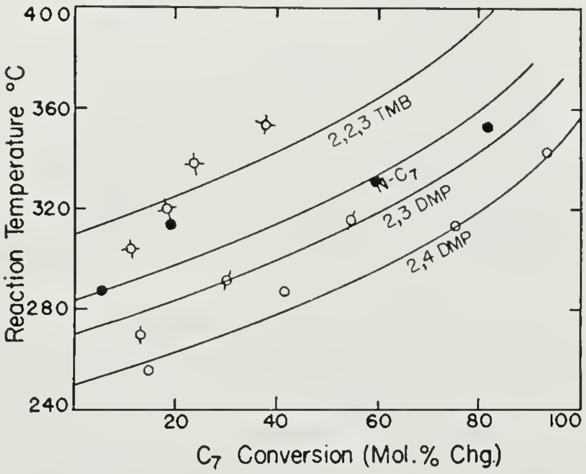


Figure 40. Isomerization of heptane isomers. Effect of temperature on conversion of heptane isomers.

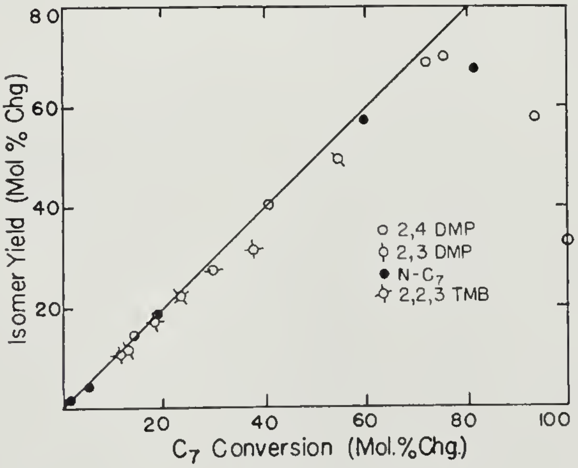


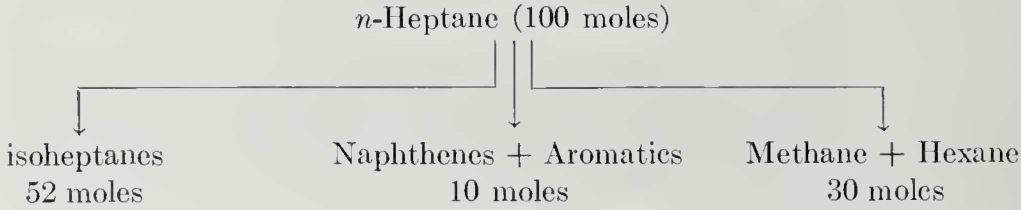
Figure 41. Isomerization of heptane isomers. Heptane isomer yields *vs.* conversion of heptanes.

Run 322 shows that at low conversions of *n*-heptane (5.9 mole per cent) the only isomers formed are the 2- and 3-methylhexanes. At higher conversions, 2,4-dimethylpentane appears in the product. The isomerization of 2,3-dimethylpentane produces all the heptane isomers with the exception of n-heptane. In Run 254, infrared analysis of the fraction containing 2,2-dimethylpentane showed that 2,2,3-trimethylbutane was present in a yield of 1.0 mole per cent based on the charge. Similarly in the isomerization of 2,4-dimethylpentane all the isomers are present at a conversion of 41.0 per cent (Run 314) with the exception of n-heptane. However, at a conversion of 75.1 per cent all the isomers are present. These results suggest that n-heptane could be formed at conversions of 2,3-dimethylpentane higher than 54.4 mole per cent (Run 254). At low conversions of 2,2,3-trimethylbutane, i.e., below 18 per cent, the only isomers found are 2,2-dimethylpentane, 2,3-dimethylpentane and 2,4-dimethylpentane. At higher conversions the methylhexanes appear in the product. At the highest conversion investigated, 37.8 per cent (Run 411), n-heptane was not found in the product.

As indicated in Tables 23 and 24, hydrocracking of the heptanes at conversions below 80 to 90 per cent occurs preferentially near the center of the molecule to form propane and butanes (see Runs 325, 254, 315 and 411). Almost equal molar quantities of these two hydrocarbons are formed. The high ratio of isobutane to n-butane, found in the products obtained using n-heptane as the feed (Run 325), indicates that isomerization of the intermediate olefin to isoheptenes precedes the cracking reaction. At higher conversions, methane and hexanes, and ethane and pentanes appear in the products (see Runs 325 and 316).

The conversion of n-heptane in the presence of a supported platinum catalyst was reported by Heinemann, Mills, Hattman and Kirsch[99]. The reaction conditions and experimental results are shown in Figure 42. Maximum isomer yields were obtained at a temperature of 874°F and a n-heptane conversion of 62 per cent. At higher temperatures, isoheptane yields decreased rapidly owing to hydrocracking reactions.

Hettinger, Keith, Gring, and Teter[104] studied the conversion of normal heptane in the presence of an alumina catalyst containing 0.6 wt. per cent platinum. Table 25 summarizes a portion of their data obtained at 500 psig and at two different weight hourly space velocities. The data show that this catalyst is quite active for the isomerization of normal heptane, even at the higher space velocity. The isomerization selectivity of the catalyst is not as high as that observed for the nickel-silica-alumina catalyst. The authors estimated that at 496°C, the primary reaction products, at conversions approaching zero, are distributed as follows at 500 psig pressure.



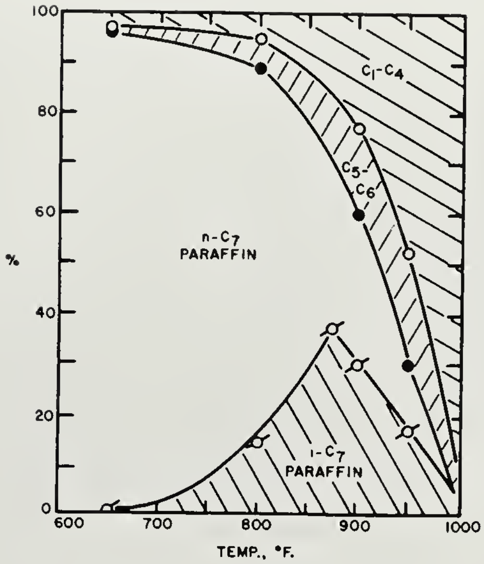


Figure 42. Isomerization of *n*-heptane—composition of product *vs.* temperature.

Table 25. Isomerization of *n*-Heptane[104]

Catalyst: 0.6 wt. % Pt on Al_2O_3
Pressure: 500 psig

Temperature, °C	468	496	468	496
WHSV, g/g/hr	5.0	5.1	48.1	49.0
H_2/HC, mole ratio	4.8	4.7	5.1	5.1
Methane, wt. % charge	1.8	3.7	0.2	0.7
Ethane	3.4	8.6	0.6	1.9
Propane	7.6	17.3	1.8	3.8
Isobutane	3.9	6.4	0.9	2.1
n-Butane	5.1	6.4	0.9	3.0
Isopentane	5.2	7.5	—	—
n-Pentane	2.3	4.1	1.4	4.1
Hexanes	6.9	7.8	1.1	1.9
n-Heptane	14.2	4.7	70.0	51.8
2-Methylpentane	13.0	5.0	20.2	23.8
3-Methylpentane	7.2	7.1		
3-Ethylpentane	2.5	0.6		
2,2- and 2,4-Dimethylpentane	2.0	1.0		
3,3-Dimethylpentane	0.4	—		
2,3-Dimethylpentane	4.6	1.6		
C_7-C_{10} Aromatics	6.1	14.6	1.0	4.9
C_5-C_7 Cycloalkanes	2.5	2.3	0.4	0.8
Alkenes	0.6	0.6	0.7	1.4
Conv. of N-C_7, mole % charge	85.8	95.3	30.0	48.2
C_7 isomer yield, mole % charge	36.4	15.3	20.2	23.8
Selectivity factor	0.42	0.16	0.67	0.49

Table 26. Isomerization of Octane Isomers[39]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. H_2/HC: 4 (mole)

Run No.	605	606	607	608	609	610	611	612	635	636	637	638
Temperature °C	260	287	316	348	316	348	364	380	259	288	320	336
Total recovery, wt. % charge	97.8	98.8	95.3	96.6	98.1	97.0	95.6	95.2	95.9	93.3	95.1	88.4
Octane	*n*-Octane								2,2,4-Trimethylpentane			
Product Distribution Moles/100 Moles of Charge (no-loss basis)												
Methane				1.4		0.7	0.7	2.8				
Ethane	1.4	0.8										
Propane	0.5	0.8	0.8	10.1	1.0	10.6	22.6	32.8	0.8	0.8	0.8	0.8
Isobutane	0.6		2.2	21.6	1.0	17.9	33.8	49.2	3.0	12.2	57.7	76.3
n-Butane			0.6	13.6	0.2	12.4	23.0	36.0	0.2	0.2	0.6	0.2
Isopentane			0.8	10.6	0.8	10.1	17.4	26.3				
n-Pentane			0.2	2.8	0.2	2.5	5.4	10.9				
Hexanes					0.7	0.5	0.3	0.8				
Heptanes					0.3	0.2	0.3	0.3				
2,5-Dimethylhexane				1.6								
2,4-Dimethylhexane				9.0		10.5	11.9	3.4				
2,3-Dimethylhexane		1.0*	5.7*	10.0*	17.5*	16.1*	8.8*	5.0*				
4-Methylheptane									0.4	0.6	1.2	1.2
3-Methylheptane		3.5	14.1	18.0	32.1	21.9	11.9	5.0				
2-Methylheptane		3.9	14.7	16.1	11.2	21.2	14.9	5.1				
n-Octane	99.2	91.1	63.2	14.6	37.0	2.1	0.0	0.6				
2,2,4-Trimethylpentane									98.2	92.9	69.0	59.1
Conv. of octane mole % charge	0.8	8.9	36.8	85.4	63.0	97.9	100.0	99.4	1.8	7.1	31.0	40.9
C_8 isomer yield mole % charge	—	8.4	34.5	54.7	60.8	69.7	47.5	17.4	0.4	0.6	1.2	1.8
Selectivity factor	—	0.95	0.94	0.64	0.97	0.71	0.48	0.17				
Wt. % C on catalyst				0.32				0.09				0.57

* Predominantly 4-Methylheptane.

Alkenes plus experimental and analytical uncertainties at low conversions are estimated to account for approximately 7 moles of the converted normal heptane. At high conversions of normal heptane, namely, 85.8 and 95.3 per cent of the charge, this catalyst is similar to that containing nickel-silica-alumina in that the hydrocracking reactions become major ones. Hydrocracking reactions similar to those described above by Haensel and Donaldson[91] also occur in the presence of this catalyst. The butane and pentane fractions contain a higher amount of the iso-compounds, which again indicates that hydrocracking follows the isomerization of the *n*-heptene to isoheptenes. The small amount of alkenes in all these runs should be noted. Even at the hydrogen pressure used, low concentrations of unsaturated hydrocarbons are always found in the reaction products obtained from all dual-functional types of catalyst.

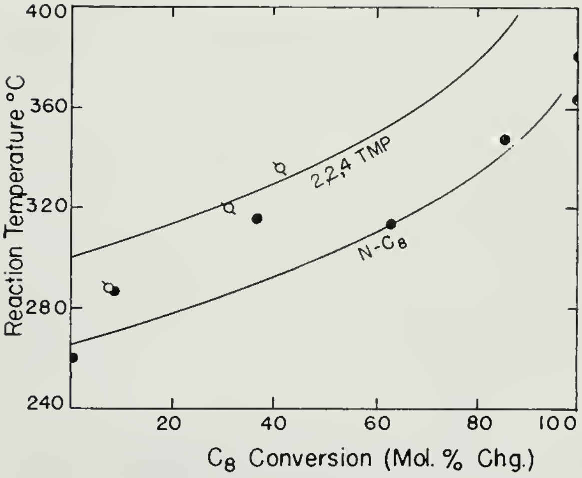


Figure 43. Isomerization of octanes. Effect of temperature on conversion of octane isomers.

These results also show that the dual-function catalysts are active dehydrocyclization catalysts. This reaction, which is important in the commercial application of the dual-function type of catalyst to the reforming of low-octane naphthas, will be discussed in more detail under the dehydrocyclization of paraffins (p. 596).

Octanes. The isomerization of *n*-octane and 2,2,4-trimethylpentane, in the presence of a 5 per cent nickel-silica-alumina catalyst, was investigated by Ciapetta and Hunter[39]. The results are summarized in Table 26 and Figures 43 and 44. Two series of runs were made using normal octane as the feed. In the first series (Runs 605 and 608) an upset occurred in the hydrogen flow prior to the second test run (606) which caused a decrease in the activity of the catalyst. At the end of this series of runs the carbon content of the catalyst was 0.32 per cent by wt. The second series of runs (609–612) was started at a higher temperature (316°C). The results showed that the catalyst had a much higher activity than the first batch of catalyst at this same temperature. At the end of the second series of runs the carbon content was 0.09 per cent by wt.

The isomerization of normal octane commenced at a lower temperature than either that found for normal heptane or normal hexane. The selectivity of the nickel catalyst for the isomerization of normal octane appears to be similar to that for the heptanes and hexanes. As indicated by the data in Table 26 and Figure 44 the selectivity factor even at a conversion of 97.9 per cent is 0.71. At a conversion of 63.0 per cent the mass spectrometer analyses of the liqud products revealed that the only isomers present were 2-, 3-, and 4-methylheptanes, and possibly 2,3-dimethylhexane. At higher conversions, 2,4-dimethylhexane is also present. Since the liquid product from this run was not prefractionated before analysis by the mass spectrometer, small amounts of other octane isomers may be present, particularly at the higher conversions.

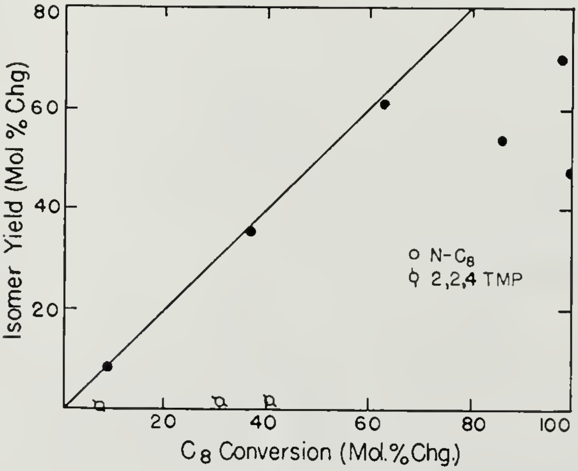


Figure 44. Isomerization of octanes. Octane isomer yields *vs.* conversion of octane.

As in the heptanes, hydrocracking occurs primarily at the center of the chain. The predominance of isobutane and isopentane shows that isomerization of the intermediate olefin precedes the hydrocracking reaction. The relative molar quantities of butanes and propane indicate that approximately three molecules of octane are cleaved into two butane molecules, for every one reacting to give a molecule of propane and one of pentane.

The data in Table 26 reveal that 2,2,4-trimethylpentane is almost completely converted into two molecules of isobutane in the presence of the nickel-silica-alumina catalyst. Only small amounts (less than 2 per cent) of octane isomers appeared in the product. These results show that in the case of a highly branched paraffin such as 2,2,4-trimethylpentane, the hydrocracking reaction proceeds at a very rapid rate. This is understandable on the basis that the intermediate olefin formed, 2,2,4-trimethylpentene, undergoes rapid de-polymerization in the presence of an acidic oxide catalyst to form two molecules of isobutylene[42].

Effect of Structure and Number of Carbon Atoms. Sufficient comparative data are available on the isomerization of alkanes over a 5 per cent nickel-silica-alumina catalyst to show the effect of carbon content and molecular structure on the reactivity of the molecule. Figure 45 shows the conversion of normal pentane, normal hexane, normal heptane, and normal octane, as a function of the reaction temperature. Comparing these normal alkanes at 50 mole per cent conversion, where the isomerization selectivity (Figure 46) is over 95 per cent for normal hexane, normal heptane, and normal octane, and 86 per cent for normal pentane, the reaction temperatures necessary to obtain this conversion are 384°C for normal pentane, 346°C for normal hexane, 323°C for normal heptane, and 302°C for normal octane. Thus, at a constant liquid space velocity, normal octane gives the same conversion as normal pentane at a temperature which is approximately 80°C lower than that used for the pentane. The increase in reactivity with increase in carbon content is similar to that observed by Greensfelder and Voge[81] for the catalytic cracking rates of the normal alkanes in the presence of cracking catalysts.

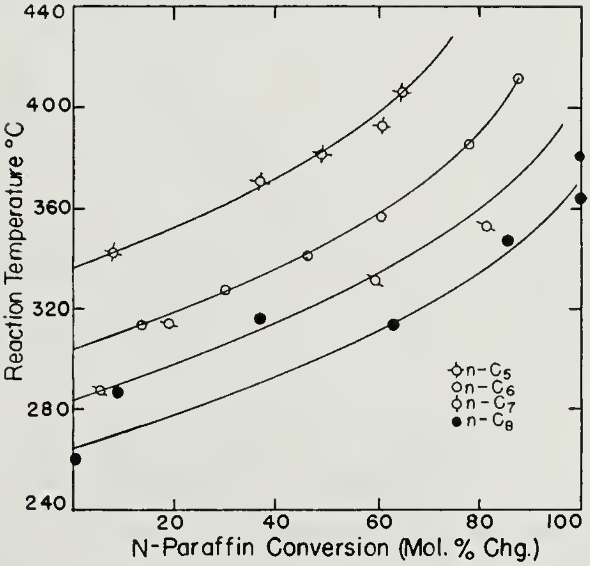


Figure 45. Isomerization of *n*-paraffins. Effect of temperature on conversion of *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane.

As shown in Figures 38 and 40, the addition of a methylene group to 2,3-dimethylbutane increases the reactivity of the molecule. For 50 mole per cent conversion of 2,3-dimethylpentane, a reaction temperature of approximately 310°C is necessary compared to 350°C for the same conversion of 2,3-dimethylbutane. However, the substitution of a methyl group for a secondary hydrogen atom in 2,2-dimethylbutane does not result in as large a change in the reactivity of the molecule. The data show that 2,2,3-trimethylbutane requires a reaction temperature of approximately 20°C lower than 2,2-dimethylbutane for the same conversion.

The analytical data shown in Tables 16, 17, 23 and 26, indicate that the initial products formed in the isomerization of *n*-hexane, *n*-heptane, and *n*-octane are the methyl isomers. Normal hexane isomerizes to 2- and 3-methyl pentanes; *n*-heptane to 2- and 3-methylhexanes; and *n*-octane to 2-, 3-, and 4-methylheptanes. These results substantiate the conclusions of Evering and Waugh[64] that the isomerization reaction occurs in a stepwise manner. For normal hexane the isomerization to the isomers appears to occur in the following manner.

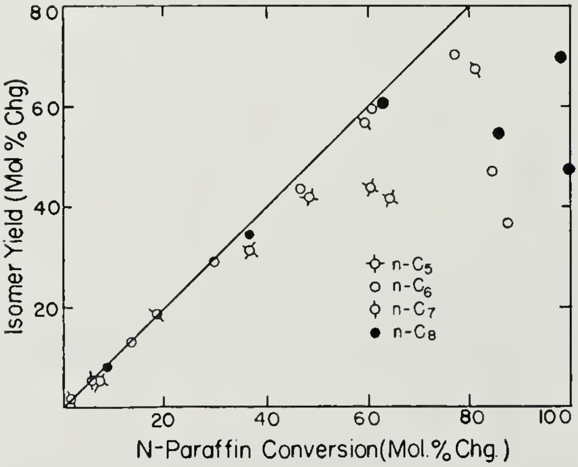
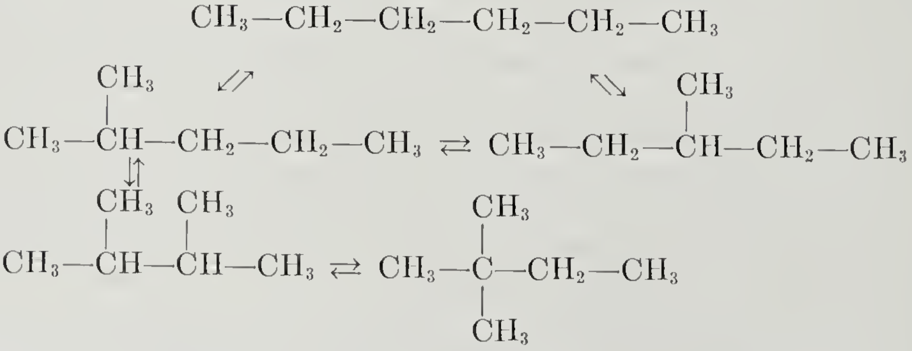


Figure 46. Isomerization of *n*-paraffins. Isomer yield *vs*. conversion of *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane.



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

$$\swarrow\!\!\nearrow \qquad\qquad \nwarrow\!\!\searrow$$

$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-CH_3 \rightleftarrows CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3$$

$$\downarrow\uparrow$$

$$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}H-CH_3 \rightleftarrows CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_3$$

Since the isomerization of 3-methylpentane was not investigated, the direct formation of 2,2-dimethylbutane from this isomer is not indicated. The results in Table 20 indicate that the formation of 3-methylpentane does not occur as a primary isomerization product from 2,2-dimethylbutane.

Isomerization of Cycloalkanes

Methylcyclopentane. The isomerization of methylcyclopentane to cyclohexane was investigated by Ciapetta[40] in the presence of a 5 per cent nickel-silica-alumina catalyst. The experimental results obtained and the reaction conditions used are shown in Table 27. Analyses of the reaction products showed that isomerization to cyclohexane was the predominant reaction at all conversions of methylcyclopentane. At the higher temperatures, hydrocracking to hexanes and lower molecular weight hydrocarbons, and isomerization-dehydrogenation to benzene also occurs. The formation of benzene shows that under these conditions, dehydrogenation of part of the cyclohexane, formed as a result of the isomerization reaction, can also

TABLE 27. ISOMERIZATION OF METHYLCYCLOPENTANE AND CYCLOHEXANE[40]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. *H_2/HC:* 4 (mole)

Run No.	627	628	629	630	623	624	625	626
Temperature, °C	288	316	344	371	287	342	371	390
Total recovery, wt. % charge	88.0	91.3	90.9	92.9	98.3	96.0	96.5	97.7
Cycloalkane	Methylcyclopentane				Cyclohexane			

Product Distribution Moles/100 Moles of Charge (no-loss basis)

	627	628	629	630	623	624	625	626
Methane								0.5
Ethane		0.6		0.6				0.3
Propane		0.4	0.4	1.0		0.4	0.4	0.8
Isobutane		0.4	0.1	1.9			0.3	1.0
n-Butane	0.4		0.1	0.3			0.1	0.4
Isopentane			0.1	0.9			0.6	0.9
n-Pentane	0.1		0.2	0.5			0.2	0.5
Hexanes		0.9	2.6	2.2			1.2	2.4
Methylcyclopentane	89.5	86.9	82.1	80.0	8.5	68.9	72.6	59.8
Cyclohexane	10.2	11.7	14.5	12.9	91.5	30.7	23.1	31.5
Benzene	0.1	0.1	0.3	1.8	0.1	0.5	1.9	3.6
Conv. of charge, mole % charge	10.5	13.1	17.9	20.0	8.5	69.3	76.9	68.5
Isomer yield mole % charge	10.2	11.7	14.5	12.9	8.5	68.9	72.6	59.8
Selectivity factor	0.95	0.89	0.81	0.65	1.0	0.99	0.95	0.87
Wt. % C on catalyst				0.32				0.36

occur in the presence of these dual functional catalysts. This reaction, which becomes a major one at higher temperatures than those indicated in Table 27, is a very important reaction in the commercial application of these catalysts to the reforming of straight run naphthas.

Figure 47 shows the conversion of methylcyclopentane as a function of the reaction temperature. The small increase in conversion with an increase in reaction temperature from 288 to 371°C is in marked contrast to the previous results obtained with this catalyst using alkanes as the feed. This is due to the equilibrium distribution of methylcyclopentane and cyclohexane at these temperature conditions. Table 28 shows a comparison of the experimentally observed concentrations of methylcyclopentane and cyclohexane with those calculated using the data of Rossini and co-workers[112a]. At the higher reaction temperatures, the experimentally observed molar concentrations of methylcyclopentane and cyclohexane agree quite closely with those calculated for the conditions used.

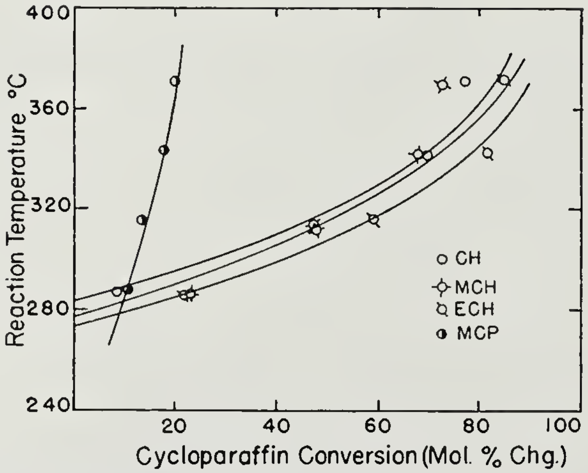


Figure 47. Isomerization of cycloparaffins. Effect of temperature on the conversion of methylcyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane.

As shown in Table 27 and Figure 48 the selectivity of this catalyst for the isomerization of methylcyclopentane to cyclohexane is similar to that observed for the isomerization of the alkanes. This high selectivity for isomerization is very important, when these dual functional catalysts are used at higher temperatures, for the conversion of alkylcyclopentanes to aromatics.

Cyclohexane. Cyclohexane is rapidly and selectively isomerized to methylcyclopentane at low reaction temperatures in the presence of a nickel-silica-alumina catalyst. The data obtained by Ciapetta[40] are shown in Table 27 and plotted in Figures 47 and 48. The high selectivity for isomer formation that prevails with this catalyst system even at a conversion of 76.9 mole per cent based on the charge, shows that this isomerization catalyst is quite unique at these high reaction temperatures for the isomerization of cyclohexane. The presence of benzene in the reaction products obtained at the higher reaction temperatures, again indicates that under these conditions, dehydrogenation of cyclohexane also can occur in the presence of this catalyst. As shown in Table 28 the observed mole per cent concentrations of cyclohexane and methylcyclopentane were approaching the calculated equilibrium values, as the reaction temperature was increased.

Table 28. Equilibrium Concentrations of Methylcyclopentane and Cyclohexane[40]

Temperature (°C)	Concentration (Mole %)			
	Methylcyclopentane		Cyclohexane	
	Exptl.	Calc. (112a)	Exptl.	Calc. (112a)
A. *Methylcyclopentane → Cyclohexane*				
288	89.8	82.1	10.2	17.9
316	88.1	84.4	11.9	15.6
344	85.0	86.2	15.0	13.8
371	86.1	87.7	14.9	12.3
B. *Cyclohexane → Methylcyclopentane*				
287	8.5	81.9	91.5	18.1
342	69.2	86.2	30.8	13.8
371	75.8	87.7	24.2	12.8

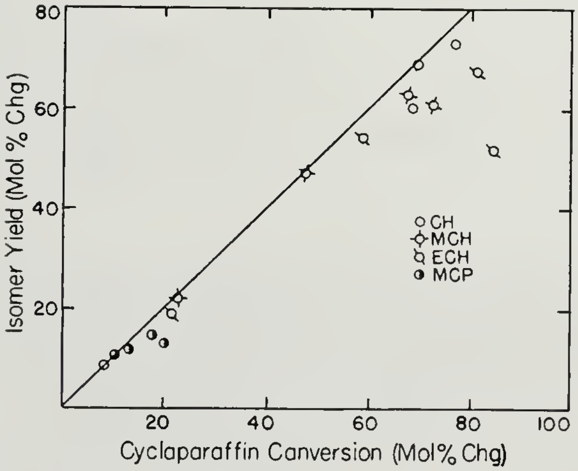


Figure 48. Isomerization of cycloparaffins. Isomer yields *vs.* conversion of methylcyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane.

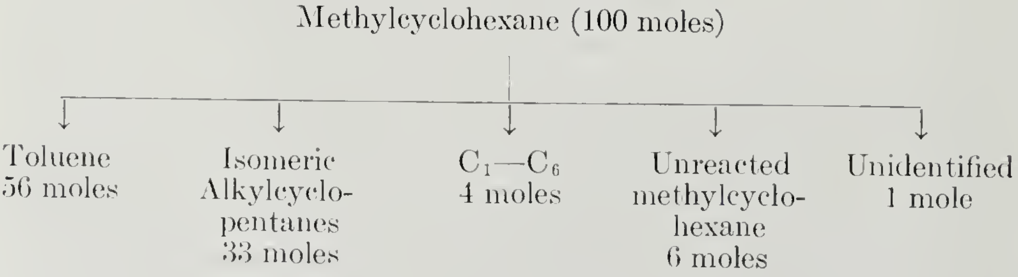
The isomerization of cyclohexane in the presence of a platinum-silica-alumina (surface area of SiO_2-Al_2O_3-430 m²/g) catalyst is shown in Table 29. As indicated by the conversions of cyclohexane, the platinum catalyst is slightly more active than the nickel catalyst at the higher temperatures. However, the selectivity of the platinum catalyst is not as high as the nickel catalyst. A larger amount of hydrocracking of the ring occurs with the platinum catalyst to form hexanes.

Methylcyclohexane. Haensel and Donaldson[91] investigated the reactions of methylcyclohexane when passed over a platinum catalyst at 700 lb psig, a liquid hourly space velocity of 2, a hydrogen to hydrocarbon mole ratio of 6.6, and an average catalyst reaction temperature of 452°C. Starting with the conversion of 100 moles of methylcyclohexane, these investigators found the following distribution of the products.

TABLE 29. ISOMERIZATION OF CYCLOHEXANE

Catalyst: 0.5% Pt/SiO_2-Al_2O_3 (430 m²/g) *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. *H_2/HC:* 4 (mole)

Temperature, °C	293	318	348	377
Recovery, wt. %	101.0	99.5	98.0	97.4
Product Distribution (Mole % Charge N.L.B.)				
Methane	0.6	0.7	0.8	1.4
Ethane	0.2	0.4	0.5	1.2
Propane	0.7	0.4	0.6	2.4
Butanes	0.4	0.2	0.4	1.5
Pentanes	0.2	0.2	0.4	1.6
Hexanes	0.1	2.8	12.2	17.8
Methylcyclopentane	5.5	29.5	66.5	68.4
Cyclohexane	93.7	67.1	21.0	10.0
Benzene	0.0	0.0	0.2	0.8
Cyclohexane conv., mole % charge	6.3	32.9	79.0	90.0
Selectivity factor	0.87	0.90	0.84	0.76



Although under these conditions the major product is toluene, the results show that 33 moles of the converted methylcyclohexane appeared in the product as isomeric alkylcyclopentanes. The complete product distribution as well as the distribution of the alkylcyclopentane isomers are shown in Table 30. All the dimethylcyclopentanes as well as ethylcyclopentane were obtained in this reaction.

Ciapetta[40] investigated the isomerization of methylcyclohexane in the presence of a 5 per cent nickel-silica-alumina catalyst (Table 31). Under the conditions employed, this investigator found that the conversion of methylcyclohexane in the presence of this catalyst, began at approximately 275°C. Figure 47 shows that at the same reaction temperature, a slightly higher conversion of methylcyclohexane (up to 50 to 60 mole per cent) is observed than that found for cyclohexane under similar conditions. Thus the presence of a tertiary carbon atom, introduced by substituting a methyl group for a hydrogen atom in the cyclohexane ring, increases the ease of reaction of the cyclohexane. The results in Table 31 and Figure 48 show that the nickel-silica-alumina catalyst is highly selective for the isomerization of this hydrocarbon. At a temperature of 370°C, and at a conversion of 72.7 mole per cent methylcyclohexane, the isomer selectivity

TABLE 30. ISOMERIZATION OF METHYLCYCLOHEXANE[91]

Pressure: 700 psig. *LHSV:* 2 v/v/hr

H_2/HC: 6.6 (mole)

Temperature, °C	
Furnace	485
Catalyst	452
Moles/100 Moles of Charge	
Hydrogen	157.1
Methane	2.8
Ethane	0.7
Propane	1.1
Butanes	0.7
Pentanes	0.2
Hexanes	0.5
Benzene	0.3
Methylcyclopentane	0.8
Heptanes	0.6
1,3-Dimethylcyclopentane	14.2
1,2-Dimethylcyclopentane	9.9
1,1-Dimethylcyclopentane	4.3
Ethylcyclopentane	5.0
Methylcyclohexane	5.7
Toluene	56.5
Unidentified	0.6

factor is 0.83. Less than 9 mole per cent of the cyclohexane converted appears in the product as paraffins. At the highest temperature investigated, 6.2 moles of methylcyclohexane are dehydrogenated to toluene. Complete analyses of the products obtained in these experiments showed that all the possible isomers of the alkylcyclopentanes are formed under these conditions. Since these analyses were obtained by use of the mass spectrometer, it was not possible to differentiate between the *cis* and *trans* isomers of

TABLE 31. ISOMERIZATION OF METHYLCYCLOHEXANE[40]

Catalyst: 5% nickel-silica-alumina — *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. — H_2/HC: 4 (mole)

Run No.	619	620	621	622
Temperature, °C	286	313	342	370
Total Recovery, wt. % charge	96.0	96.3	99.7	97.4
Product Distribution Moles/100 Moles of Charge (no-loss basis)				
Ethane				0.3
Propane		0.4	0.9	0.9
Isobutane			0.8	1.2
n-Butane	1.2	0.3	0.8	2.2
Isopentane				0.8
n-Pentane			0.8	1.1
Heptanes	0.1	0.1	1.1	2.1
1,1-Dimethylcyclopentane	1.3	4.8	7.6	7.8
1,2-Dimethylcyclopentane	6.4	18.3	23.2	21.0
1,3-Dimethylcyclopentane	6.2	13.6	22.6	22.6
Ethylcyclopentane	8.0	10.2	9.3	8.9
Methylcyclohexane	77.3	52.5	32.6	27.3
Toluene	0.1	0.2	1.5	6.2
Conv. of charge, mole % charge	22.7	47.5	67.4	72.7
Isomer yield, mole % charge	21.9	46.9	62.7	60.3
Selectivity factor	0.97	0.99	0.93	0.83
Wt. % C on catalyst				0.32

TABLE 32. EQUILIBRIUM CONCENTRATIONS OF METHYLCYCLOHEXANE AND ITS ISOMERS[40]

Temperature (°C)	342		370	
	Exp.	Calc.	Exp.	Calc.
1,1-Dimethylcyclopentane	8.0	9.2	8.9	9.1
1,2-Dimethylcyclopentane	24.3	20.3	24.0	21.2
1,3-Dimethylcyclopentane	23.7	23.5	25.8	25.2
Ethylcyclopentane	9.8	10.5	10.2	11.8
Methylcyclohexane	34.2	36.5	31.2	32.7

1,2- and 1,3-dimethylcyclopentanes. In agreement with the results found by Haensel and Donaldson[91], the 1,1-dimethylcyclopentane is also found in the reaction products using the nickel-silica-alumina catalyst.

TABLE 33. ISOMERIZATION OF ETHYLCYCLOHEXANE[40]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm. *H_2/HC:* 4 (mole)

Run No.	663	664	665	666
Temperature, °C	286	317	343	372
Total recovery, wt. % charge	99.5	94.1	95.7	98.1
Product Distribution Moles/100 Moles of Charge (no-loss basis)				
Ethane	0.4			0.4
Propane	0.5	0.5	1.0	4.6
Isobutane		0.6	2.5	8.1
n-Butane		0.6	0.6	4.5
Isopentane			1.1	4.0
n-Pentane			0.2	1.4
Hexanes				1.0
Octanes	0.2	1.2	4.2	5.3
Cyclohexane	2.4	2.8	2.9	3.5
Methylcyclopentane				0.3
C_7 Naphthenes	0.5		1.1	2.1
1,1,2-Trimethylcyclopentane	0.6	1.7	2.6	2.6
1,2,3-Trimethylcyclopentane	2.3	7.8	12.4	11.3
Isopropylcyclopentane	1.4	1.3	0.5	0.1
1,1-Dimethylcyclohexane	3.6	8.1	12.0	9.7
1,2-Dimethylcyclohexane	11.0	35.0	40.0	28.0
Ethylcyclohexane	78.4	41.1	18.7	15.7
Benzene	0.1	0.1	0.3	0.7
Toluene		0.1	0.5	1.9
Ethylbenzene + xylenes		0.6	3.0	7.8
Conv. of charge, mole % charge	21.6	58.9	81.2	84.3
Isomer yield, mole % charge	18.9	53.9	67.5	51.7
Selectivity factor	0.88	0.92	0.83	0.61
Wt. % C on catalyst				0.37

Table 32 shows a comparison of the experimental mole per cent of each of the alkylcyclopentanes and methylcyclohexane, obtained at reaction temperatures of 342 and 370°C, with those calculated using the data of Rossini and co-workers[63] under the conditions employed. The good agreement between the experimental values and the calculated values, at both temperatures, shows that the thermodynamic equilibrium concentrations of the isomers are obtained under these conditions.

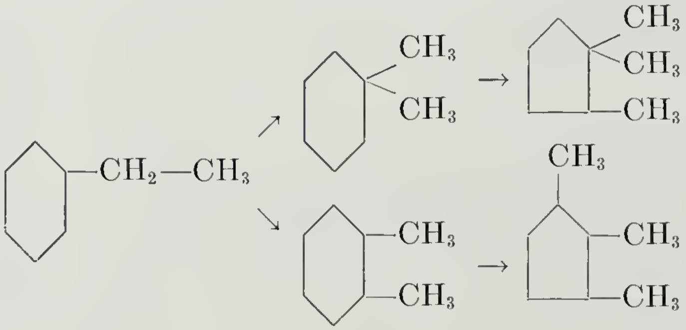
Ethylcyclohexane. The isomerization of ethylcyclohexane was also investigated in the presence of a 5 per cent nickel-silica-alumina catalyst by Ciapetta[40]. The experimental data as well as the reaction conditions employed are shown in Table 33. The conversion of ethylcyclohexane as a function of reaction temperature is shown in Figure 47. The data show that ethylcyclohexane is more reactive than cyclohexane and methylcyclohexane at the same reaction temperature.

The results shown in Table 33 and Figure 48 clearly indicate that the nickel-silica-alumina catalyst is highly active and selective for the isomerization of ethylcyclohexane. At a conversion of 58.9 mole per cent, the selectivity factor for isomerization is 0.92. Even at a conversion of 81.3 per cent the selctivity factor was 0.83. The selectivity drops off at the highest conversion reached, namely, 84.3 per cent, because of an increase in the hydrocracking reaction, and in the dehydrogenation reaction to form aromatics.

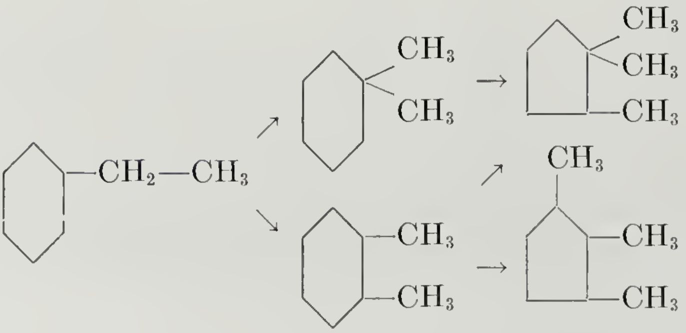
In the presence of this catalyst, ethylcyclohexane is isomerized primarily to the dimethylcyclohexanes and trimethylcyclopentanes, showing that the isomerization involves both the side chain and the ring. Although 1,1- and 1,2-dimethylcyclohexanes were the only dimethylcyclohexanes identified, small amounts of the 1,3- and 1,4- isomers may be present. Of the possible trimethylcyclopentanes, only 1,1,2- and 1,2,3-trimethylcyclopentanes were found. Isopropylcyclopentane was also definitely identified, in small concentrations, in the products.

The isomers found in the isomerization of ethylcyclohexane indicate that the reaction proceeds by either reaction (A) or (B).

(A)



(B)



The above reactions indicate that 1,1,2-trimethylcyclopentane may result from both the isomerization of 1,1-dimethylcyclohexane or 1,2-dimethylcyclohexane. To explain the formation of isopropylcyclopentane, it is necessary to conclude that 1,1-dimethylcyclohexane can isomerize further to form a five-membered ring isomer, since the direct formation of isopropylcyclopentane from any of the other isomers is highly improbable. The complete absence of methylethylcyclopentanes is in agreement with the results obtained by other investigators[62].

As in the case of methylcyclopentane and cyclohexane, the reaction products obtained at the highest reaction temperature, namely, 372°C, contain appreciable amounts of aromatic hydrocarbons. The presence of these aromatic hydrocarbons in the product show that the hydrogenation agent, nickel, retains its ability to catalyze the dehydrogenation of cyclohexanes to the corresponding aromatic hydrocarbons.

The results in Table 33 also show that at the higher reaction temperatures, hydrocracking of the side chain and the ring occurs to form octanes and lower molecular weight alkanes and cycloalkanes. The absence of methane, and the very low yields of ethane, show that the hydrocracking reactions take place in the center of the molecule after the opening of the cyclopentane or the cyclohexane ring.

The isomerization of ethylcyclohexane in the presence of a nickel-silica-alumina catalyst was also investigated by Pines and Shaw[133]. To determine the mechanism of the rearrangement of ethylcyclohexane, these investigators used ethyl-α-C^{14}-cyclohexane and ethyl-β-C^{14}-cyclohexane as their feed stocks, at 360°C, 25 atmospheres hydrogen pressure, a molar hydrogen-to-hydrocarbon ratio of 4:1, and an hourly liquid space velocity of 1 and 3. Analysis of the non-geminal alkylcyclohexanes was carried out by selectively dehydrogenating them to the corresponding aromatic hydrocarbons, under conditions where 1,1-dimethylcyclohexane was not dehydrogenated. The aromatic hydrocarbons were oxidized to the corresponding aromatic acids, which were isolated, purified, and assayed. By use of an isotope dilution technique, the conversion and composition of the alkylcyclohexanes were determined. The composition of the alkylcyclohexanes in the product obtained from the isomerization of ethyl-α- and β-C^{14}-cyclohexanes is given in Table 34. The product distribution was calculated from dilution data. No attempt was made in this investigation to determine the concentration of alkylcyclopentanes obtained in the reaction.

The results in Table 34 show that all three of the isomeric dimethylcyclohexanes are produced under the conditions investigated. The relative concentrations of 1,2-, 1,3-, and 1,4-dimethylcyclohexanes were found to be approximately the same as those calculated for the thermodynamic equilibrium between ethylcyclohexane and dimethylcyclohexanes.

The radioactive distribution data show that an extensive rearrangement of the carbon skeleton of the alkylcyclohexanes took place during the isomerization reaction in the presence of the nickel-silica-alumina catalyst. In the case of ethyl-α-C^{14}-cyclohexane, a nearly statistical distribution of the radioactivity between the ring and side chain of 1,2-, 1,3-, and 1,4-dimethylcyclohexanes was observed. This rearrangement of the carbon skeleton of the alkylcyclohexanes is similar to that observed for the rearrangement of the carbon atoms in propane-1-C^{13} and normal butane-1-C^{13} when they are contacted with aluminum bromide in the presence of a small amount of water. The carbonium ion intermediate mechanism is used to explain the skeletal isomerization reactions which occur in the presence of the nickel-silica-alumina catalyst.

TABLE 34. ISOMERIZATION OF ETHYLCYCLOHEXANE[133]

Catalyst: 5% Ni-SiO_2-Al_2O_3 *Temperature:* 360°C
Pressure: 25 atm. *H_2/HC:* 4.0 (mole)

Charge	Ethyl-α-C^{14}-Cyclohexane		Ethyl-β-C^{14}-Cyclohexane	
LHSV (v/v/hr)	1.0	1.0	1.0	3.0
Products, wt. %				
Ethylcyclohexane[1]	56.6	56.4	55.0	69.5
Ethylcyclohexane[2]	3.3	3.6	3.2	2.4
1,2–Dimethylcyclohexane	5.2	4.4	3.8	2.9
1,3–Dimethylcyclohexane	13.2	11.8	10.5	7.9
1,4–Dimethylcyclohexane	7.0	6.8	6.6	4.7
Conversion of EtCH[1], wt. %	43.4	43.6	45.0	30.5

[1] Recovered unreacted EtCH
[2] Recovered reacted EtCH

Isomerization of Aromatics

The experimental results obtained in the isomerization of methylcyclopentanes and alkylcyclohexanes show conclusively that dual-function catalysts are very active for the isomerization of constituents attached to these rings. Hence it is reasonable to conclude that, under the proper operating conditions of temperature and hydrogen pressure, these catalysts should be active for the isomerization of alkyl aromatic hydrocarbons. Thermodynamic equilibrium calculations show that low pressures (below 700 psig) and temperatures of 850°F or higher are favorable to the formation of aromatic hydrocarbon in the products. For example, in the case of the cyclohexane-benzene equilibrium, at 300 psig, and a hydrogen to hydrocarbon mole ratio of 4, the equilibrium concentration of benzene in the product is approximately 96 mole per cent at a reaction temperature of 950°F. If we increase the hydrogen pressure to 600 psi, then the equilibrium concentration of benzene at the same temperature is 94 mole per cent. At 800°F, the equilibrium concentration of benzene is 72 per cent at 300 psig, and 31 per cent at 600 psi.

Xylenes. The isomerization of *meta*-xylene was investigated by Pitts, Connor and Leum[135] in the presence of a platinum catalyst supported on a low surface area silica-alumina base. Starting with a feed containing 98.1 per cent *meta*-xylene, and approximately 1 per cent of each of the other xylenes, these investigators obtained the results summarized in Table 35.

TABLE 35. ISOMERIZATION OF *META*-XYLENE[135]

Catalyst: Pt/SiO_2-Al_2O_3 (Low area) *LHSV:* 1.0 v/v/hr
Pressure: 175 psig *H_2/HC:* 10 (mole)

		Single Pass		Two-Stage Second Pass	
Temperature, °F		850	900	850	900
Total recovery, wt. % charge	(Feed)	97.5	99.0	95.4	97.2
Products (Wt. % Charge—no-loss basis)					
C_1–C_5 paraffins		2.5	2.1	2.5	4.0
C_6 + paraffins		1.4	0.6	0.8	0.1
C_6 + naphthenes		0.9	0.3	1.1	0.2
p-Xylene	1.0	22.4	22.8	22.4	21.6
m-Xylene	98.1	44.6	44.0	43.8	42.2
o-Xylene	0.8	23.9	24.2	24.1	24.9
Ethylbenzene		0.2	0.1	3.3	3.3
Other aromatics		4.2	5.9	2.1	3.7
Conversion of *meta*-xylene, wt. % charge		54.4	55.1	55.3	56.8

The data show that at a hydrogen pressure of 175 psig, *meta*-xylene is effectively isomerized to *para*-xylene and *ortho*-xylene at a temperature of 850 and 900°F. The low yields of ethyl benzene (0.1 to 0.2 per cent) indicate that the isomerization of xylenes to ethyl benzene is a very slow reaction under the conditions investigated. It was suggested by these investigators that some intermediate, whose concentration is inversely proportional to temperature, is involved in a consecutive reaction system from feed to intermediate to final state.

To obtain evidence for the above mechanism these investigators studied the isomerization of *meta*-xylene by a two-step process. In the first step, *meta*-xylene was partially hydrogenated in the presence of the same catalyst at 723°F and a space velocity of two volumes per hour per volume of catalyst. The product of this step was then fed into a higher temperature step, where the conversion to aromatics was completed to a large extent and the isomerization continued. The results of this two-step process are also shown in Table 35. In the two-step process essentially the same yields of *para*-xylene, *meta*-xylene, and *ortho*-xylene were obtained as in the one-step process. However, the yield of ethyl benzene increased from 0.2 per cent or less to 3.3 per cent.

Ethylbenzene. The isomerization of ethylbenzene was also investigated by Pitts, Connor and Leum[135] in the presence of a platinum catalyst supported on a low surface area silica-alumina base. The results are shown in Table 36. Under the conditions employed, at a temperature of 800°F, approximately 41 per cent of the ethylbenzene was converted to other products. Xylenes were formed to the extent of 32 wt. per cent based on the feed, and contained all the isomeric xylenes. These investigators found that as the reaction temperature was increased above 800°F the conversion of ethylbenzene decreased and the yield to xylenes decreased correspondingly. A higher conversion of ethylbenzene to xylenes was obtained by using the two-step process similar to that employed in studying the isomerization of *meta*-xylene. The analyses of the products obtained in the first and second step are shown in Table 37.

TABLE 36. ISOMERIZATION OF ETHYLBENZENE[135] ONCE THROUGH OPERATION

Catalyst: Pt/SiO_2-Al_2O_3 (low area) *LHSV:* 1.0 v/v/hr
Pressure: 175 psig *H_2/HC:* 10 (mole)

Temperature, °F	(Feed)	800	850	900	950
Total recovery, wt. % charge		94.4	95.9	95.7	95.7
Products (Wt. % of Charge—no loss basis)					
C_1–C_5 paraffins		2.2	1.3	2.2	1.6
C_6^+ paraffins		0.5	0.1	—	—
Naphthenes		3.2	0.9		
p-Xylene	0.7	7.5	5.9	5.2	4.0
m-Xylene	1.2	14.9	11.3	8.8	5.8
o-Xylene	1.0	11.5	9.2	7.5	4.5
Ethylbenzene	97.0	57.5	69.3	73.6	76.5
Other aromatics	0.1	3.0	2.0	2.9	7.5
Conversion of ethylbenzene, wt. % charge		40.9	28.6	24.0	21.1
Xylenes, wt. % charge		32.0	24.2	19.2	11.8

Isopropylbenzene. Haensel and Donaldson[91] investigated the reactions of cumene (isopropylbenzene) in the presence of a platinum catalyst[86] at 500 psig, an average catalyst temperature of 459°C, a liquid hourly space velocity of two, and a hydrogen to hydrocarbon mole ratio of 4. The composition of the total products from this experiment are shown in Table 38. The data show that the major reaction is the hydrocracking of cumene into benzene and propane. The selectivity of the hydrocracking reaction is well illustrated by the very extensive formation of benzene and propane as compared to the formation of toluene, xylene, methane, and ethane.

The benzene formed in the hydrocracking of cumene undergoes hydrogenation to cyclohexane which in turn rearranges to methylcyclopentane. The calculated equilibrium concentrations at the experimental conditions are 35 per cent benzene, 60.8 per cent methylcyclopentane, and 4.2 per cent cyclohexane, as compared to 62.5 per cent benzene, 29.2 per cent methylcyclopentane, and 8.3 per cent cyclohexane obtained in the experimental run. These results show that the conversion of benzene to cyclohexane occurs at a more rapid rate than the isomerization of cyclohexane to methylcyclopentane under the conditions investigated.

Table 37. Isomerization of Ethylbenzene[135]

Two-Stage Operation

Catalyst: Pt/SiO_2-Al_2O_3 (low area) *H_2/HC:* 10 (mole)

Pressure: 175 psig

	(Feed)	1st Stage	2nd Stage			
Temperature, °F		723	793	842	894	943
LHSV, v/v/hr		2.0	1.0	1.0	1.0	1.0
Total recovery, wt. % charge		99.8	95.6	95.8	96.5	95.1
Product (Wt. % of Charge—no-loss basis)						
C_1–C_5 paraffins		0.5	0.9	1.1	2.2	1.3
C_6^+ paraffins			2.1	1.0	0.4	—
Naphthenes		30.0	4.8	1.5	0.2	—
p-Xylene	0.7		12.2	11.1	9.6	8.4
m-Xylene	1.2		24.2	21.5	18.7	16.0
o-Xylene	1.0		16.6	15.7	13.1	11.4
Ethylbenzene	97.0	66.1	37.1	45.9	48.9	55.2
Other aromatics	1.0	3.4	2.3	2.3	7.1	7.9
Conversion of ethylbenzene, wt. % charge			61.8	52.7	49.6	43.1
Xylenes, wt. % charge			51.8	46.9	39.8	34.0

The isomerization of isopropylbenzene was also investigated by Pitts, Connor and Leum[135], using a platinum-silica-alumina catalyst. The results in Table 39 show that under the conditions employed isopropylbenzene is

TABLE 38. ISOMERIZATION OF CUMENE[91]

Pressure: 500 psig *H_2/HC:* 4 (mole)
LHSV: 2 v/v/hr

Temperature, °C	459
Moles/100 Moles Cumene	
Methane	1.5
Ethane	1.2
Propane	56.2
Isobutane	0.6
n-Butane	0.4
Hexanes	1.7
Heptanes	0.6
Methylcyclopentane	13.7
Cyclohexane	3.6
Benzene	29.3
Toluene	1.6
Xylenes	1.0
Isomeric C_9 naphthenes	4.6
Cumene	16.4
n-Propylbenzene	1.8
1,2,4-Trimethylbenzene	9.9
1,3,5-Trimethylbenzene	2.8
1,2,3-Trimethylbenzene	1.0
ortho-Ethyltoluene	3.7
m-Ethyltoluene	3.2
p-Ethyltoluene	1.5
Unidentified	1.0
Hydrogen consumed	166.5

TABLE 39. ISOMERIZATION OF CUMENE-ONCE THROUGH OPERATION[135]

Catalyst: Pt/SiO_2-Al_2O_3 (low area) *LHSV:* 1.0 v/v/hr
Pressure: 350 psig *H_2/HC:* 4 (mole)

Temperature, °F	(Feed)	750	850	950
Recovery, wt. %		97.0	92.0	96.4
Products (Wt. %—no-loss basis)				
C_1-C_2 paraffins		0.4	0.2	0.5
Propane		21.9	24.0	28.6
C_4–C_5 paraffins		3.6	3.5	5.0
C_6 + paraffins		—	2.3	1.1
Naphthenes		17.6	4.8	0.9
Benzene	0.2	43.0	53.3	58.2
Trimethylbenzenes	95.8	7.9	5.5	1.1
Methylethylbenzenes				
Cumene				
Other aromatics	4.0	5.6	6.4	4.6

cracked to give primarily benzene and propane. At a temperature of 750°F a portion of the aromatic charge (17.6 wt. per cent) is converted to alkylcycloalkanes. At the higher reaction temperatures the yield of alkylcycloalkanes decreased, and the hydrocracking of isopropylbenzene to propane and benzene increases. These results show that under conditions where isomerization of aromatics occurs, the reactivity of the isopropyl group is such that the major reaction involves the splitting of this group from the aromatic ring.

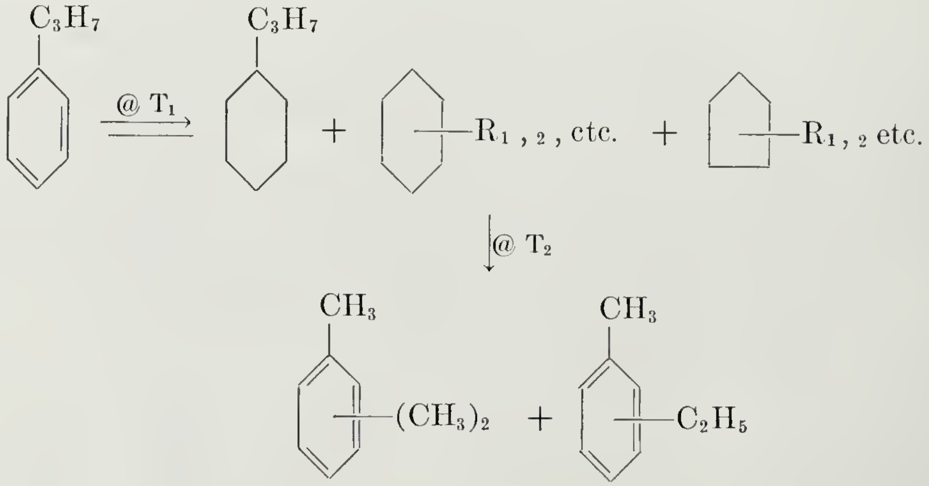
These investigators found that the isomerization of cumene can be carried out in two stages to give a good yield of the isomeric trimethylbenzenes and methylethylbenzenes. As shown in Table 40 the first stage of the reaction was carried out at a temperature of 587°F and a pressure of 500 psig. Under the conditions shown in Table 40 the cumene is almost completely converted into the corresponding alkylcycloalkane. When the product from the first stage is then passed over the same catalyst at higher temperatures (800 to 900°F) and a lower pressure (350 psig), high yields of the corresponding isomers of cumene are obtained. The results show that both the trimethylbenzenes and methylethylbenzenes are formed during the isomerization of cumene. As mentioned previously, these investigators found that the isomerization of ethylbenzene by the two-step procedure also gave higher yields of the isomeric aromatics than when the single-stage procedure was employed. Thus by carrying out the first stage, under conditions of temperature and pressure where hydroisomerization of the aromatic occurs, and then subjecting the products to a second stage at a higher

TABLE 40. ISOMERIZATION OF CUMENE-TWO STAGE OPERATION[135]

Catalyst: Pt/SiO_2-Al_2O_3 (low area) *H_2/HC:* 4 (mole)
LHSV: 1.0 v/v/hr

	1st Stage	2nd Stage		
Temperature, °F	587	800	850	900
Pressure, psig	500	350	350	350
Recovery, wt.%	101.9	96.1	90.7	89.8
	Products (Wt.%—no-loss basis)			
C_1–C_2 paraffins	0.1	0.8	0.9	1.7
Propane	4.4	2.9	4.0	3.6
C_4–C_5 paraffins	0.4	5.8	6.4	8.4
C_6^+ paraffins	4.8	10.6	5.4	2.4
C_6–C_8 naphthenes	27.7	16.1	7.7	2.8
C_9 naphthenes	61.8	3.2	0.9	
Benzene	0.3	1.9	3.8	2.9
Trimethylbenzenes	0.3	38.5	48.6	48.7
Methylethylbenzenes	0.1	11.0	11.2	16.5
Other aromatics	0.1	7.3	11.1	13.1

temperature, or lower pressure, higher yields of the isomeric aromatics are obtained. In the case of cumene the isomerization by the two-step procedure is visualized as occurring by the following mechanism.



Hydrogenation Reactions of Dual-Function Catalysts

Hydrogenation of Unsaturated Hydrocarbons

The hydrogenation of unsaturated hydrocarbons in the presence of nickel catalyst has been known for a long time. This reaction occurs very readily at low temperatures and low hydrogen pressures. It is not surprising therefore to find that the nickel-silica-alumina catalyst used by Ciapetta and Hunter[38] in studying the isomerization of saturated hydrocarbons should be very active for the hydrogenation of alkene hydrocarbons. The results in Table 41 (Run 591) show that this catalyst will hydrogenate normal hexene completely to normal hexane, at a temperature of 196°C, under a pressure of 24.8 atmospheres. Under these conditions the normal hexene gives primarily *n*-hexane with little or no side reactions.

The results, shown in Table 40, obtained by Pitts, Connor and Leum[135], in the two-step isomerization of cumene also show that the platinum-silica-alumina catalyst is a very active catalyst for the hydrogenation of aromatics. These data show that the metal components in dual-function catalysts are very active hydrogenation agents.

Hydroisomerization of Alkenes. The hydrogenation of 1-pentene and 1-hexene in the presence of a nickel-silica-alumina catalyst was investigated by Ciapetta[41]. These alkenes were contacted with the catalysts under conditions similar to those used for the isomerization of saturated hydrocarbons. The results obtained with these alkenes are shown in Table 41. Included in the data are the highest and lowest temperatures observed in the catalyst bed. The reaction products were almost completely saturated.

Table 41. Hydro-Isomerization of Alkenes[41]

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 24.8 atm *H_2/HC:* 4 (mole)

Run No.	651	652	653	654	591	592	593	594	596	597	598
Temperature, °C											
Top of Catalyst	283	301	321	346	196	211	232	286	309	337	357
Bottom of Catalyst	212	239	268	296	121	126	149	204	229	258	288
Total recovery, wt. % charge	97.4	97.6	98.4	95.1	94.4	95.8	98.5	97.6	97.6	98.2	97.8
Alkene	1-Pentene				1-Hexene						
Product Distribution Moles/100 Moles of Charge (no-loss basis)											
Methane											
Ethane							0.6				0.3
Propane	0.3	0.5	1.0	0.7	0.4	0.4	0.4	0.8	0.8	2.5	3.1
Isobutane	0.5	0.7	1.2	1.5				0.4	1.2	2.8	5.6
n-Butane	0.5	1.0	1.7	2.0					0.6	0.4	1.6
Isopentane	23.1	30.1	35.4	40.2			0.1	1.1	1.6	2.5	4.3
n-Pentane	67.8	57.9	51.0	44.9	0.4	0.2	0.5	1.1	0.5	1.3	2.4
Isohexanes					—	2.2	6.4	17.0	29.0	41.1	45.4
n-Hexane					99.2	97.0	90.9	77.6	64.1	48.5	36.8
Higher mole wt. HC	6.2	8.2	9.0	9.0	0.3	0.4	1.5	2.7	3.3	3.4	5.1
Conv. alkene, mole % charge	32.2	42.1	49.0	55.1	0.8	3.0	9.1	22.4	35.9	51.5	63.2
C_6 isomer yield, mole % charge	23.1	30.1	35.4	40.2	0.0	2.2	6.4	17.0	29.0	41.1	45.5
Selectivity factor	0.72	0.72	0.72	0.73	—	0.73	0.70	0.76	0.81	0.80	0.72
Wt. % C on catalyst				4.2			3.1				1.32

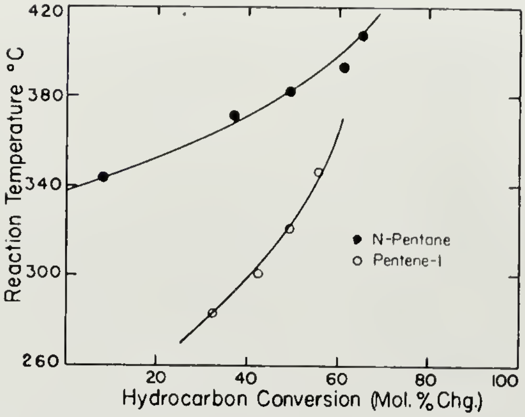


Figure 49. Hydroisomerization of pentene-1. Effect of temperature on conversion of pentene-1.

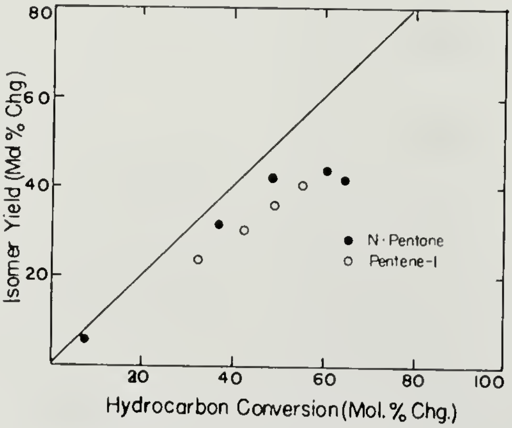


Figure 50. Hydroisomerization of pentene-1. Isomer yield *vs.* conversion of pentene-1.

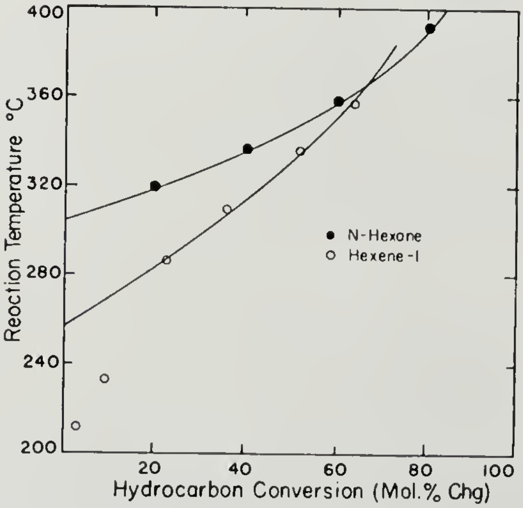


Figure 51. Hydroisomerization of hexene-1. Effect of temperature on conversion of hexene-1.

Only small amounts of unsaturated hydrocarbons were observed in the reaction products. The conversions of the alkenes are based on the concentrations of the corresponding saturated normal hydrocarbons in the product.

The conversions of 1-pentene and 1-hexene as a function of the highest observed catalyst temperature are shown in Figures 49 and 51. Also shown for comparison purposes are the results previously obtained for *n*-pentane and *n*-hexane over the same catalyst. The data show that the conversion of alkene hydrocarbons is obtained at substantially lower reaction temperatures than found for the corresponding saturated hydrocarbons. Analysis of the products obtained from 1-pentene and 1-hexene showed that isomerization occurred simultaneously with the hydrogenation. In Figures 50 and 52 are shown the isomer yields as a function of the conversion of the hydrocarbons. With 1-pentene as a feed, the isomer yields at the same conversion of the charge, is less starting with the olefin as a feed instead of the corresponding paraffin. As indicated in Figure 52 this is also true for the isomerization of 1-hexene. The lower selectivity factors found for the alkenes than for the alkanes is not due to increased hydrocracking reactions. The data in Table 41 show that the products from 1-pentene and 1-hexene contain small amounts (1 to 10 per cent) of saturated hydrocarbons, higher in molecular weight than the feed stock. These hydrocarbons are formed by polymerization reactions at the surface of the silica-alumina followed by subsequent hydrogenation. This is also indicated by the higher carbon contents found in the used catalyst. In the investigation of the isomerization of alkanes and cycloalkanes, hydrocarbons heavier than the feed were not found.

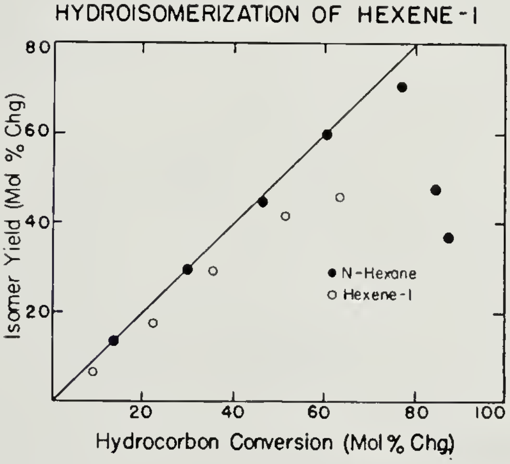


Figure 52. Hydroisomerization of hexene-1. Isomer yield *vs.* conversion of hexene-1.

Hydroisomerization of Cycloalkenes. The hydroisomerization of cyclohexene and methylcyclopentene was investigated by Mills, Heinemann, Milliken and Oblad[124] over a dual-function catalyst. The reaction was studied at a temperature of 950°F, a hydrogen pressure of 300 psi, a liquid hourly space velocity of 3, and a hydrogen to hydrocarbon mole ratio of 4. Under these conditions a major portion of the cyclohexene was dehydrogenated to benzene. Approximately 11 per cent by volume of the liquid product consisted of cycloalkanes, in which the ratio of C_6 to C_5 rings was approximately 1:4. These results indicate that cyclohexene is isomerized, under the conditions used, to methylcyclopentene, which is then hydrogenated to methylcyclopentane. Using methylcyclopentene as the charge, these investigators found that a major amount of the product consisted of benzene. However, approximately 13 volume per cent consisted of cycloalkanes in which the ratio of C_6 to C_5 rings was 1:25.

Table 42. Hydroisomerization of Benzene[44]

Catalyst: 5% nickel-silica-alumina
Pressure: 350 psig
LHSV: 1.0 v/v/hr
H_2/HC: 4:1 (mole)
Diluent: n-Hexane (50 mole%)

Temperature, °F					
Furnace	600	650	700	750	800
Catalyst	631	671	720	775	806
Yields, wt.% of benzene, no loss basis					
Methylcyclopentane	72.5	83.1	81.6	62.5	30.5
Cyclohexane	27.3	15.9	14.0	10.1	4.3
Benzene	0.2	1.0	4.4	27.4	65.2
Conversion, wt.% of benzene	99.8	99.0	95.6	72.6	34.8

The Hydroisomerization of Aromatic Hydrocarbons. The hydroisomerization of benzene and toluene in the presence of a nickel-silica-alumina catalyst was investigated by Ciapetta and Hunter[44]. The results obtained are shown in Tables 42 and 43. Since the hydrogenation reaction released large amounts of heat, the aromatic hydrocarbon was diluted with 50 mole per cent of *n*-hexane. At a furnace temperature of 600°F and under the conditions shown in Table 42, the products obtained from benzene consisted completely of methylcyclopentane and cyclohexane. The conversion of benzene at this condition was 99.8 per cent. As the reaction temperature was increased to 800°F the conversion of benzene decreased to 34.8 per cent. The composition of the total product as a function of temperature is shown in Figure 53. As expected from the thermodynamic equilibrium the major product formed at all conditions is methylcyclopentane. At temperatures of 650°F and above, the distribution of methylcyclopentane and cyclohexane in the product is approximately that expected from the equilibrium calculations under the conditions used. Figure 54 shows the composition of the product as a function of the benzene conversion.

TABLE 43. HYDROISOMERIZATION OF TOLUENE[44]

Catalyst: 5% nickel-silica-alumina
Pressure: 350 psig
LHSV: 1.0 v/v/hr
H_2/HC: 6:1 (mole)
Diluent: n-Hexane (50 mole%)

Temperature, °F						
Furnace	442	495	545	600	651	700
Catalyst (Max.)	476	528	566	627	675	700
Yields, wt.% of toluene, no loss basis						
1,1-Dimethylcyclopentane	1.9	2.1	1.8	7.0	4.3	1.5
1,2-Dimethylcyclopentane	5.8	10.3	10.5	17.3	12.3	3.3
1,3-Dimethylcyclopentane	0.6	0.9	8.2	19.9	24.1	6.5
Ethylcyclopentane	5.6	9.2	12.3	11.4	8.1	2.1
Methylcyclohexane	85.8	77.4	67.3	42.7	19.4	3.1
Toluene	0.4	0.2	0.0	1.7	31.8	83.6
Conversion, wt.% of toluene	99.6	99.8	100.0	98.3	68.2	16.4

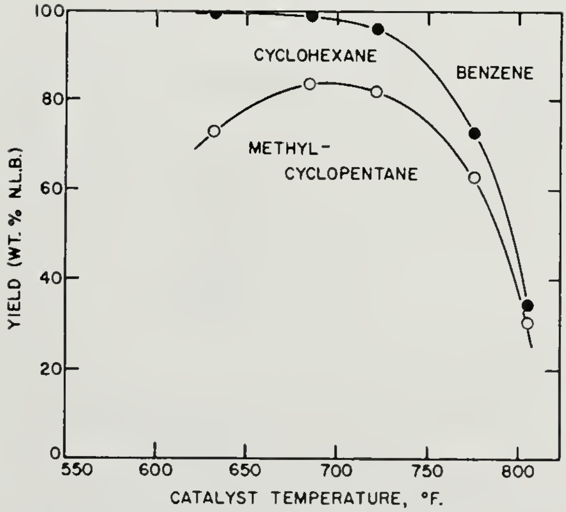


Figure 53. Hydroisomerization of benzene. Composition of product *vs.* temperature.

The results in Table 43 show that at a furnace temperature of 442°F toluene is completely hydrogenated to cycloalkanes. Analyses of the products showed that even at this temperature hydroisomerization of toluene occurred to form dimethylcyclopentanes and ethylcyclopentane. As shown in the Figure 55 where the composition of the total product is plotted as a function of the reaction temperature, complete hydrogenation of toluene occurs at temperatures up to 625°F. Above this temperature the toluene conversion decreases due to the equilibrium between the aromatic and the cycloalkane hydrocarbons. As the temperature is increased to about 650°F the yield of methylcyclohexane decreases while the yield of alkylcyclopentane increases. This is shown graphically in Figure 56 where the distribution of the product is plotted as a function of the conversion of toluene.

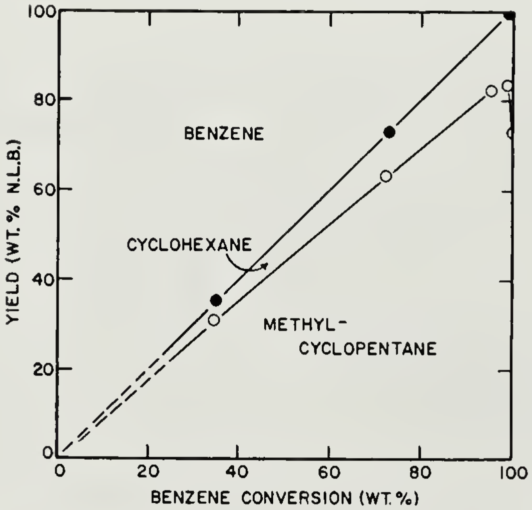


Figure 54. Hydroisomerization of benzene. Composition of product *vs.* conversion of benzene.

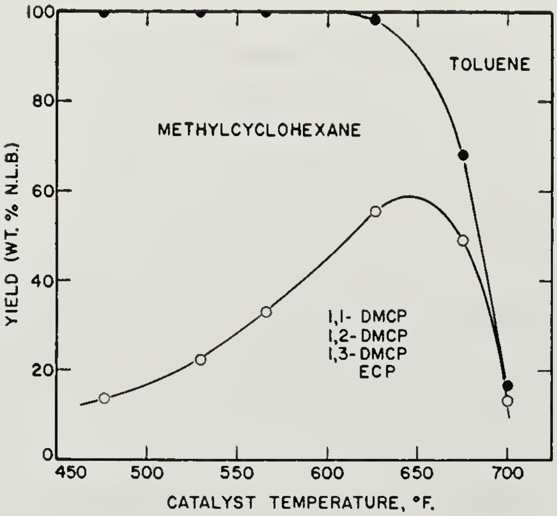


Figure 55. Hydroisomerization of toluene. Composition of product *vs.* temperature.

These results show that the nickel-silica-alumina catalysts are very active catalysts for the hydroisomerization of aromatic hydrocarbons. Due to their dual functional nature the isomerization occurs simultaneously with the hydrogenation reaction, so that the aromatic hydrocarbon is converted not only to the corresponding cycloalkane but also to the isomeric cycloalkanes.

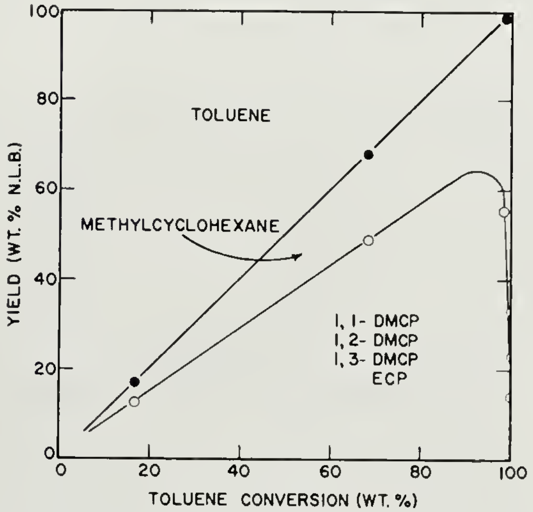


Figure 56. Hydroisomerization of toluene. Composition of product *vs*. conversion of toluene.

Table 44. Dehydrogenation of Cyclohexane[99]

LHSV: 3 v/v/hr *H_2/HC:* 4 (mole)

Pressure (psig)	Temp. (°F.)	Mole % Benzene in Product	
		Observed	Calculated
300	800	70	72
300	900	90	89
300	950	93	95
600	800	33	31
600	95	92	94

Dehydrogenation Reactions of Dual-Function Catalysts

Dehydrogenation of Naphthenes

The dehydrogenation of cyclohexanes to aromatics occurs very readily in the presence of dual-function catalysts, at reaction temperatures of 800 to 950°F. The dehydrogenation of cyclohexane and methylcyclohexane were studied by Heinemann, Mills, Hattman and Kirsch[99] in the presence of a platinum containing catalyst. The results at various temperatures and pressures for both cyclohexane and methylcyclohexane are shown in Tables 44 and 45. Also shown in these tables are the equilibrium values calculated for benzene and toluene under the conditions given. At 300 psi hydrogen pressure, increasing the temperature from 800 to 950°F increased the mole per cent benzene in the product from 70 to 93 per cent. In the case of methylcyclohexane, increasing the temperature from 800 to 900°F increased the concentration of toluene from 83 to 92 per cent. Thus at the higher reaction temperatures, namely above 900°F, and at a pressure of 300 psi, more than 90 per cent of the cyclohexane can be converted to the corresponding aromatic hydrocarbon. As indicated by the calculated equilibrium concentrations of benzene and toluene, dehydrogenation of cyclohexane and methylcyclohexane in the presence of the platinum catalyst gives equilibrium yields of benzene and toluene.

Table 45. Dehydrogenation of Methylcyclohexane[99]

LHSV: 3 v/v/hr *H_2/HC:* 4 (mole)

Pressure (psig)	Temp. (°F.)	Mole % Aromatics Observed	Mole % Aromatics Calculated
300	800	83	85
300	900	92	96
600	800	48	45

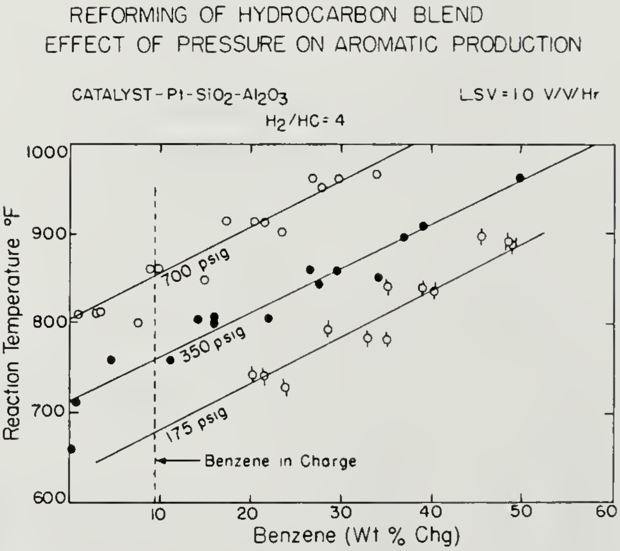


Figure 57. Dehydrogenation of cyclohexane. Effect of temperature and pressure on yield of benzene. *Catalyst:* Pt-SiO_2-Al_2O_3 ; LHSV: 1.0 v/v/hr; H_2/HC: 4 (mole).

Haensel and Donaldson[91] also studied the dehydrogenation of methylcyclohexane over a platinum containing catalyst. These investigators found (Table 30) that at a pressure of 700 psi, an hourly liquid space velocity of 2, and a hydrogen to hydrocarbon mole ratio 6.6, using an average catalyst temperature of 452°C, 56.5 moles of the methylcyclohexane charge appeared in the product as toluene.

The conversion of cyclohexane to benzene was investigated by Ciapetta, Pitts and Leum[45] at various temperatures and pressures using a platinum-silica-alumina catalyst. The feed consisted of a hydrocarbon blend containing 9.5 per cent benzene, 40.5 per cent cyclohexane and 50 per cent *n*-heptane. Figure 57 shows the effect of the reaction temperature on the yield of benzene at pressures of 175, 350 and 700 psig. As expected from the thermodynamic calculations, as the pressure is increased, a higher temperature is required to obtain the same yield of benzene. As indicated in Figure 57, at 175 psi hydrogen pressure, complete conversion of cyclohexane to benzene occurs at approximately 900°F. At 350 psi a reaction temperature

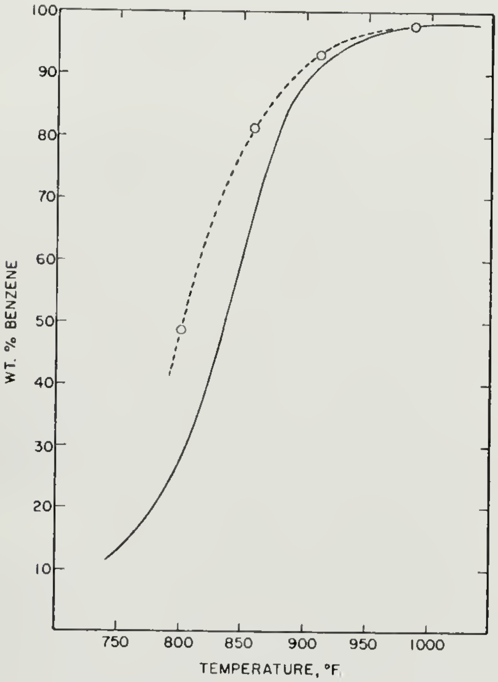


Figure 58. Benzene-Cyclohexane equilibrium experimental (– – –) and calculated (———). Concentrations of benzene *vs.* average catalyst temperature. *Catalyst:* Pt-SiO_2-Al_2O_3 LHSV—1.0 v/v/hr. *Pressure:* 500 psig H_2/HC: 10 (mole).

Table 46. Dehydrogenation of Cyclohexanes[104]

Catalyst: 0.6% Pt on Al_2O_3 *WHSV:* 100–103 v/v/hr
Pressure: 200 psig *H_2/HC:* 5.0–5.1 (mole)
Temperature: 925°F

Hydrocarbon Feed	Cyclohexane	Methyl Cyclohexane	Ethyl Cyclohexane
		Mole % Conversion to	
Benzene	51		
Toluene		80	
Ethylbenzene			71

of approximately 950°F was required to obtain complete conversion of cyclohexane to benzene. At 700 psig pressure a temperature of approximately 1100°F would be required in order to convert most of the cyclohexane to benzene. Under the conditions used by these investigators equilibrium concentrations of benzene were obtained at the higher reaction temperatures. This is shown in Figure 58 for the benzene-cyclohexane equilibrium at 500 psig.

The dehydrogenation of cyclohexane, methylcyclohexane, and ethylcyclohexane was investigated by Hettinger, Keith, Gring and Teter[104] in the presence of a platinum-alumina catalyst. The reaction conditions used by those investigators and the products obtained are shown in Table 46. The results show that the platinum-alumina catalyst used is extremely active for the dehydrogenation of cyclohexanes to the corresponding aromatics. Even at the high weight hourly space velocities used by these investigators (100–103 g feed/g catalyst/hr), cyclohexane was dehydrogenated to the extent of 51 per cent, methylcyclohexane to the extent of 80 per cent, and ethylcyclohexane to the extent of 71 per cent.

Dehydroisomerization of Alkylcyclopentanes

Heinemann, Mills, Hattman and Kirsch[99] investigated the dehydroisomerization of methylcyclopentane in the presence of a platinum catalyst. The reaction conditions employed and the results obtained are shown in Table 47. The data show that the formation of aromatics, at 900°F, accounts for almost 50 per cent of the reacted methylcyclopentane. Even at 950°F at a conversion of methylcyclopentane of 80 per cent, 50 per cent of the methylcyclopentane converted appeared in the product as benzene. These results also show that while methylcyclopentane conversion increases with temperature, catalytic hydrocracking also increased between 900 and 950°F, as shown by the larger ratio of C_4 to dry gas.

The dehydroisomerization of methylcyclopentane in the presence of a platinum-low surface area silica alumina catalyst was investigated by Connor, Ciapetta, Leum and Fowle[48]. The results are shown in Table 48. The reaction was studied at 500 psig, a liquid hourly space velocity of 3.0, and a hydrogen to hydrocarbon mole ratio of 10:1. Under these conditions the conversion of methylcyclopentane to other products increased from 53.7 mole per cent at 850°F to 83.3 per cent at 1000°F. The conversion of methylcyclopentane and the yield of benzene as a function of the reaction temperature are plotted in Figure 58a. The data in Table 48 show that hydrocracking of the methylcyclopentane ring to hexanes is a major reaction under all conditions investigated. All the isomers of hexane appear in the product. The data also show that butanes and pentanes are obtained in only minor quantities throughout the temperature range investigated. The other reac-

Table 47. Dehydroisomerization of Methylcyclopentane[99]

Catalyst: Pt/acidic oxide *LHSV:* 6 v/v/hr
Pressure: 300 psig *H_2/HC:* 4 (mole)

Temperature °F	900	950	975
Product Distribution (Wt.% Charge NLB)			
Hydrogen	3.4	3.2	3.2
C_1–C_4	4.2	7.0	9.8
C_6^+ paraffins	24.9	25.5	26.6
Aromatics	33.5	38.6	40.0
Methylcyclopentane	33.0	25.7	20.4
MCP conversion, wt.%	66.0	74.3	79.6

Table 48. Dehydroisomerization of Methylcyclopentane[48]

Catalyst: 0.5% Pt/SiO_2-Al_2O_3 (low area) *LHSV:* 3.0 v/v/hr
Pressure: 500 psig *H_2/HC:* 10 (mole)

Temperature, °F	850	900	950	1000
Recovery, wt.% charge	98.5	98.2	97.5	96.0
Product Distribution (Mole % Charge)				
Methane	1.8	1.9	1.9	2.1
Ethane	0.9	0.9	1.9	3.2
Propane	1.8	1.8	3.9	5.0
Isobutane	—	—	—	1.7
n-Butane	—	0.3	0.4	0.5
Isopentane	—	0.4	0.5	0.3
n-Pentane	—	0.4	0.6	0.9
Cyclopentane	0.1	0.6	0.3	0.1
n-Hexane	9.0	9.4	9.8	7.7
2,2-Dimethylbutane	0.4	0.2	0.5	0.1
2,3-Dimethylbutane	4.1	2.1	0.5	1.5
2-Methylpentane	10.0	11.1	9.3	7.8
3-Methylpentane	9.9	9.5	6.5	7.0
Methylcyclopentane	44.8	35.7	28.2	16.2
Cyclohexane	3.6	1.9	1.0	0.7
Benzene	16.5	27.9	41.2	54.8
Toluene	0.1	0.2	0.3	0.3
Higher mole wt. aromatics	0.1	0.1	0.2	0.2
Methylcyclopentane conv., mole % charge*	53.7	63.2	70.9	83.3
Hexane yield, mole % charge*	32.8	31.7	26.0	23.5

* No loss basis.

tion which increases with temperature, and becomes an important reaction, is the hydrocracking of hexanes to propane. However, even at 1000°F, only 5 mole per cent yield of propane is obtained at a methylcyclopentane conversion of 83.3 per cent. As predicted from thermodynamic calculations for the equilibrium system benzene-cyclohexane-methylcyclopentane, the yield of cyclohexane is very low throughout this temperature range.

These investigators also determined the effect of other hydrocarbons on the activity and selectivity of platinum-low surface area silica-alumina catalysts for the dehydroisomerization of methylcyclopentane to benzene. The results at 500 psig hydrogen pressure using synthetic blends of cyclohexane and methylcyclopentane are shown in Figure 59. The methylcyclopentane concentration was varied from zero per cent to pure methylcyclopentane. The 45° line in this figure represents 100 per cent conversion of the reacted methylcyclopentane plus cyclohexane to benzene. The results using pure cyclohexane show that the platinum-silica-alumina catalyst is a very selective dehydrogenation catalyst. Even at a conversion of cyclohexane of 70 per cent, the major product obtained is benzene. As the cyclohexane concentration in the feed is decreased, the selectivity of conversion of methylcyclopentane to benzene decreases at any fixed conversion of the feed. The lowest selectivity is obtained when the feed consists only of methylcyclopentane.

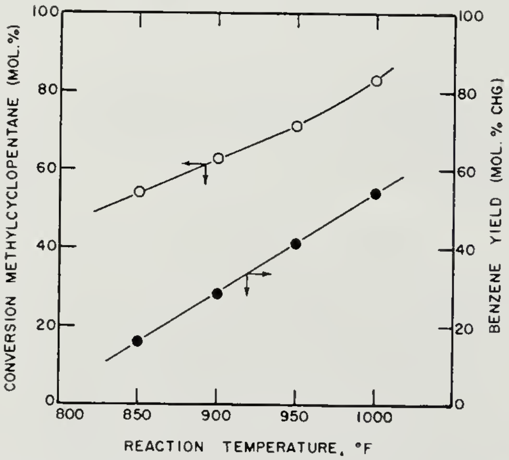


Figure 58a. Dehydroisomerization of methylcyclopentane. Methylcyclopentane conversion and benzene yield *vs.* temperature.

These data indicated that the presence of increasing amounts of benzene, at reaction conditions, reduces the hydrocracking of methylcyclopentane. Hence, these investigators investigated other synthetic hydrocarbon feeds to determine if this was the cause for this increased selectivity. In this study a hydrocarbon blend was used which contained 40 per cent hexane-30 per cent methylcyclopentane-3 per cent cyclohexane-27 per cent benzene. The latter two hydrocarbons were present in approximately the equilibrium concentrations for the reaction conditions used. In this way the hydrogenation-dehydrogenation reaction was kept to a minimum, and the only major naphthene reaction was the dehydroisomerization of methylcyclopentane. The data in Table 49 shows that high selectivity was obtained at high naphthene conversions which appears to confirm the role of benzene as an inhibitor. These results confirm those of Heinemann, Mills, Hattman and Kirsch[99] who had previously shown that benzene has an appreciable inhibiting effect on the hydrocracking of n-heptane in the presence of a platinum catalyst.

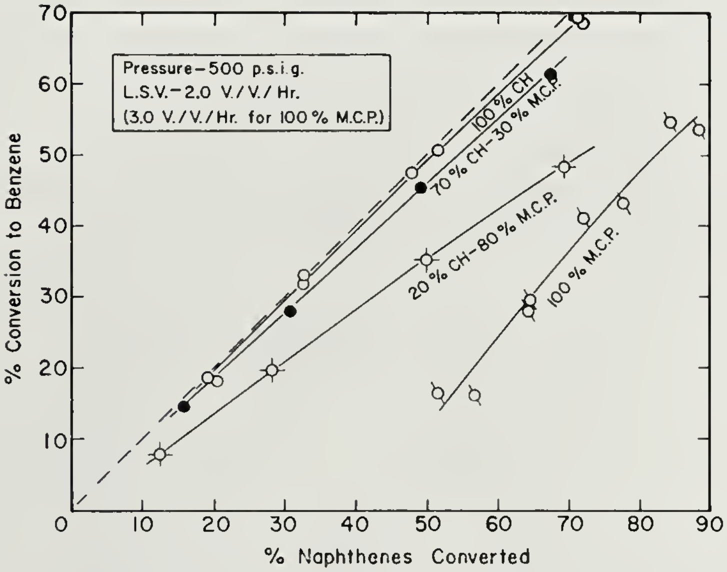


Figure 59. Dehydroisomerization of methylcyclopentane. Effect of cyclohexane on benzene yields.

Table 49. Dehydroisomerization of Methylcyclopentane[48]

Effect of Benzene on Selectivity

Charge: 40% n-C_6—30% MCP—3% CH—27% Benzene

LHSV: 6.0 v/v/hr *H_2/HC:* 10 (mole)

175 psig

Temp. (°F.)	% Naphthenes Converted	Selectivity
850	39.2	0.99
900	62.5	0.85
950	77.7	0.98

An appreciable effect of pressure on the selectivity of the platinum-silica-alumina catalyst was found in the dehydroisomerization of methylcyclopentane[48]. Results obtained at 175 psig hydrogen pressure and 500 psig are shown in Table 50. The results clearly indicate that increasing the hydrogen pressure results in a large decrease in selectivity for the dehydroisomerization of methylcyclopentane to benzene.

In Figure 59a the experimentally observed benzene yields obtained in the presence of the platinum-low surface area silica-alumina catalyst are compared with those calculated from Rossini's[69] data (solid lines) for the system methylcyclopentane-cyclohexane-benzene. In these experiments a synthetic blend consisting of 40 per cent *n*-hexane—30 per cent methylcyclopentane—30 per cent cyclohexane was used. The results show the effect of hydrogen pressure (175 and 500 psig) and the effect of liquid hourly space velocity (1.5 to 6.0) on the yield of benzene at various reaction temperatures.

TABLE 50. DEHYDROISOMERIZATION OF METHYLCYCLOPENTANE[48]
Effect of Pressure on Naphthene Selectivity
Charge: 40% *n*-C_6—30% MCP—30% CH
LHSV: 3.0 v/v/hr H_2/HC: 10 (mole)

	175 psig		500 psig	
Temp. (°F)	% Naphthenes Converted	Selectivity	% Naphthenes Converted	Selectivity
750	27.1	1.04		
800	44.0	1.06	10.8	0.46
850	61.7	1.05	24.4	0.69
900	77.6	1.04	51.6	0.77
950			78.2	0.72

$$\text{Selectivity} = \frac{\text{Moles Benzene Produced}}{\text{Moles Naphthenes Reacting}}.$$

Dehydrocyclization of Paraffins

The dehydrocyclization of *n*-heptane in the presence of dual-function catalysts was extensively studied by Hettinger, Keith, Gring and Teter[104]. The data at various space velocities, temperatures, and hydrogen pressures, in the presence of a catalyst consisting of 0.6 per cent platinum supported on a alumina support are shown in Table 51. The results show that under most of the conditions investigated, dehydrocyclization of *n*-heptane to toluene is a major reaction occurring over these catalysts. The mole per cent conversion of *n*-heptane to aromatics plus naphthenes as a function of the reciprocal weight hourly space velocity is shown in Figure 60. As expected, the yield of aromatics plus naphthenes is highest at the lower reaction pressures. This effect of pressure is more clearly shown in Figure 61, in which the mole per cent conversion of *n*-heptane to aromatics plus naphthenes is plotted as a function of the total reaction pressure, at a fixed temperature and weight hourly space velocity.

As mentioned previously, and also indicated by the data in Table 51, small amounts of olefin hydrocarbons are always found in the products in the presence of these dual functional catalysts.

These investigators also studied the dehydrocyclization activity of other metal-acidic oxide catalysts. The data for iridium, palladium, rhodium, and platinum, all supported on alumina are shown in Table 52. Figure 23, compares the activity of these metal acidic oxides for the conversion of normal heptane to aromatics plus naphthenes. The results, in Figure 23, show that platinum and iridium are the most active catalysts under the same reaction conditions. Rhodium and palladium show the lowest activity for the dehydrocyclization of n-heptane.

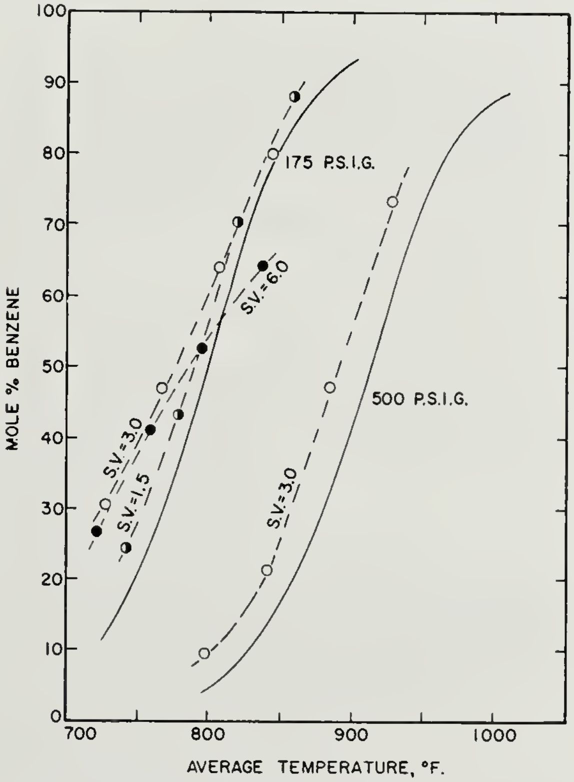


Figure 59a. Benzene-cyclohexane-methylcyclopentane equilibrium. Experimental (– – –) and calculated (———). Concentrations of benzene *vs.* average catalyst temperature. *Charge:* 40% n-C_6, 30% MCP, 30% CH. *Catalyst:* Pt-SiO_2-Al_2O_3.

The above results, plus those obtained by Donaldson, Pasik, and Haensel[56], show that these metal acidic oxide catalysts are extremely active and quite selective for the dehydrocyclization of paraffins to aromatics. The latter investigators studied the dehydrocyclization activity of a platinum

TABLE 51. DEHYDROCYCLIZATION OF *n*-HEPTANE[104]

Catalyst: 0.6% on Al_2O_3 *H_2/HC:* 4.7–5.1 (mole)

Temperature, °F	875	875	925	925	925	925	925	925	925	875	875	875	925	925	925	925
Pressure, psig	200	200	200	200	200	100	350	350	350	500	500	500	500	500	500	500
WHSV, g/g/hr	10.2	5.0	19.7	5.3	2.0	2.0	10.0	5.0	2.0	10.0	5.0	48.1	59.0	9.9	5.1	2.0
Yield, wt. % of charge																
Hydrogen	0.6	1.2	1.2	1.9	2.1	3.9	1.0	0.8	−0.2	−0.1	−0.1	−0.1	−0.3	0.2	−0.2	−1.8
Methane	0.7	1.4	1.2	2.9	3.0	2.0	2.2	3.2	6.5	1.0	1.8	0.2	0.7	2.2	3.7	7.9
Ethane	2.0	2.9	3.2	6.2	7.3	5.1	4.2	6.3	10.7	2.5	3.4	0.6	1.9	4.5	8.6	12.5
Propane	4.4	6.0	4.8	10.8	10.5	8.7	9.2	13.7	19.4	4.0	7.6	1.8	3.8	9.2	17.3	26.3
Isobutane	2.5	3.6	2.1	5.7	5.9	5.6	3.5	6.0	8.8	2.4	3.9	0.9	2.1	4.4	6.4	9.3
n-Butane	3.3	4.4	4.4	6.4	7.5	4.9	6.0	7.6	9.7	4.0	5.1	0.9	3.0	6.8	6.4	12.3
Isopentane	2.7	3.4	2.9	8.2	7.5	6.4	4.8	6.0	8.8	3.1	5.2	—	—	5.6	7.5	10.0
n-Pentane	1.2	1.9	1.6	2.9	4.4	2.0	5.0	5.2	5.3	1.3	2.3	1.4	4.1	4.0	4.1	6.5
C_2–C_5 olefins	0.6	0.5	0.1	1.1	1.0	0.5	0.8	0.0	0.0	1.0	0.6	0.0	0.0	0.8	0.9	0.4
Hexanes	3.0	4.1	3.2	6.4	6.2	3.5	8.0	8.5	7.3	4.2	6.9	1.1	1.9	6.6	7.8	5.0
n-Heptane	29.1	16.3	27.8	4.0	2.5	0.3	8.4	8.0	0.4	23.5	14.2	70.0	51.8	10.1	4.7	0.4
Isoheptanes	35.3	32.9	24.7	5.0	0.5	2.1	22.2	13.3	1.6	45.0	39.7	20.2	23.8	29.7	15.3	1.9
Cycloalkanes	2.4	2.3	2.7	1.3	1.2	0.7	2.4	1.8	1.0	2.4	2.5	0.4	0.8	2.4	2.3	0.7
Benzene				1.5	1.8	2.6			2.0							
Toluene	10.9	18.0	18.2	34.4	37.0	49.4	21.3	23.2	17.6	4.6	6.1	1.0	4.9	12.6	14.6	9.7
Higher aromatics				0.5	1.0	1.5			0.7							
Olefins, total	1.3	1.1	1.9	0.8	0.6	0.8	1.0	0.7	0.4	0.7	0.6	0.7	1.4	0.9	0.6	0.3
n-Heptane remaining, mole %	29.2	16.3	27.8	4.0	2.5	0.3	8.4	4.0	0.4	23.5	14.2	70.0	51.8	10.1	4.8	0.4
Isomerization, mole %	35.3	32.9	24.7	5.0	0.5	2.1	22.2	13.3	1.6	45.0	39.7	20.2	23.8	29.7	15.3	1.9
Hydrocracking, mole %	19.8	27.7	23.0	49.3	52.0	38.2	42.8	55.0	75.1	23.4	36.4	7.6	16.9	43.2	61.2	86.2
Conv. to olefins, mole %	1.3	1.1	1.9	0.8	0.6	0.8	1.0	0.7	0.4	0.7	0.6	0.7	1.4	0.9	0.6	0.3
Dehydrocyclization, mole %	14.4	22.0	22.6	40.9	44.4	58.8	25.6	27.2	22.5	7.4	9.1	1.5	6.1	16.1	18.2	11.2

catalyst using a paraffinic naphtha obtained from a Fischer-Tropsch product. Dehydrocyclization of paraffins contributes to the over-all octane number obtained in the reforming of virgin naphthas. This is particularly true when the reforming operation is carried out at either low pressures or at very high temperatures.

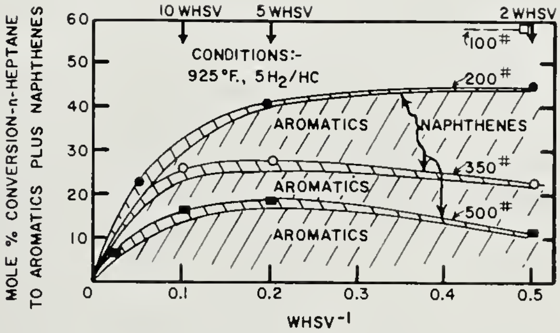


Figure 60. Dehydrocyclization of *n*-heptane. Effect of space velocity and pressure on yield of aromatics plus naphthenes.

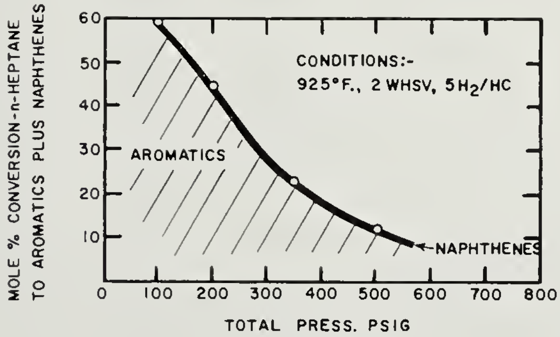


Figure 61. Dehydrocyclization of *n*-heptane. Effect of total pressure on yields of aromatic plus naphthenes.

Effect of Reaction Conditions

Hydrogen to Hydrocarbon Mole Ratio. Ciapetta and Hunter[38] investigated the effect of hydrogen to hydrocarbon mole ratio on the activity and selectivity of a standard nickel silica-alumina catalyst for the isomerization of *n*-hexane. The mole ratio of hydrogen to hydrocarbon was varied from 0.5:1 to 8:1. The liquid space velocity was varied from 0.6 ml/ml/hr for a hydrogen to hydrocarbon ratio of 8:1, to 2.2 for a ratio of 0.5:1 in order to maintain the total gas (hexane + hydrogen) volume space velocity constant. The experimental data are shown in Table 53.

The conversion of *n*-hexane at constant reaction temperature is plotted as a function of the hydrogen to hydrocarbon mole ratio in Figure 62. The results show that at constant reaction temperature, the conversion of *n*-hexane is independent of the hydrogen partial pressure and the hydrocarbon partial pressure in the feed. The apparent decrease in conversion at the higher reaction temperatures (Table 52, Run 508) for a hydrogen to hydrocarbon mole ratio of 0.5:1 appears to be due to the inactivation of the catalyst by carbon deposition. The carbon content of the used catalyst was 0.65 per cent by wt. compared to 0.03 per cent for the used catalyst at higher hydrogen to hydrocarbon mole ratios.

Figure 63 reveals that there is little or no effect of the molar ratio of hydrogen to hydrocarbon on the isomer yield at the same conversion of normal hexane. Thus, provided hydrocracking is low, and since there is no consumption of hydrogen during the isomerization reaction, the nickel silica-alumina catalyst shows high selectivity for the isomerization of *n*-hexane even at low mole ratios of hydrogen to hydrocarbons.

TABLE 52. DEHYDROCYCLIZATION OF *n*-HEPTANE[104]
Effect of Metal Component

Pressure: 200 psig *WHSV:* 4.5–4.9 g/g/hr
Temperature: 925°F *H_2/HC:* 4.8–5.3 (mole)

Catalyst Composition	0.6% Pt Al_2O_3	0.32% Rh Al_2O_3	1.0% Pd Al_2O_3	0.59% Ir Al_2O_3
Yields, wt. % of charge				
Hydrogen	1.3	0.1	−0.6	1.0
Methane	3.1	1.5	0.8	3.0
Ethylene				0.3
Ethane	6.8	4.5	6.7	7.6
Propylene		0.6	0.5	0.5
Propane	12.0	10.3	11.0	12.4
Isobutane	5.7	5.9	7.2	5.1
m-Butane	7.9	6.7	6.4	9.8
Butylenes	0.5		1.3	0.4
C_5^+ product	62.7	70.4	66.7	59.9
Mole % conversion of *n*-heptane to aromatics plus naphthenes	29.9	13.4	10.5	25.1
Yield of aromatics, vol. % charge	20.8	8.8	7.1	17.2
Yield of naphthenes, vol. % charge	1.2	1.2	3.0	1.3

Liquid Space Velocity. The effect of liquid space velocity on the activity of nickel-silica-alumina catalyst for the isomerization of *n*-hexane was investigated by Ciapetta and Hunter[38]. The charge rate of *n*-hexane was varied from 0.2 to 2.0 volumes of feed per volume of catalyst per hour. The results are shown in Table 54. In these runs the total gas space velocity (hydrogen plus *n*-hexane) was varied from 172 to 1716 volumes of gas at

TABLE 53. ISOMERIZATION OF n-HEXANE[38]
Effect of Hydrogen to Hydrocarbon Ratio
Catalyst: 5% nickel-silica-alumina *Pressure:* 350 psig

Run No.	505	506	507	508	501	502	503	504	497	498	499	500
Temperature, °C	316	348	376	402	316	345	376	404	316	344	374	404
Total recovery, wt. % charge	96.8	94.4	99.6	98.5	95.9	95.8	92.6	92.7	95.5	95.2	97.6	95.2
Liquid space velocity, v/v/hr	2.2				1.32				0.55			
H_2/HC, mole ratio	0.5				2.0				8.0			
Product Distribution (Mole % Charge—NLB)												
Methane		0.5	1.1	1.6		1.6	16.6	39.7	1.6	1.6	1.6	59.6
Ethane		1.1		0.3			0.6	2.6			0.9	4.3
Propane	0.2	0.2	2.2	7.8	0.6	0.6	2.0	11.7	1.0	0.8	7.6	11.9
Isobutane			1.2	2.1			0.7	3.3				3.0
n-Butane		0.1	0.1	0.7	0.7		0.7	4.0				7.7
Isopentane		0.5	1.3	1.0		0.2	7.1	15.2			0.8	12.3
n-Pentane	0.2	0.5	1.2	1.9	0.2	1.1	4.9	8.6	0.1	0.1	3.6	16.6
2,2-Dimethylbutane	1.2	2.3	1.0		0.8	3.2	6.1	3.8		1.1	2.0	0.2
2,3-Dimethylbutane	1.5	4.0	4.1	3.3	1.5	4.6	6.4	4.8		2.1	3.4	1.6
2-Methylpentane	10.8	24.7	29.6	19.4	8.4	24.4	28.2	20.6	9.6	25.8	32.4	12.0
3-Methylpentane	8.6	19.4	22.3	17.0	8.4	18.7	21.9	16.3	8.0	20.3	26.3	12.1
n-Hexane	77.6	48.3	38.8	51.8	79.9	47.5	22.2	15.4	81.5	50.0	27.6	17.4
Conv. n-hexane, mole % charge	22.4	51.7	61.2	48.2	20.1	52.5	77.8	84.6	18.5	50.0	72.4	82.6
C_6 Isomer yield, mole % charge	22.1	50.4	57.0	39.7	19.1	50.9	64.6	45.5	17.6	49.3	64.1	25.9
Selectivity factor	0.99	0.98	0.93	0.82	0.95	0.97	0.83	0.54	0.95	0.99	0.89	0.31
Wt. % C on catalyst				0.65				0.03				0.03

S.T.P. per volume of catalyst per hour. As shown in Figure 64 the conversion of *n*-hexane decreases at constant reaction temperature as the liquid space velocity of the feed is increased. The rate of decrease of conversion with space velocity is less at the higher reaction temperatures owing to the hydrocracking reaction which becomes the major reaction above conversions of *n*-hexane of 70 to 80 mole per cent. Since this reaction is highly exothermic, control of the catalyst temperature becomes more difficult. As the catalyst temperature increases, the hydrocracking reaction is acceler-

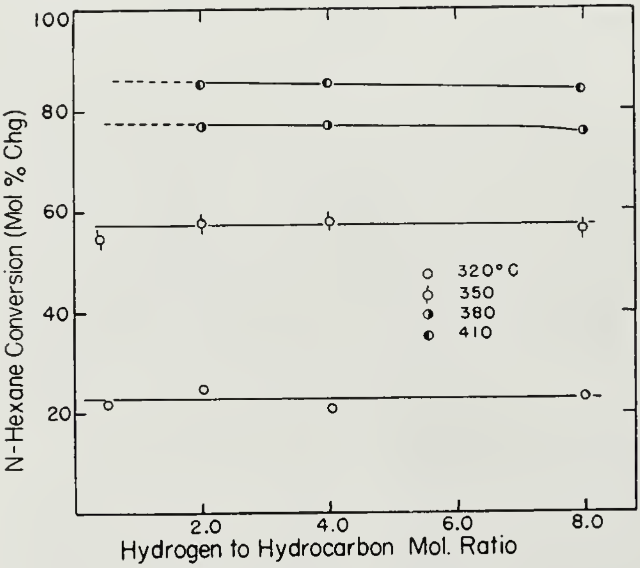


Figure 62. Isomerization of *n*-hexane. Effect of hydrogen to hydrocarbon ratio on *n*-hexane conversion at constant reaction temperatures.

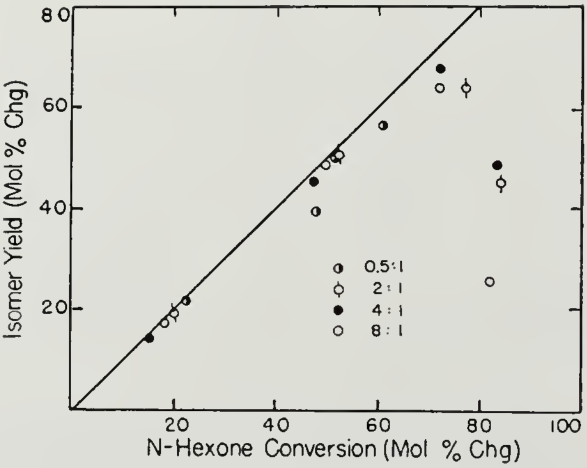


Figure 63. Isomerization of *n*-hexane. Effect of hydrogen to hydrocarbon ratio on isomer yield.

TABLE 54. ISOMERIZATION OF n-HEXANE[38]

Effect of Liquid Space Velocity

Catalyst: 5% nickel-silica-alumina *H_2/HC:* 4 (mole)
Pressure: 350 psig

Run No.	528	529	530	531	493	494	495	496	525	526	527	528
Temperature, °C	316	341	372	401	315	343	371	404	317	344	376	404
Total recovery, wt. % charge	87.4	100.2	99.5	96.7	94.7	93.7	95.7	96.5	99.7	98.3	98.3	96.7
Liquid space velocity, v/v/hr	0.2				0.5				2.0			
Product Distribution (Mole % Charge—NLB)												
Methane	0.5	3.2	3.2	41.3	0.5	0.5	4.3	45.5	1.1	0.5	1.6	11.8
Ethane		0.6	0.6	3.7		0.6	0.6	3.2	0.9	0.3	0.3	0.6
Propane	0.6	0.2	5.7	11.1	0.8	1.4	1.0	11.9	1.6		2.0	4.3
Isobutane	0.4	1.3	1.8	5.8		0.4		0.6	0.9		0.9	1.0
n-Butane	0.4	0.9	4.0	8.3				7.6		0.4		1.9
Isopentane		6.2	9.4	25.7			0.1	29.8	0.1		0.6	6.9
n-Pentane	1.0	4.1	5.5	11.7		0.2		14.5			2.0	5.4
2,2-Dimethylbutane		1.6	1.7	0.6		0.9	1.5	1.8		3.6	0.6	4.2
2,3-Dimethylbutane	1.4	2.9	3.1	0.6		2.0	4.5	1.8		2.7	2.8	4.9
2-Methylpentane	21.6	33.8	33.2	14.0	13.3	24.4	32.8	13.9	7.2	16.0	34.1	30.7
3-Methylpentane	17.6	23.4	23.4	12.4	10.1	20.3	26.4	11.7	7.5	12.8	24.8	23.0
n-Hexane	57.5	27.2	19.7	17.1	76.1	51.2	29.1	14.5	83.3	64.4	33.3	20.0
Conv. n-hexane, mole % charge	42.5	72.8	80.3	82.9	23.9	48.8	70.9	85.5	16.7	35.6	66.4	80.0
C_6 isomer yield, mole % charge	40.6	61.7	61.4	27.6	23.4	47.6	65.2	29.2	14.7	35.1	62.3	62.8
Selectivity factor	0.96	0.85	0.76	0.33	0.98	0.98	0.92	0.34	0.88	0.99	0.94	0.79
Wt. % C on catalyst				0.14				0.05				0.11

ated, so that smaller changes in conversion are observed with increase in liquid space velocity than at the lower temperatures where isomerization to hexane isomers is the major reaction.

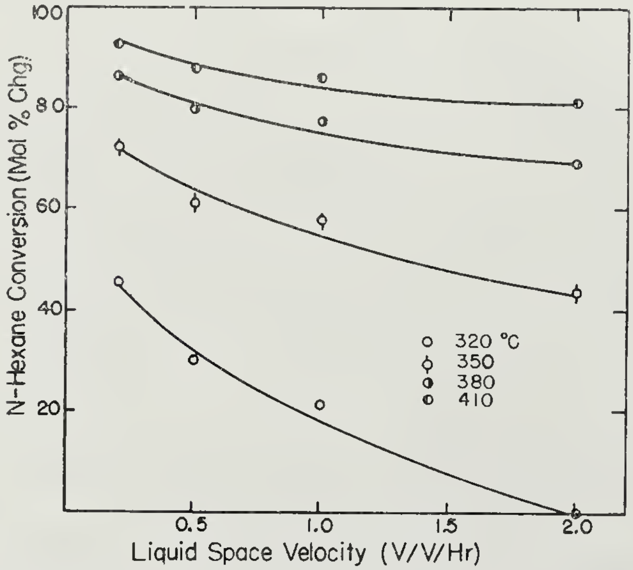


Figure 64. Isomerization of n-hexane. Effect of liquid space velocity on n-hexane conversion at constant reaction temperatures.

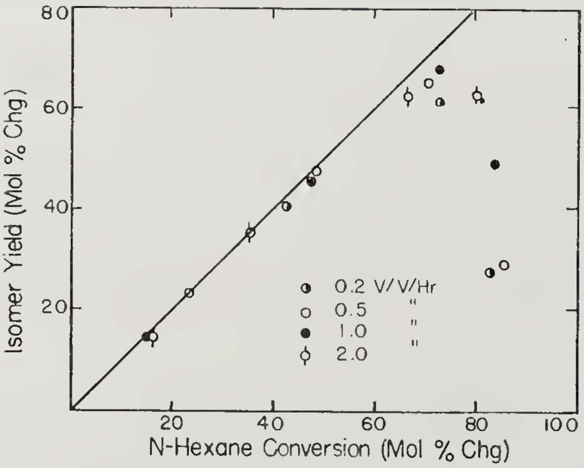


Figure 65. Isomerization of n-hexane. Effect of liquid space velocity on isomer yield.

Figure 65 shows there is very little effect of liquid space velocity on the selectivity of the isomerization reaction up to conversions of 65 to 70 mole per cent. These results reveal that within the contact times employed, this catalyst shows a preferential activity for the isomerization reaction. The apparent energy of activation of the isomerization reaction, calculated at a

Table 55. Isomerization of n-Hexane[38]
Effect of Reaction Pressure

Catalyst: 5% nickel-silica-alumina *H_2/HC:* 4 (mole)

Run No.	513	514	509	510	511	512	521	522	523	524
Temperature, °C	316	346	316	344	376	400	318	345	376	406
Total recovery, wt. % charge	91.8	96.9	92.4	95.3	96.4	101.1	98.2	97.6	98.6	98.8
Pressure, psig	90		175				700			
Liquid space velocity, v/v/hr	0.26		0.5				2.0			
Product Distribution (Mole % Charge—NLB)										
Methane	8.1	33.9	1.1	5.9	58.5	48.3	1.1	1.1	1.1	4.3
Ethane	0.9	1.7		0.3	4.3	3.2		0.6	0.6	0.6
Propane	3.7	0.6	0.8		7.0	14.6	0.8	1.4	2.5	3.9
Isobutane	1.2	0.6		0.4	1.8	3.0			0.9	0.6
n-Butane	1.6	3.0			6.2	3.7		0.9	0.9	0.9
Isopentane		14.3		0.7	25.2	14.9			0.9	3.5
n-Pentane	6.1	8.2	0.2	5.1	12.1	13.0	0.8	0.9	0.6	2.1
2,2-Dimethylbutane		2.8	0.7		1.8	2.8			0.2	3.1
2,3-Dimethylbutane	1.6	4.3	1.9	3.0	2.4	3.4			1.0	2.7
2-Methylpentane	25.4	25.5	15.0	30.4	15.0	17.0	6.3	17.9	35.6	38.4
3-Methylpentane	22.8	19.4	13.7	25.8	13.3	14.8	6.8	13.1	25.3	27.1
n-Hexane	39.3	20.3	68.0	34.4	14.9	16.5	85.5	66.5	34.0	19.7
Conv. n-hexane, mole % charge	60.7	79.7	32.0	65.6	85.1	83.5	14.5	33.5	66.0	80.3
C_6 isomer yield, mole % charge	49.8	52.0	31.3	59.2	32.5	38.0	13.1	31.0	62.1	71.3
Selectivity factor	0.82	0.65	0.98	0.90	0.38	0.46	0.91	0.93	0.94	0.89
Wt. % C on catalyst		.04				0.08				.07

constant conversion of 50 mole per cent, is of the order of 52 to 56 kcal per mole.

Reaction Pressure. The effect of total reaction pressure on the isomerization of *n*-hexane in the presence of a standard nickel-silica-alumina catalyst was investigated by Ciapetta and Hunter[38]. Reaction pressures from 90 to 700 psig were studied. The complete experimental data are shown in Table 55. In order to maintain all the other variables constant the liquid space velocity was varied from 0.26 ml/vol. of catalyst per hour at 90 psig pressure, to 2.0 ml/ml/hr at 700 psig pressure. In this manner, using a constant hydrogen to hydrocarbon mole ratio of 4:1, it was possible to maintain the total gas contact time (hydrogen + normal hexane) constant.

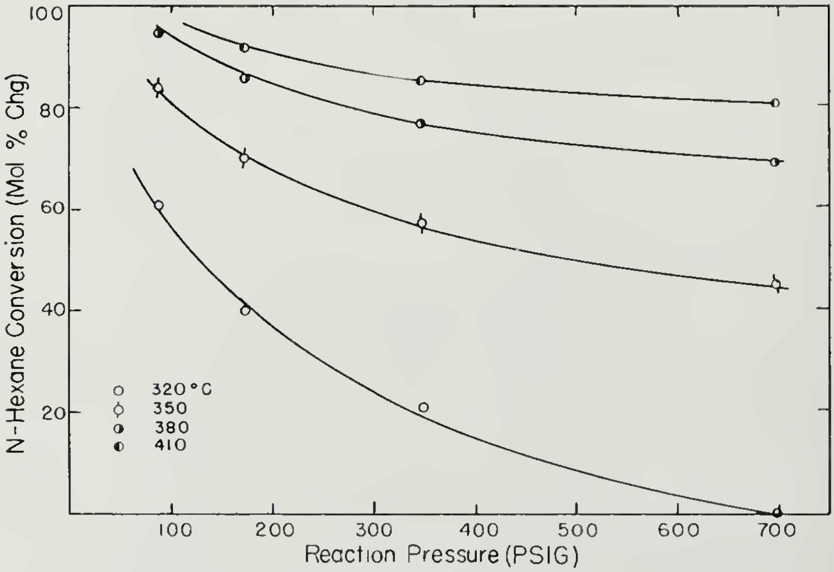


Figure 66. Isomerization of *n*-hexane. Effect of reaction pressure on *n*-hexane conversion at constant reaction temperatures.

The data plotted in Figure 66 show that the conversion of *n*-hexane, at the same temperature, decreases as the total reaction pressure is increased. Thus at a reaction temperature of 320°F the conversion of *n*-hexane at 90 psig pressure is 61 mole per cent, while at 700 psig pressure the conversion of *n*-hexane is less than 15 per cent. Since the reaction is apparently of zero order with respect to the partial pressure of hydrogen and normal hexane, increasing the partial pressure of the reactants by increasing the total pressure should cause a decrease in conversion, provided the total gas contact time is maintained constant. Thus in changing the pressure from 350 to 700 psig, we have increased the partial pressure of *n*-hexane by a factor of 2. Hence, in order to obtain the same conversion of *n*-hexane, it would be necessary to double the contact time.

As shown in Figure 67 and Table 56, the selectivity of the isomerization reaction is not affected by the total reaction pressure within the pressure range investigated.

At atmospheric pressure, these authors found that hydrocracking is the primary reaction observed on passing *n*-hexane with hydrogen over the nickel-silica-alumina catalyst. At 330°C a liquid space velocity of 0.5 ml/ml/hr, 20 per cent of the *n*-hexane was converted to other products. The yield of isohexanes was only 4.4 per cent based on the charge; the remainder of the converted *n*-hexane appears as lower molecular weight hydrocarbons (predominantly methane).

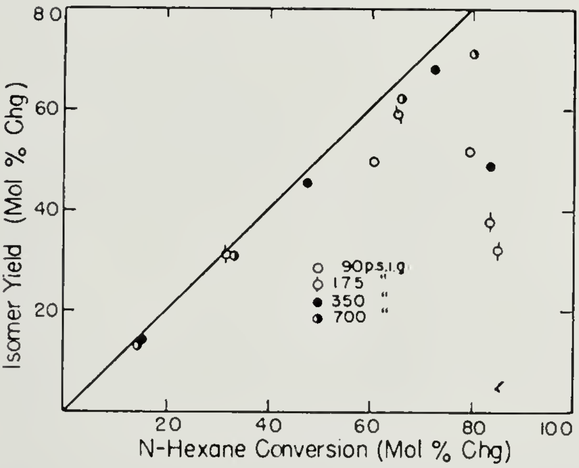


Figure 67. Isomerization of *n*-hexane. Effect of reaction pressure on isomer yield.

Effect of Catalyst Variables

Hydrogenation-Dehydrogenation Component. As previously discussed, the hydrogenation-dehydrogenation activity of the metal component of a dual-function catalyst is extremely important in terms of the over-all activity and selectivity of these catalysts for the reactions of hydrocarbons. The vast amount of previous work directed toward determining the activity of various metal catalysts for the hydrogenation or dehydrogenation reactions of hydrocarbons has clearly shown that metals like platinum, palladium, nickel and cobalt are much more active than metals like iron, copper and zinc for these reactions. As reported above, this order of activity was observed by Ciapetta and Hunter[38] in their investigation of the isomerization of normal hexane in the presence of platinum, cobalt, or nickel dual-function catalysts.

Method of Catalyst Preparation. Ciapetta and Hunter[38] prepared nickel on silica-alumina catalysts by several procedures in order to investigate the effect of catalyst preparation on the isomerization of *n*-hexane. The

TABLE 56. ISOMERIZATION OF n-HEXANE[55]

Effect of Method of Preparation

Pressure: 350 psig *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	428	429	431	430	424	425	426	427	437	438	439	440
Temperature, °C	329	357	372	387	331	359	387	404	331	362	393	404
Total recovery, wt. % charge	97.3	93.8	93.1	92.1	94.6	96.0	90.5	97.3	96.1	96.3	91.7	95.9
Catalyst	SA-5N (X)				SA-5N (VIII)				SA-5N (XVI)			
Product Distribution (Mole % Charge—NLB)												
Methane	0.5	0.5	2.2	5.9	0.5	1.6	9.7	20.4	1.1	2.7	16.6	31.1
Ethane				0.6			0.9	1.4			1.4	2.6
Propane		1.0	1.0	3.5	0.4	0.4	1.4	9.6	1.0	1.4	4.3	9.2
Isobutane				1.0			1.2	1.9		0.4	1.5	1.0
n-Butane			0.3	0.3	0.4		0.7	2.2			1.8	1.5
Isopentane			1.1	3.2		0.5	8.7	8.6		1.3	10.1	9.3
n-Pentane		0.4	1.0	1.8		0.5	3.4	5.0		1.7	6.5	6.8
2,2-Dimethylbutane		1.9	6.1	8.1		3.0	7.3	6.3		1.0	4.8	2.1
2,3-Dimethylbutane	1.0	3.5	5.8	6.5		4.5	6.4	6.0	1.3	3.9	4.2	4.7
2-Methylpentane	14.3	30.4	32.2	30.2	21.3	31.8	29.0	25.2	18.3	34.8	30.5	28.2
3-Methylpentane	11.5	21.8	22.4	20.3	14.1	23.4	20.6	18.4	12.3	27.6	23.0	22.6
n-Hexane	73.1	41.5	30.7	25.8	64.1	36.0	24.2	20.8	67.6	28.9	15.6	15.9
Conv. n-hexane, mole % charge	26.9	58.5	69.3	74.2	35.9	64.0	75.8	79.2	32.4	71.1	84.4	84.1
C_6 Isomer yield, mole % charge	26.8	57.6	66.5	65.1	35.4	62.7	63.3	55.9	31.9	67.3	62.5	57.6
Selectivity factor	1.00	0.99	0.96	0.88	0.99	0.98	0.83	0.71	0.99	0.95	0.74	0.69
Wt. % C on catalyst				0.35				0.15				0.19

standard catalyst was prepared by slurrying fresh silica-alumina in a solution of nickel nitrate, and precipitating nickel carbonate by the addition of an aqueous solution of ammonium carbonate. Catalyst SA-5N(XVI) was prepared by first precipitating nickel carbonate from solutions of nickel nitrate and ammonium carbonate. A slurry of the washed nickel carbonate was then mixed with the water slurry of silica-alumina. The final catalyst was dried and activated by the same procedure as the standard catalyst. Catalyst SA-5N (X) was prepared by first forming nickel carbonate using aqueous solutions of nickel nitrate and sodium carbonate. The sodium carbonate precipitated nickel carbonate was then washed free of sodium ions, slurried in water and the resulting suspension mixed with a water slurry of silica-alumina catalyst. Catalyst SA-5N (VIII) was prepared by impregnating the silica-alumina with a nickel nitrate solution, thermally decomposing the nitrate to the corresponding oxide, and finally

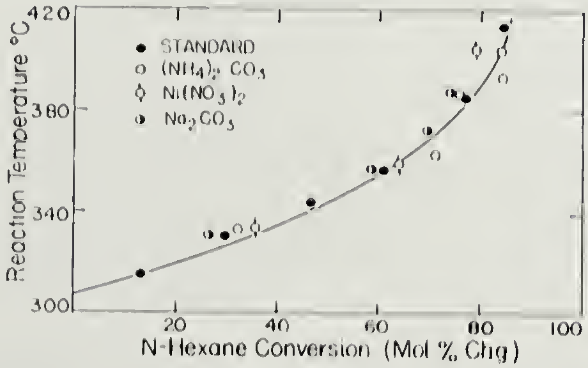


Figure 68. Isomerization of *n* hexane. Effect of catalyst preparation method on conversion of *n* hexane.

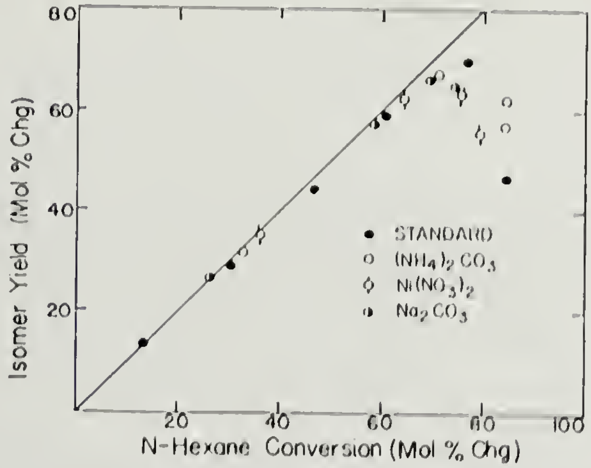


Figure 69. Isomerization of *n* hexane. Effect of catalyst preparation method on isomer yield.

Table 57. Isomerization of n-Hexane[38]

Effect of Catalyst Activation Temperature

Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr

Pressure: 350 psig *H_2/HC:* 4 (mole)

Run No.	475	471	472	473	462	458	459	460	517	518	519
Temperature, °C	303	332	358	392	304	331	360	398	331	359	392
Total recovery, wt. % charge	96.3	96.5	95.6	93.8	97.7	97.7	92.8	87.7	91.9	91.1	90.3
Activation temp., °C	371				427				496		
Product Distribution (Mole % Charge—NLB)											
Methane	0.5	2.2	8.6	60.8	0.5	1.6	7.5	64.0	4.8	9.1	52.1
Ethane			0.6	4.3			0.6	4.0	0.6	1.2	2.9
Propane			1.0	4.1			0.6	5.3	2.7	2.0	5.9
Isobutane			0.4	3.3			0.6	3.6	0.9	1.1	4.0
n-Butane				7.7			0.3	9.2	0.9	0.4	7.4
Isopentane			5.1	14.0			1.6	21.8	1.0	3.2	18.7
n-Pentane		0.4	0.8	18.9		0.4	6.6	21.5	1.0	3.9	14.3
2,2-Dimethylbutane		0.2	0.6	2.4		0.5	3.5	2.1		1.2	3.2
2,3-Dimethylbutane			1.0	2.6			4.0	3.1	1.1	1.3	2.0
2-Methylpentane		1.5	7.6	12.2		4.8	11.8	12.0	13.6	30.8	20.0
3-Methylpentane		0.9	7.3	9.2		1.5	9.3	9.6	13.0	21.6	14.2
n-Hexane	100.0	97.7	76.0	23.6	99.9	92.5	62.3	16.2	66.9	34.7	11.5
Conv. n-hexane, mole % charge	0.0	2.3	24.0	76.4	0.1	7.5	37.7	83.8	33.1	65.3	88.5
C_6 isomer yield, mole % charge	0.0	2.6	16.5	26.4	0.0	6.8	28.6	26.8	27.7	54.9	39.4
Selectivity factor		1.00	0.69	0.35	0.0	0.91	0.76	0.32	0.83	0.84	0.45
Wt. % C on catalyst				0.03				0.12			0.16

activating the catalyst in the same manner as a standard catalyst. The results obtained in the isomerization of *n*-hexane, using the latter three catalysts are shown in Table 56. The conversion of *n*-hexane as a function of the temperature, and the isomer yields as a function of *n*-hexane conversions are plotted in Figures 68 and 69. It is obvious from the data that these methods of preparing the catalyst are comparable to that used in making the standard catalyst.

TABLE 58. ISOMERIZATION OF *n*-HEXANE[38]
Effect of Catalyst Activation Temperature
Catalyst: 5% nickel-silica-alumina *LHSV:* 1.0 v/v/hr
Pressure: 350 psig *H_2/HC:* 4 (mole)

Run No.	463	464	465	466	467	468	469	470
Temperature, °C	331	359	388	416	329	359	387	416
Total recovery, wt. % charge	97.1	96.4	94.6	92.0	95.6	96.0	94.9	92.0
Activation temp., °C	593				649			
Product Distribution (Mole % Charge—NLB)								
Methane			0.5	1.6				0.5
Ethane				0.6				0.6
Propane		1.0	2.7	13.9		1.4	2.7	11.1
Isobutane		0.4	0.1	0.7			0.3	0.6
n-Butane			0.1	0.6			0.2	0.6
Isopentane			0.2	1.3			0.2	0.7
n-Pentane			0.6	1.1		0.1	0.2	0.4
2,2-Dimethylbutane	1.4	3.1	3.5	2.7		0.4	1.7	1.9
2,3-Dimethylbutane	0.6	3.5	7.1	6.2	0.9	0.0	2.2	3.5
2-Methylpentane	8.3	17.9	25.8	30.1	1.9	7.2	10.3	13.2
3-Methylpentane	3.0	9.3	18.9	22.0	1.2	2.3	6.3	8.5
n-Hexane	86.7	65.5	41.9	28.6	96.0	89.5	77.5	65.5
Conv. *n*-hexane, mole % charge	13.3	34.5	58.1	71.4	4.0	10.5	22.5	34.5
C_6 isomer yield, mole % charge	13.3	33.8	55.3	61.0	4.0	9.9	20.5	27.1
Selectivity factor	1.00	0.98	0.95	0.86	1.00	0.94	0.91	0.79
Wt. % C on catalyst				0.12				0.05

Catalyst Activation Temperature. The activity and selectivity of nickel-silica-alumina catalysts for the isomerization of *n*-hexane were observed, by Ciapetta and Hunter[38], to depend very markedly on the temperature at which they are activated. These authors activated various batches of the standard catalyst at temperatures of 371, 427, 496, 593, and 649°C for 16 hours using the same hydrogen flow rate. The results obtained for these catalysts in the isomerization of *n*-hexane are shown in Tables 57 and 58.

The conversion of *n*-hexane at the same reaction temperature is plotted as a function of the activation temperature in Figure 70. At reaction temperatures of 330 to 390°C, the conversion of *n*-hexane increases as the activation temperature is increased, passes through a maximum between activation temperatures of 500 to 550°C, and then decreases for catalysts activated at higher temperatures.

The yields of isomers obtained at the same reaction temperature as a function of the activation temperature of the catalyst is shown in Figure 71. Since extensive hydrocracking occurs at conversions higher than 75 to 80 per cent, Figure 71 shows only the isomer yields for conversions of *n*-hexane below this value. For all reaction temperatures, the isomer yield is low with catalysts activated at low temperatures (371 and 427°C); it increases to a maximum for activation temperatures of 500 to 550°C, and then decreases for higher activation temperatures. The data plotted in Figure 72 (yields of methane and pentanes as a function of the activation temperature) show that the catalysts activated at the lower reaction temperatures possess a higher hydrocracking activity than those catalysts activated at the higher temperatures.

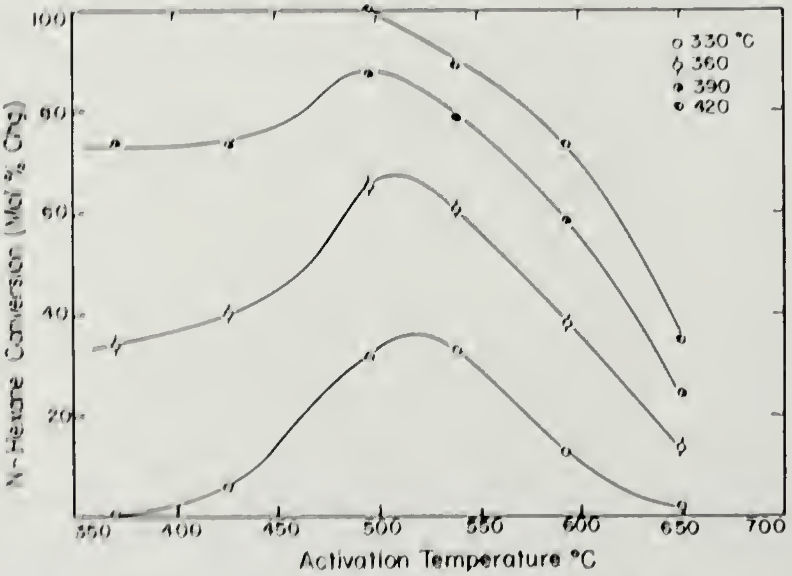


Figure 70. Isomerization of *n*-hexane. Effect of catalyst activation temperature on conversion of *n*-hexane at constant reaction temperatures.

Determination of the extent of reduction of the catalyst at 427°C showed that under the conditions used (16 hr and 6 liters of hydrogen per hr) only 40 to 50 per cent reduction of the nickel oxide occurred compared to 90 to 95 per cent reduction for the catalyst activated at 538°C. These results show that incomplete reduction of nickel oxide produces a catalyst which is not only less active for the conversion of *n*-hexane, but also less selective for the isomerization reaction.

At reduction temperatures above 550°C the activity of the catalyst decreases for the conversion of *n*-hexane under comparable reaction condi-

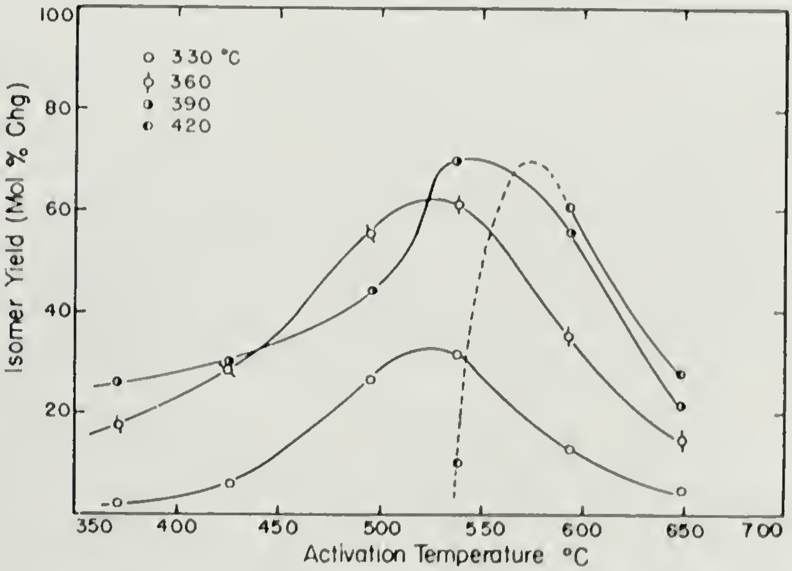


Figure 71. Isomerization of *n* hexane. Effect of catalyst activation temperature on isomer yield at constant reaction temperatures.

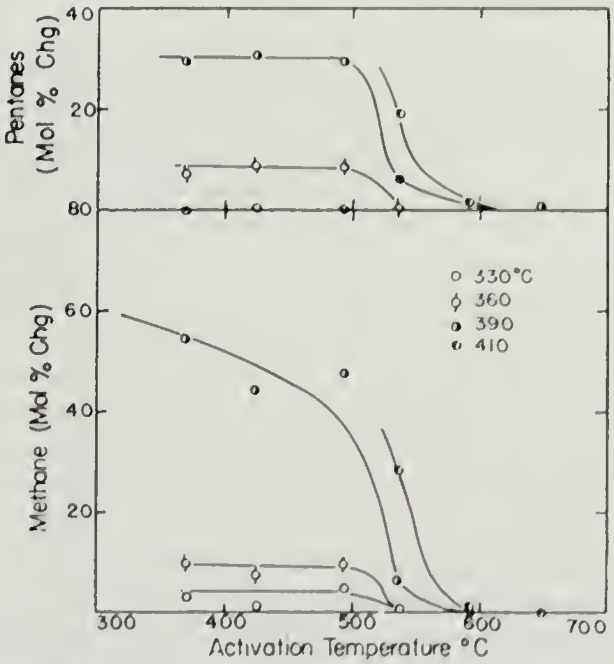


Figure 72. Isomerization of *n* hexane. Effect of catalyst activation temperature on yields of methane and pentanes at constant reaction temperatures.

tions without affecting the selectivity at comparable conversions. As shown in Figure 72, at temperatures above 551°C, very little hydrocracking of *n*-hexane to methane and pentanes occurs under these reaction conditions.

The effect of activation temperature on the BET surface area of the catalyst is shown in Table 59. The unreduced catalyst has a surface area, as measured by nitrogen adsorption, of 336 m^2/g which decreased to 280 m^2/g after activation with hydrogen at 538°C. Thus, these catalysts retain much of the pore structure of the silica-alumina cracking catalyst.

Metal Concentration. The effect of nickel concentration in nickel-silica-alumina catalysts was investigated by Ciapetta and Hunter[38]. Tables 60 and 61 show the results obtained in the isomerization of *n*-hexane using nickel-silica-alumina catalysts containing 2.5, 5, 7.5, 10, 15 and 20 per cent nickel by weight. These catalysts were prepared by adding the required amount of freshly precipitated and washed nickel carbonate slurry to a water slurry of silica-alumina. The catalysts were all treated in the same manner prior to use and tested under similar conditions.

TABLE 59. EFFECT OF ACTIVATION TEMPERATURE ON SURFACE AREA[38]

Catalyst: 5% nickel-silica-alumina

Temperature*, °C	Unred.†	427	538	593
BET area, m^2/g	336	324	279	282

* Catalyst heated in H_2 for 16 hr

† Evacuated at 316°C for 0.5 hr

Surface area of fresh silica-alumina—420 m^2/g

Figure 73 shows the conversion of *n*-hexane as a function of the nickel concentration in the catalyst, at constant reaction temperatures. For the catalyst containing 2.5 per cent nickel, changing the reaction temperature from 320 to 410°C only increased the conversion of *n*-hexane from 10 to 25 per cent, while with the catalyst containing 5 per cent nickel the conversion increased from 25 to 85 per cent. Increasing the nickel content to 10 per cent does not affect the conversion, but for the catalysts containing 15 and 20 per cent nickel the conversion increased markedly for the same reaction temperatures. The hexane isomer yields as a function of the nickel content of the catalyst at constant reaction temperatures are shown in Figure 74. The low isomer yields for the catalyst containing 2½ per cent nickel are expected on the basis of the low conversion of *n*-hexane shown by this catalyst at all temperatures. The isomer yield appears to pass through a maximum at approximately 4 to 6 per cent nickel and then decreases at higher nickel contents. This maximum becomes more evident at the higher reaction temperature, provided the selectivity factor is still high.

Table 60. Isomerization of n-Hexane[38]

Effect of Nickel Concentration

Pressure: 350 psig *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	533	534	535	536	537	538	539	540	541	542	543	544
Temperature, °C	316	345	373	399	317	346	375	406	316	348	371	403
Total recovery, wt. % charge	96.7	99.7	95.9	100.7	97.5	93.4	95.8	86.0	98.6	96.8	100.7	93.9
Catalyst	SA-2.5N (XXI)				SA-5N (XXII)				SA-7.5N (XXIII)			
Wt. % nickel	2.5				5.0				7.5			
Product Distribution (Mole % Charge—NLB)												
Methane	0.5			0.5	0.5	1.1	3.8	36.6	1.6	18.3	25.2	88.1
Ethane				1.1		0.6	0.6	2.3	0.3	0.3	0.9	4.0
Propane	2.0	0.8	1.8	10.8	1.2	0.4	1.4	9.6	2.2	0.8	1.6	9.0
Isobutane			0.2	0.9		0.4	0.6	4.6	1.5	0.6	1.0	2.1
n-Butane		0.4	0.6	1.3			0.6	4.8	1.2	1.2	1.6	3.6
Isopentane			0.1	0.6			2.3	20.6	0.7	7.0	4.7	5.6
n-Pentane	1.2	1.0	0.6	0.7	0.1	0.5	2.6	14.8	2.5	8.1	3.3	4.5
2,2-Dimethylbutane			0.5				5.1	2.4	0.8	2.4	2.9	2.2
2,3-Dimethylbutane		0.1	3.1			0.5	5.0	3.0	0.2	2.2	4.4	2.8
2-Methylpentane	3.5	5.5	6.1	8.9	11.5	30.8	32.3	16.9	9.4	24.6	27.3	19.5
3-Methylpentane	4.6	7.1	7.6	5.8	10.1	20.9	23.7	12.5	7.6	16.4	21.6	12.4
n-Hexane	89.8	86.0	80.7	76.8	77.5	46.8	27.6	16.4	75.8	36.5	30.6	28.4
Conv. n-hexane, mole % charge	10.2	14.0	19.3	23.2	22.5	53.2	72.4	83.6	24.2	63.5	69.4	71.6
C_6 isomer yield, mole % charge	8.1	12.7	17.3	14.7	21.6	52.2	66.1	34.8	18.0	45.6	56.2	36.9
Selectivity factor	0.80	0.91	0.90	0.63	0.96	0.98	0.91	0.42	0.74	0.72	0.81	0.52
Wt. % C on catalyst				0.12				0.11				0.38

Table 61. Isomerization of n-Hexane[38]

Effect of Nickel Concentration

Pressure: 350 psig *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	545	546	547	548	549	550	551	552	553	554	555	556
Temperature, °C	288	319	347	379	272	287	321	347	276	290	318*	346*
Total recovery, wt. % C	96.6	96.8	100.4	95.4	99.9	96.9	97.0	98.9	99.9	96.3	97.4	92.0
Catalyst	SA-10N (XXIV)				SA-15M (XXV)				SA-20N (XXVI)			
Wt. % nickel	10				15				20			
Product Distribution (Mole % Charge—NLB)												
Methane	1.1	9.1	30.6	48.4	1.1	3.2	45.6	22.0	3.8	12.9	45.1	167.0
Ethane		0.3	0.9	2.0		0.6	0.3	0.3	0.9	0.3	0.9	3.2
Propane	0.4	0.4	0.8	4.1	0.4	0.6	1.6	0.8	0.4	0.4	0.8	2.3
Isobutane	0.5	0.5	0.7	1.0			0.9	1.0	0.7		0.4	1.6
n-Butane			1.3	2.7			3.6	2.1		0.9		0.9
Isopentane		0.7	2.7	6.5			4.9	4.4		1.1	0.6	2.4
n-Pentane	1.1	7.4	6.8	5.1	0.4	2.9	19.8	5.0	3.6	10.4	2.0	6.1
2,2-Dimethylbutane			2.0	2.1		0.6	0.3	0.8				0.7
2,3-Dimethylbutane			2.7	3.9				2.0				1.4
2-Methylpentane	2.1	9.7	20.1	24.8	1.3	2.5	12.1	27.6	1.4	3.5	8.1	14.8
3-Methylpentane	3.5	7.3	15.3	18.6	1.3	2.3	8.1	19.4	2.0	2.8	6.5	11.5
n-Hexane	92.8	73.8	44.4	26.6	96.7	91.3	46.3	35.6	91.8	79.8	73.8	29.4
Conv. n-hexane, Mole % charge	7.2	26.2	55.6	73.4	3.3	8.7	53.7	64.4	8.2	20.2	26.2	70.6
C_6 isomer yield, Mole % charge	5.6	77.0	40.1	49.4	2.6	5.4	20.5	49.8	3.4	6.3	14.6	28.4
Selectivity factor	0.78	0.65	0.72	0.67	0.79	0.62	0.78	0.77	0.41	0.31	0.56	0.40
Wt. % C on catalyst				0.24				0.17				0.33

* Cooling air used to control temperature.

The effect of nickel concentration on the extent of hydrocracking is clearly shown in Figures 75 and 76. The hydrocracking of *n*-hexane to produce methane and pentane increases as the nickel content of the catalyst increases above 5 per cent. Thus, as the nickel content of the catalyst increases we obtain reactions which are more characteristic of the metal part of these dual function catalysts. The demethanation activity of the 20 per cent nickel catalyst is similar to that reported by Haensel and

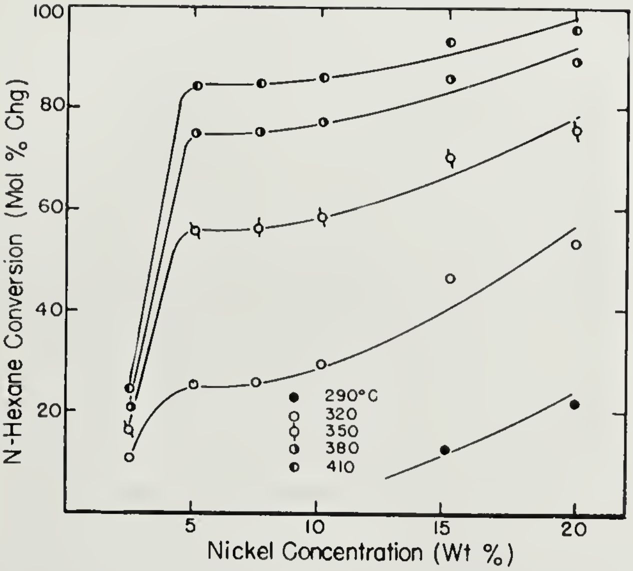


Figure 73. Isomerization of *n*-hexane. Effect of nickel concentration on conversion of *n*-hexane at constant reaction temperatures.

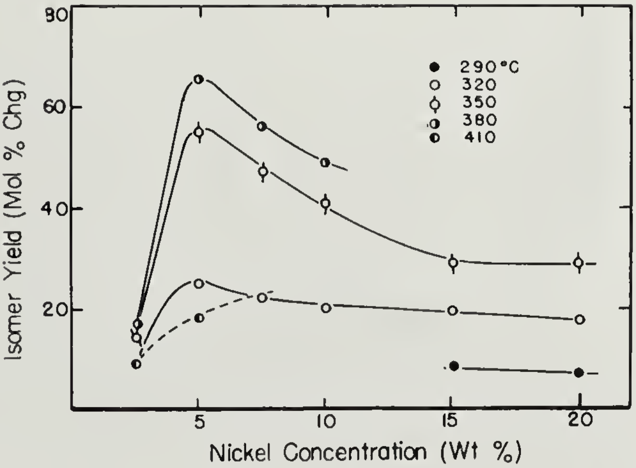


Figure 74. Isomerization of *n*-hexane. Effect of nickel concentration on isomer yield at constant reaction temperatures.

Ipatieff[92] in their study on the demethanation of hydrocarbons in the presence of catalysts containing high concentrations of nickel.

Effect of Alumina Content. To determine the effect of the amount of alumina present in nickel-silica-alumina catalyst, Ciapetta and Hunter[38] prepared a series of catalysts using washed hydrogels of nickel carbonate, silica and alumina. The alumina content in the finished catalyst was varied from 2 to 95 per cent. In all catalysts the concentration of nickel was maintained constant at approximately 5 per cent. The results obtained in the isomerization of n-hexane under comparable reaction conditions are shown in Tables 62 and 63. The conversion of normal hexane as a function of the reaction temperature is shown in Figure 77. The conversion of n-hexane for catalysts containing 13 and 80 per cent alumina are ap-

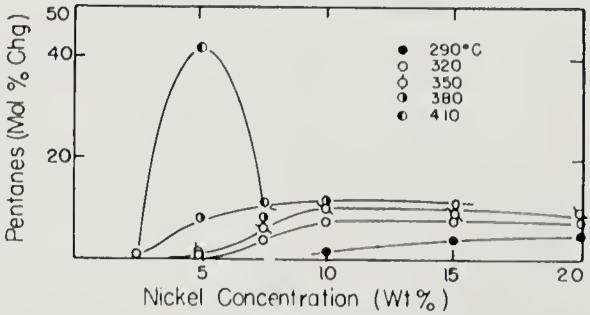


Figure 75. Isomerization of n-hexane. Effect of nickel concentration on yield of pentanes at constant reaction temperature.

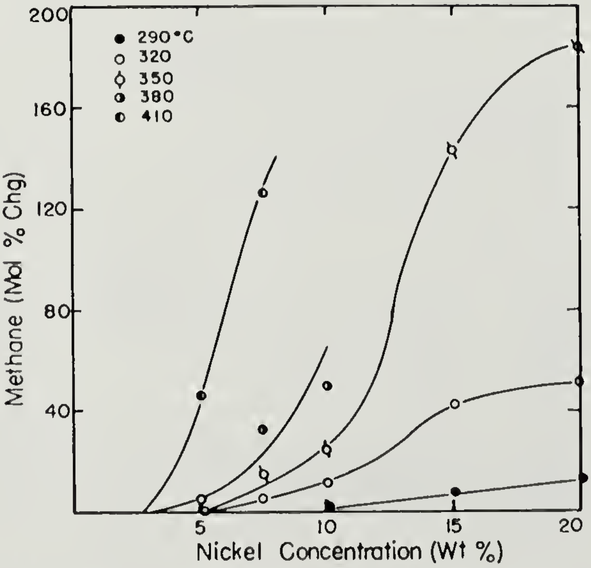


Figure 76. Isomerization of n hexane. Effect of nickel concentration on yield of methane at constant reaction temperature.

proximately the same, but the catalysts containing 2 and 60 per cent alumina are less active at the same reaction temperature. Increasing the alumina content to 95 per cent gives a poor conversion catalyst.

As shown by Figure 78 both the 13 per cent and 60 per cent alumina catalysts show a high selectivity for isomerization, while the 2 per cent and 80 per cent alumina catalysts show a higher hydrocracking activity resulting in lower yields of hexane isomers at the same conversion of *n*-hexane.

TABLE 62. ISOMERIZATION OF *n*-HEXANE[38]

Effect of Alumina Concentration

Pressure: 350 psig *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	432	433	450	451	452	454	455	456	457
Temperature, °C	330	361	329	359	392	332	357	386	414
Total recovery, wt. % charge	95.6	96.1	93.6	95.8	93.9	99.3	95.8	96.0	96.4
Catalyst	SA-5N (XI)		SA-5N (XII)			SA-5N (XIV)			
Wt. % Al_2O_3	2		13			60			
Product Distribution (Mole % Charge—NLB)									
Methane	5.4	20.4	1.6	3.8	37.6		0.5	0.5	0.5
Ethane		0.9			2.3		0.6		
Propane		1.0		1.0	4.7		1.0	1.0	5.5
Isobutane		0.1		1.0	2.5			1.5	0.2
n-Butane		1.9			5.9			0.4	0.1
Isopentane	0.2	0.7		1.3	8.9				0.2
n-Pentane	4.4	8.0		2.0	6.3			0.2	0.6
2,2-Dimethylbutane		0.6			2.0		0.6	1.6	4.1
2,3-Dimethylbutane		1.0		2.0	3.1			2.3	6.2
2-Methylpentane	2.1	3.4	9.8	28.1	28.8	3.7	13.0	23.9	29.2
3-Methylpentane	0.4	3.3	5.8	25.3	22.1	1.4	6.4	14.1	20.4
n-Hexane	92.5	78.5	84.3	40.1	16.5	94.9	79.1	56.0	36.3
Conv. *n*-Hexane, mole % charge	7.5	21.5	15.7	59.9	83.5	5.1	20.9	44.0	63.7
C_6 Isomer Yield mole % charge	2.5	8.3	15.6	55.4	56.0	5.1	20.0	41.9	59.9
Selectivity factor	0.33	0.39	0.99	0.93	0.67	1.00	0.96	0.95	0.94
Wt. % C on catalyst		0.03			0.07				0.07

DEVELOPMENT OF NAPHTHA REFORMING CATALYSTS

The major constituents of petroleum naphthas are the alkanes, cycloalkanes, and aromatic hydrocarbons. Rossini and his co-workers[139a] have shown that the relative amounts of these hydrocarbons vary depending on the crude source. In most virgin petroleum naphthas the concentration of aromatics is usually less than 15 per cent of the total hydrocarbons present. The analyses of 21 virgin naphthas, obtained from various parts of the world, showed that the paraffin content of these naphthas varied from 27 to 72 per cent, the remainder of the saturated hydrocarbons being cycloalkanes. The cycloalkane fraction of virgin naphthas consists of cyclopentanes and cyclohexanes. In many of these naphthas the concentration of cyclopentanes is higher than the cyclohexanes, but this depends on the source of the original naphthas.

TABLE 63. ISOMERIZATION OF *n*-HEXANE[38]

Effect of Alumina Concentration

Pressure: 350 psig *LHSV:* 1.0 v/v/hr

H_2/HC: 4 (mole)

Run No.	571	569	572	441	442	433	444
Temperature, °C	287	316	348	329	359	387	442
Total recovery, wt. % charge	95.0	93.5	98.0	94.0	99.3	99.1	96.9
Catalyst	SA-5N (XXVII)			SA-5N (XV)			
Wt. % Al_2O_3	80			95			
Product Distribution (Mole % Charge—NLB)							
Methane	1.1	3.8	45.1	0.5	1.6		0.5
Ethane			1.4		0.9	0.6	0.6
Propane	0.4	0.4	1.4	1.0	3.9	1.0	1.4
Isobutane			1.2		1.0		
n-Butane			5.5		1.0	0.4	0.4
Isopentane			2.4				
n-Pentane	0.5	3.9	26.4				0.1
2,3-Dimethylbutane				1.7	1.2	0.4	
2-Methylpentane	0.7	1.5	4.7	1.1	0.9	0.8	4.9
3-Methylpentane	1.7	1.3	2.9	8.0	5.9	2.3	2.9
n-Hexane	96.8	93.0	54.0	88.4	88.0	95.6	90.9
Conv. *n*-Hexane, Mole % charge	3.2	7.0	46.0	11.6	12.0	4.4	9.1
C_6 isomer yield, Mole % charge	2.4	2.8	7.6	10.8	8.0	3.5	7.8
Selectivity factor	0.75	0.40	0.17	0.93	0.67	0.80	0.86
Wt. % C on catalyst			0.04				0.06

As shown in Table 2 and Figure 9 the most desirable constituents, in high octane motor and aviation gasolines, are the isoalkanes and the aromatic hydrocarbons. However, Figure 9a shows that the octane number of equilibrium mixtures of the alkanes decreases with increasing carbon number. Therefore the over-all contribution of isoalkanes to the octane number becomes increasingly less as the molecular weight increases. Hence, in the reforming of virgin naphthas the ability of the catalyst system to produce high concentrations of aromatics becomes more important above clear octane numbers of 90.

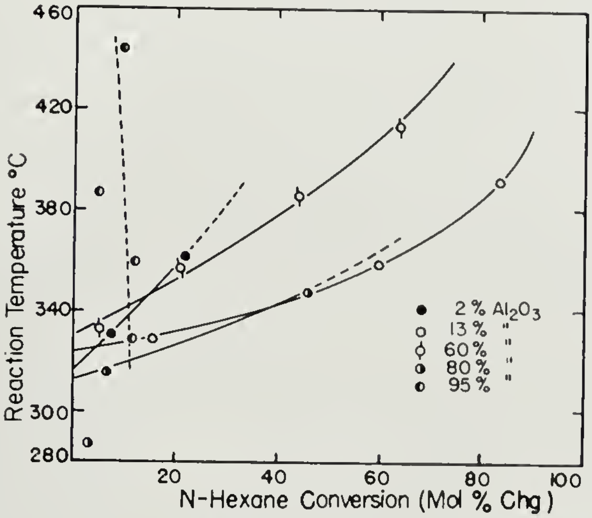


Figure 77. Isomerization of *n*-hexane. Effect of alumina concentration on conversion of *n*-hexane.

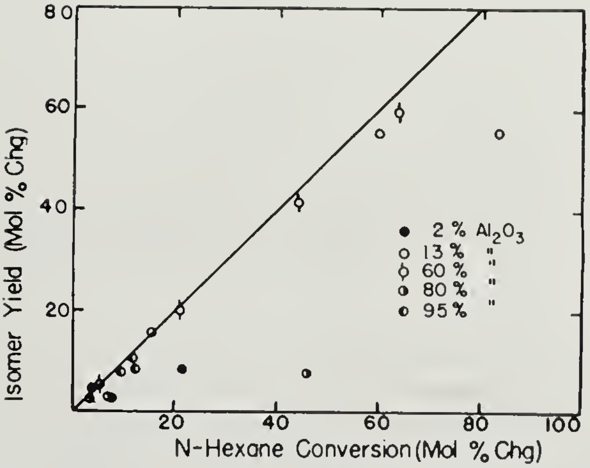


Figure 78. Isomerization of *n*-hexane. Effect of alumina concentration on isomer yield.

As indicated in Figures 1, 2a, and 57, temperature above 700 to 751°F are required to produce high concentrations of aromatics by dehydrogenation of the cyclohexanes, at hydrogen pressures of 100 to 500 psig. Figures

58a and 59a show that temperatures above 800 to 850°F are required to produce aromatics from alkylcyclopentanes by dehydroisomerization. Temperatures above 900°F (Table 51) are required to produce appreciable aromatics by dehydrocyclization of alkanes.

For the formation of aromatics from cyclohexanes, the data in Tables 44, 45, and 46 and Figure 57 show that the only requirement is an active hydrogenation-dehydrogenation catalyst. This is more clearly shown by the data in Table 64. A pure hydrocarbon blend consisting of 50 per cent *n*-heptane and 50 per cent cyclohexane was passed over a 0.4 per cent platinum-silica gel catalyst. The silica gel had a surface area of 500 m^2/g and contained less than 0.02 per cent alumina. The results show that this catalyst has essentially only one function—a high dehydrogenation activity for the conversion of cyclohexane to benzene. The lack of appreciable isomerization activity even at 950°F indicates that this catalyst would have little activity for the dehydroisomerization of alkylcyclopentanes to benzene.

TABLE 64. REFORMING OF 50% *n*-HEPTANE—50% CYCLOHEXANE BLEND[43]

Catalyst: 0.4% Pt-SiO_2(500 m^2/g) *H_2/HC:* 4 (Mole)
Pressure: 350 psig *LHSV:* 2 v/v/hr

Temperature of	750	800	850	900	950
Conversion, mole % charge					
n-Heptane	0	0	1	27	49
Cyclohexane	50	83	97	100	100
Yield, mole % charge					
Isoheptanes	0	0	1.0	7	9
Benzene	44	78	94	96	96
Methylcyclopentane	—	1	2	4	4

The results in Table 18 show that if platinum is deposited on a high area silica-alumina cracking catalyst, the resulting dual-function catalyst is very active for the isomerization of *n*-hexane. If a similar catalyst is used for the conversion of a 50 per cent *n*-heptane-50 per cent cyclohexane blend, we get the results shown in Table 65. At a temperature of 750°F, this catalyst has a high activity for the isomerization of *n*-heptane to isoheptanes and cyclohexane to methylcyclopentane. As the reaction temperature is increased, however, the selectivity for isomerization of *n*-heptane decreases. At 900°F only 2 per cent of isoheptanes was found in the product, although 97 per cent of the *n*-heptane was converted to other products. At this temperature, in the presence of the high area silica-alumina catalyst, the *n*-heptane is almost completely hydrocracked to lower molecular weight hydrocarbons. As shown by the data in Table 65, the dehydrogenation activity of this catalyst is very high for the conversion of cyclohexane to benzene at temperatures of approximately 850 to 900°F.

Ciapetta[36] found that by lowering the surface area of the silica-alumina support, it was possible to decrease the hydrocracking reactions and obtain a higher yield of isomers at the temperatures required for high conversions of cyclohexanes and cyclopentanes to aromatics. The effect of the surface area of the silica-alumina support on the isomerization activity of a platinum catalyst, for the conversion of n-heptane, is shown in Table 66.

TABLE 65. REFORMING OF 50% n-HEPTANE—50% CYCLOHEXANE BLEND[43]

Catalyst: 0.5% $Pt\text{-}SiO_2\text{-}Al_2O_3$ (420 m^2/g) *H_2/HC:* 4 (mole)
Pressure: 350 psig *LHSV:* 2 v/v/hr

Temperature of	750	800	850	900
Conversion, mole % charge				
n-Heptane	83	89	93	97
Cyclohexane	92	94	97	99
Yield, mole % charge				
Isoheptanes	51	38	22	2.0
Benzene	6	24	51	89
Methylcylopentane	68	50	24	8

TABLE 66. ISOMERIZATION OF n-HEPTANE OVER $Pt\text{-}SiO_2\text{-}Al_2O_3$ CATALYSTS[36]
Effect of Surface Area

Pt. Concentration: 0.25 wt.% *LHSV:* 2.0 v/v/hr
Pressure: 350 psig *H_2/HC:* 4 (mole)

Surface area m^2/g	420	320	225	110	43
Acidity (mg KOH/G)	8.4	7.8	6.1	3.7	1.3
Temp., °F for 70% conversion	703	743	783	843	878
Isoheptanes, Mole % charge	56.4	50.5	54.0	50.5	46.0
Selectivity factor	0.80	0.72	0.77	0.72	0.67

These results show that by lowering the surface area, higher reaction temperatures are required to obtain the same conversion of n-heptane (70 mole per cent based on the charge). The results also show that the isomer selectivity is essentially unchanged even for the lowest area support, although the reaction temperature is 175°F higher.

The results obtained in the reforming of a blend of pure hydrocarbons consisting of 50 per cent n-heptane and 50 per cent cyclohexane, in the presence of various platinum-silica-alumina catalysts, are shown in Figures 79, 80, and 81. The surface area of the silica-alumina supports has been modified by high temperature steaming, from 420 m^2/g to 43 m^2/g. Figure 79 shows that as the surface area of the silica-alumina support is decreased,

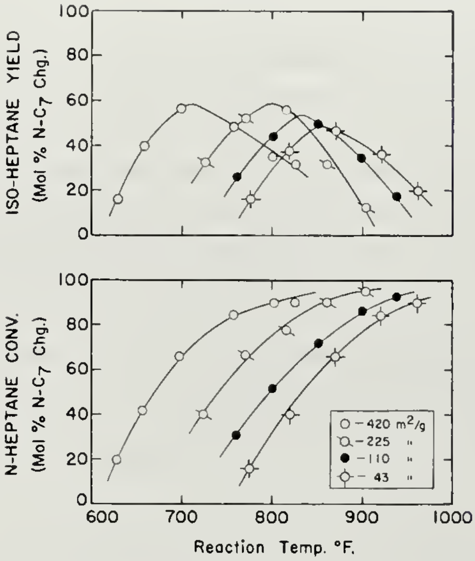


Figure 79. Reforming of hydrocarbon blend. Effect of surface area of silica-alumina support on n-heptane conversion and isoheptane yield. *Catalyst:* $Pt/SiO_2/Al_2O_3$ *LHSV:* 2 v/v/hr. *Pressure:* 350 psig *H_2/HC:* 4.

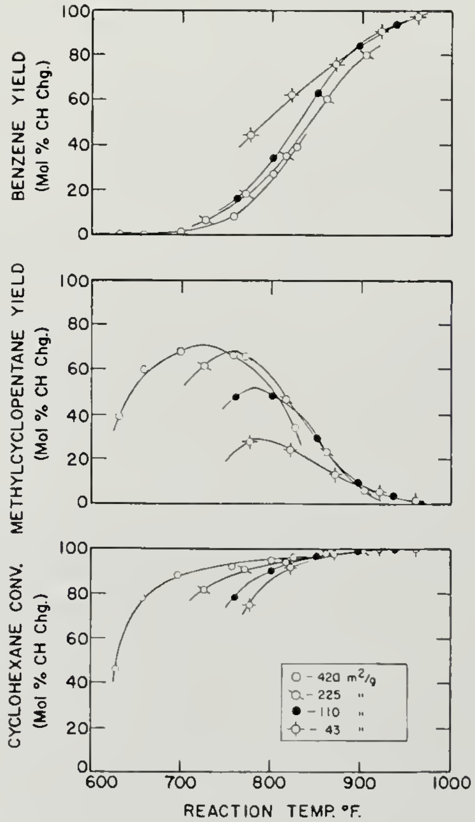


Figure 80. Reforming of hydrocarbon blend. Effect of surface area of silica-alumina support on cyclohexane conversion, methylcyclopentane and benzene yields. *Catalyst:* $Pt/SiO_2/Al_2O_3$ *LHSV:* 2 v/v/hr. *Pressure:* 350 psig *H_2/HC:* 4.

higher reaction temperatures are required for the same conversion of *n*-heptane. The yield of isoheptanes, for any one catalyst, passes through a maximum with increasing temperature, and then decreases at higher conversions of *n*-heptanes. However, as the surface area is decreased, the maximum isomer yield occurs at higher and higher reaction temperatures.

As shown in Figure 80 the conversion of cyclohexane also depends on the surface area of the silica-alumina support at temperatures below 800°F. The lower conversions of cyclohexane below 800°F are not due to a difference in the dehydrogenation activity of the various catalysts. In the presence of these dual-function catalysts cyclohexane undergoes two reactions (1) isomerization to methylcyclopentane, and (2) dehydrogenation to benzene. At temperatures below 800°F under the conditions used, the isomerization activity of the catalyst determines the extent of reaction of cyclohexane. Hence, the higher area supports, or as previously discussed, the higher acidic supports, are much more active for the isomerization of cyclohexane to methylcyclopentane. Although the low surface area supports show

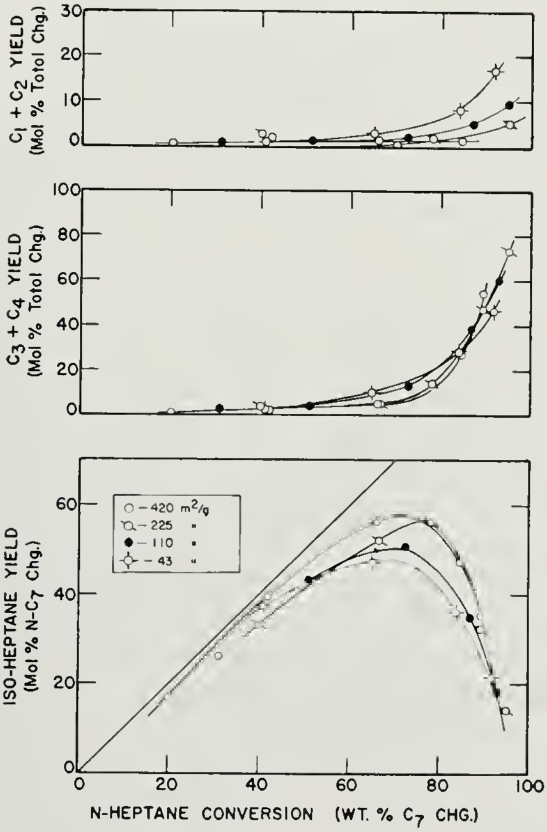


Figure 81. Reforming of hydrocarbon blend. Effect of surface area of silica-alumina support on isoheptane, $C_3 + C_4$ and $C_1 + C_2$ yields. *Catalyst:* $Pt/SiO_2/Al_2O_3$ *LHSV:* 2 v/v/hr. *Pressure:* 350 psig *H_2/HC:* 4.

appreciable isomerization, the rate of isomerization will be a determining factor in the extent of conversion of cyclohexane. At reaction temperatures above 800°F, the yields of methylcyclopentane decrease and the yield of benzene increases. At approximately 900°F, where complete conversion of cyclohexane occurs on all catalysts, yields of benzene are 80 per cent or higher, while the yields of methylcyclopentane are less than 10 per cent. The yields of methane plus ethane, and propane plus butane, and the isoheptane yields are plotted as a function of the *n*-heptane conversion in Figure 81. The data show, within experimental error, that the yields of isoheptanes and the lower molecular weight hydrocarbons are approximately the same for all the platinum catalysts at the same conversion of *n*-heptane. This effect of the surface area of silica-alumina supports for platinum catalysts was used to develop a commercial platinum reforming catalyst[71].

The relative acidities of silica-alumina cracking catalysts can be determined by titration with an aqueous solution of sodium or potassium hydroxide using a standard procedure. The results in Table 66 show that, as the surface area of the silica-alumina support decreases, the acidity of the base is also decreased. Thus the isomerization activity and selectivity of the catalyst used in obtaining the data shown in Figures 79 to 81 depend on the acidity of the silica-alumina support. In most researches directed toward developing a suitable naphtha reforming catalyst, the major problem is the adjustment of the acidity of the support and the concentration of the metal to obtain the proper balance among the main naphtha reforming reactions. As mentioned previously, in naphtha reforming these reactions include isomerization, dehydrogenation, dehydroisomerization and hydrocracking.

The acidity of silica-alumina catalysts can also be adjusted by (1) adding controlled amounts of alkali metal oxides such as Na_2O or K_2O[37], and (2) by adding controlled amounts of alumina to pure silica gel[32]. The effect of adding a small amount of alumina to silica gel on the isomerization activity of a platinum catalyst is shown in Table 67. The initial silica gel had a surface area of approximately 500 m^2/g. The data show that the pure silica gel in combination with platinum has practically no activity for the isomerization of *n*-heptane at a reaction temperature of 800°F. At this temperature the platinum-silica gel catalyst has a high dehydrogenation activity. The addition of 1.1 per cent alumina to the silica gel gives a platinum catalyst which shows a very high activity for the conversion of *n*-heptane to isoheptane. Although the conversion of cyclohexane increases, the yield of benzene is markedly decreased because the isomerization activity of the catalyst converts a large portion of the cyclohexane to methylcyclopentane. Increasing the alumina content to 2.4

per cent gives a more active n-heptane conversion catalyst, which still shows a high selectivity for the isomerization to isoheptanes. Thus, it becomes possible to control the acidity of the silica support by determining the amount of alumina necessary to give a balanced dual-function catalyst under conditions used in the reforming of naphthas.

TABLE 67. PLATINUM-SILICA CATALYST[32]

Effect of Alumina Additions

Charge 50% n-Heptane, 50% cyclohexane
Catalysts: ≈0.2% Pt on SiO_2 (≈500 m^2/g)
Pressure: 350 psig
LHSV: 2 v/v/hr
H_2/HC: 4 (mole)
Temperature: 800°F

Wt. % Al_2O_3 added	0	1.1	2.4	7.2
Conversion, Mole % charge				
n-Heptane	2	69	84	87
Cyclohexane	80	92	94	94
Yield, mole % charge				
Isoheptanes	3	46	44	35
Benzene	67	29	25	25
Methylcyclopentane	8	51	51	51

TABLE 68. PLATINUM-ALUMINA CATALYSTS[32]

Effect of Silica Additions

Charge 50% n-Heptane, 50% cyclohexane
Catalysis: 0.25% Pt on Al_2O_3
Pressure: 350 psig
LHSV: 2 v/v/hr
H_2/HC: 4 (mole)
Temperature: 800°F

Wt. % SiO_2 added	0.1	5.0	10.0	20.0
Conversion, Mole % charge				
n-Heptane	2.0	13.0	46.0	64.0
Cyclohexane	86.0	87.0	89.5	92.5
Mole % charge				
Isoheptanes	1.0	13.0	40.0	48.0
Benzene	82.0	73.0	30.0	28.0
Methylcyclopentane	4.0	13.0	46.0	55.0

A number of commercial platinum reforming catalysts use alumina as the acidic oxide support. The acidity of the alumina base may be controlled by adding small amounts of various materials[43]. The results in Table 68 show that by adding increasing amounts of silica to a platinum-alumina catalyst, the isomerization activity at the same reaction temperature is increased. Table 69 shows that we can also increase the isomerization activity of a platinum-alumina catalyst by adding increasing amounts of chlorine to the catalyst. Active dual-function catalysts can also be prepared by adding boria to the alumina. The results for platinum-alumina catalysts containing increasing amounts of boria are shown in Table 70.

TABLE 69. PLATINUM-ALUMINA CATALYSTS[32]

Effect of Chlorine Additions

Charge 50% *n*-Heptane — *Pressure:* 350 psig
50% Cyclohexane — *LHSV:* 2 v/v/hr
Catalysts: 0.25% Pt on Al_2O_3 — H_2/HC: 4 (mole)
Temperature: 800°F

Wt./chlorine added	0.06	0.49	1.2
Conversion, Mole % charge			
n-Heptane	8.0	46.0	79.0
Cyclohexane	85.0	93.0	96.0
Mole % charge			
Isoheptanes	6.0	33.0	46.5
Benzene	78.0	40.0	43.0
Methylcyclopentane	4.0	36.0	35.5

TABLE 70. PLATINUM-ALUMINA CATALYSTS[32]

Effect of Boria Additions

Charge 50% *n*-Heptane — *Pressure:* 350 psig
50% Cyclohexane — *LHSV:* 2 v/v/hr
Catalyst: 0.25% Pt on Al_2O_3 — H_2/HC: 4 (mole)
Temperature: 800°F

Wt. % boria added	0.0	3.4	11.3
Conversion, mole % charge			
n-Heptane	8.0	60.0	76.0
Cyclohexane	85.0	92.5	94.0
Mole % charge			
Isoheptane	6.0	49.0	50.0
Benzene	78.0	35.0	35.5
Methylcylopentane	4.0	42.0	42.0

REFORMING OF PETROLEUM NAPHTHAS

Thermal Processes

Thermal Reforming. In 1931, the petroleum industry successfully met its first octane number challenge by the development of thermal reforming. A number of processes appeared almost simutaneously, and the technique soon became an established refining tool. Octane improvement is realized primarily by cracking of paraffins and naphthenes to produce shorter paraffins and olefins, together with high octane cyclo-olefins. Figure 82 shows the changes in product distributions of thermal reformates from East Texas naphtha as the octane number is increased[72]. Coke formation is not a problem in thermal reforming and high conversions per pass can be obtained without its forming. The greatest increases in octane number are obtained by high-conversion, once-through operation; so recycle is rarely used.

Thermal reforming is carried out at severe conditions. Temperatures range from 1000 to 1075°F at pressures of 500 to 1000 psig. Time at reaction temperature (soaking time) can vary between 20 and 40 seconds.

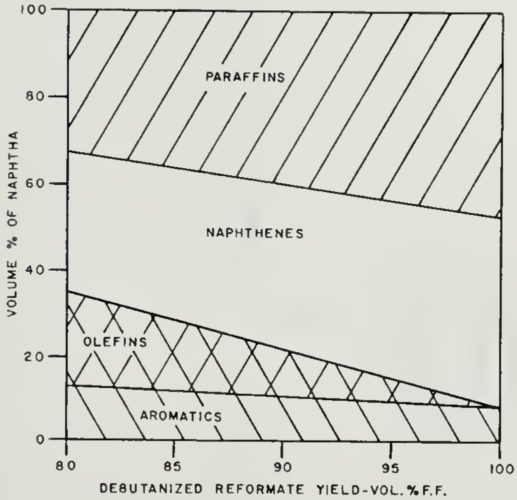


Figure 82. Composition of thermal reformates from East Texas naphtha.

No pretreating of feed stock is usually employed beyond the removal of the higher octane number front ends of the charge. Sulfur is not removed by the reaction as in catalytic reforming, and its presence in the gasoline has deleterious effects on lead susceptibility and storage properties.

General descriptions of thermal reforming processes have been given by Sachanen[143], Egloff and Nelson[61] and Goldtrap[74]. A flow diagram of a typical thermal reformer is shown in Figure 83. The plants in use today differ very little from the early designs.

Owing to the higher temperatures used and the relatively short soaking time, reaction chambers are usually not employed and the reaction takes place in tubes. The effluent from the tubes passes into a main fractionator where the tarry residuum formed from the condensation reactions is removed. The liquid product then passes into a separator where light gases are removed and then into a stabilizer where the product is depropanized or debutanized as desired. According to Sachanen[143] yields of reformed gasoline vary between 70 and 90 vol. per cent at octane numbers of 70 (motor method, clear). The average balance of reforming products under a variety of conditions has been given as 75 vol. per cent gasoline, 18 vol. per cent gas, and 7 vol. per cent residuum based on charge.

The product distribution from thermal reforming of an East Texas naphtha is given in Table 71. The yield of gasoline is very low, 72 vol. per cent, and its volatility is high, 13.4 lb RVP. A further liquid yield loss would result on removal of the light ends to produce 10 lb RVP gasoline.

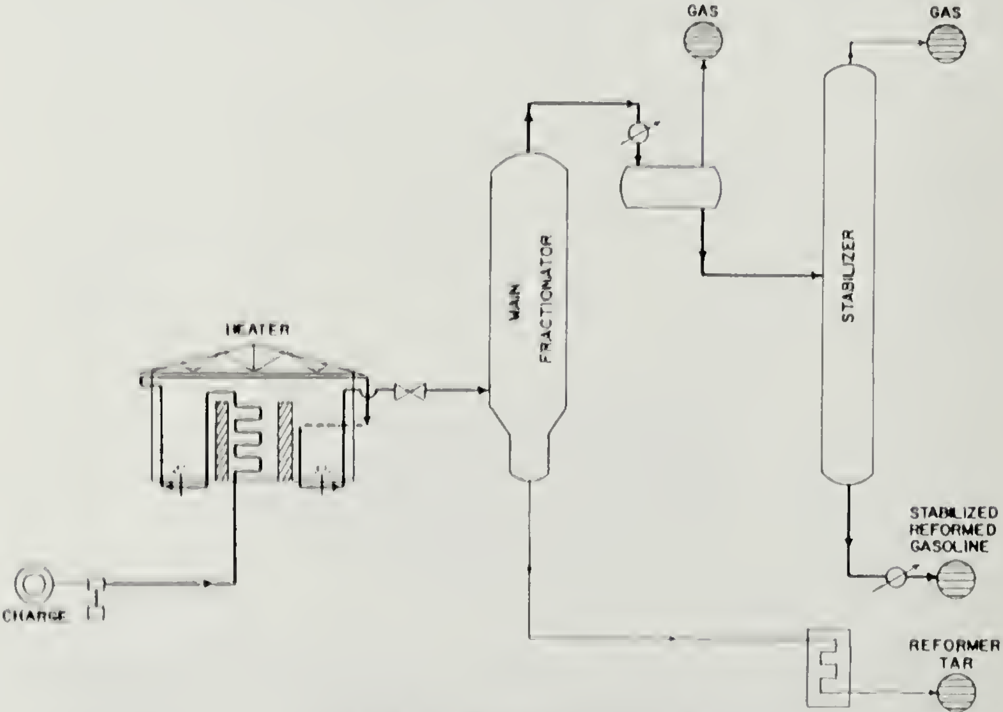


Figure 83. Thermal reforming.

Because of the reactions which take place in thermal reforming, the process is limited in octane potential. Above levels of 85 to 90 octane number (F-1, clear), almost no octane gain could be obtained from thermal reforming of straight-run naphthas and yield losses are prohibitive. While no significant octane increases can be obtained, several supplementary processes have been developed which produce higher gasoline yields. The most important of these is catalytic polymerization, which makes use of the C_3 and C_4 olefins produced in large quantities in thermal reforming. The over-all gasoline yield improvement by the addition of polymer gasoline and the decrease in vapor pressure resulting from the removal of butenes from the thermal reformate for use as feed are shown in Table 71. Experimental data showing the improved yield-octane relationships realized by the use of catalytic polymerization at various thermal reforming severities for two naphthas have been given by Mase and Turner[119].

TABLE 71. THERMAL REFORMING VS. FIXED-BED HYDROFORMING OF EAST TEXAS VIRGIN HEAVY NAPHTHA[1] (Ref. 121)

	Thermal Reforming	Fixed-Bed Hydroforming
Temperature, °F	1045	930
Pressure, psig	1000	200
Soaking volume factor	9.68	
Space velocity, v/hr/v	—	0.5
Recycle gas rate, SCF/bbl	—	2890
Hydrogen in recycle, vol. %	—	70
Yields, Wt. % Feed		
Gas		
$H_2 + CH_4$	5.5	4.0[2]
C_2H_4	0.6	—
C_2H_6	5.6	2.0
C_3H_6	3.2	—
C_3H_8	6.7	4.6
	21.6	10.6
Gasoline (400°F E.P.)	70.6	86.9
Tar	7.8	
Carbon	—	0.2
Gasoline (400°F E.P.)		
Vol. % feed	72.1	—
Gravity, °API	54.1	—
RVP, lb	13.4	—
Oct. No., CFRM, clear	80.1	—
	Basis Reforming Plus Catalytic Polymerization of Propylene and Butylene	
C_4 + Gasoline		
Vol. % feed	74.1	85.2
Gravity, °API	51.8	46.4
RVP, lb	7.9	6.5
Oct. No., CFRM, clear	80.3	81.3
CFRR, clear		91.4
CFRR + 3 ml Tel.		99.3

[1] Gravity, °API = 50.3; boiling range = 248 – 396°F; sulfur = 0.01 wt. %

[2] 1.3 wt. % H_2 ; 2.7 wt. % CH_4

After about 1935 most refiners operating thermal reformers used catalytic polymerization as a supplementary process. The most widely used process was developed by the Universal Oil Products Company and uses a phosphoric acid catalyst.

In 1952, investment costs for a 10,000 bbl/day thermal reformer with catalytic polymerization were estimated at about \$300/bbl of feed, and direct operating costs were about 30¢/bbl[145]. As of January 1957, there were 34 operable thermal reforming units in this country with combined capacities of about 220,000 bbl/day.

Polyforming and Gas Reversion. Efforts during the 1930's to improve gasoline yields from thermal reforming resulted in the development of pyrolytic processes in addition to the catalytic polymerization process discussed above. The most widely used of these were the Polyforming and Gas Reversion processes[30]. Both involved the use of thermal polymerization of the C_3 and C_4 olefins concurrent with thermal reforming of the feed naphtha. In Polyforming, C_3 and C_4 hydrocarbons from the thermal reforming reaction or from an outside source were added to fresh naphtha prior to the furnace coil. In Gas Reversion, the C_3 and C_4 hydrocarbons and naphtha were heated in two separate coils, and then combined in a third coil where the final conversion took place. Coil outlet temperatures were in the order of 1100°F and pressures ranged from 1000 to 2000 psig. The yields and product properties were about the same for both processes. While the yields were dependent on the amount of outside gases fed to the process, the process octane limitations were about the same as for the combination of thermal reforming and catalytic polymerization.

Catalytic Reforming

Fixed-Bed Hydroforming. In 1939 the first catalytic process for upgrading low octane number naphthas was introduced. This was the Fixed-Bed Hydroforming process developed jointly by Esso Research and Engineering Company, M. W. Kellogg Company, and Standard Oil Company of Indiana. The first unit went on stream in November, 1940, at the Pan American Refining Company, Texas City, Texas.

This process was a radical departure from the previous processes which employed heat and pressure to effect the desired reaction. Where thermal reforming produced few aromatics and relied mainly on the cracking of long-chain paraffins and of naphthenes and the formation of olefins for octane improvement, the principal octane improving reactions of this process were the catalytic dehydrogenation and dehydroisomerization of naphthenes to form aromatics. A molybdenum oxide-alumina catalyst was used and the process was carried out in the presence of recycle hydrogen derived from the process. Coke was laid down and deactivated the catalyst; this necessitated regeneration facilities. Together with the dehydrogenation reactions mentioned above, the other reactions taking place in this process are those now commonly called the reforming reactions: (a) dehydrocyclization of paraffins to form aromatics, (b) hydrocracking to form short-chain saturated hydrocarbons, (c) isomerization of low octane paraffins, and (d) desulfurization.

The commercial catalyst consisted of about 9 wt. per cent molybdenum oxide deposited on 2 to 4 mesh activated gel alumina granules. This catalyst was very resistant to poisoning and the life amounted to 9 to 12 months in the unit before replacement[121]. As with other catalytic reforming processes, straight-run naphthas were the usual feed stocks in Fixed-Bed Hydroforming operating to produce motor gasolines. The more naphthenic stocks gave the highest octane increases at normal operating conditions and hence the most favorable yield-octane relationships. The more paraffinic stocks produced more cracked materials, particularly where high octane products were being made. The catalyst, as used, was not easily poisoned by sulfur or nitrogen, and pretreatment of the feed for removal of these components was not practiced.

Typical operating conditions for Fixed-Bed Hydroformers were: temperatures—850 to 1000°F, pressures—150 to 300 psig, recycle gas (about 75 per cent hydrogen) 2000 to 4000 cu ft/bbl of feed, and space velocity equal to about 0.5 vol./hr/vol. of catalyst.

A simplified flow diagram of a Fixed-Bed Hydroforming unit is given in Figure 84. Detailed descriptions of the operating procedures and the equipment have appeared in the literature[9, 105, 121]. A conventional unit had four reactors filled with the granulated catalyst. Two reactors were always on stream and two undergoing regeneration. Fresh feed naphtha and the hydrogen-rich recycle gas were brought to reaction temperature in separate coils of a combination furnace and then passed into the first reactor. In this reactor the temperatures of the reactants drop 85 to 100°F owing to the endothermic dehydrogenation reactions taking place. The reaction temperatures were restored by passing the product stream through a reheat furnace before it entered the second reactor. The drop in the second vessel amounted to only 30 to 60°F. Gaseous products separating from the liquid were passed through an absorption tower to produce a C_4-free, hydrogen-rich (about 75 per cent) recycle gas which was then charged with fresh feed. The liquid ends were depropanized and passed through a re-run tower where the heavy polymer (3 to 4 vol. per cent) was removed and the gasoline then sent to the blending tanks.

After 4 to 8 hours on stream the catalyst had to be regenerated to remove coke. Partially reduced molybdenum oxides were reoxidized and the sulfur which had reacted with the molybdenum oxide was removed as SO_2; about 90 per cent of the sulfur in the feed was removed in this way[105]. Regeneration was accomplished by passing a heated flue gas-air mixture containing 2 to 3 vol. per cent oxygen over the catalyst. Catalyst temperatures were controlled to 1050 to 1100°F. Both upflow and downflow burning were used to insure complete regeneration. The switching of the reactors and gas streams through the cycle (on-stream, purging, regeneration, repurging) was controlled by motor valves energized by an electric cycle timer[9].

This first catalytic reforming process offered a considerable advantage over thermal reforming plus catalytic polymerization. Higher octane levels could be obtained and gasoline yields were much better. As with thermal reforming, light gas was the principal by-product although it was present in much lower amounts due to the mild temperatures and more selective (center) cracking. In Hydroforming, this light gas is saturated and cannot be polymerized.

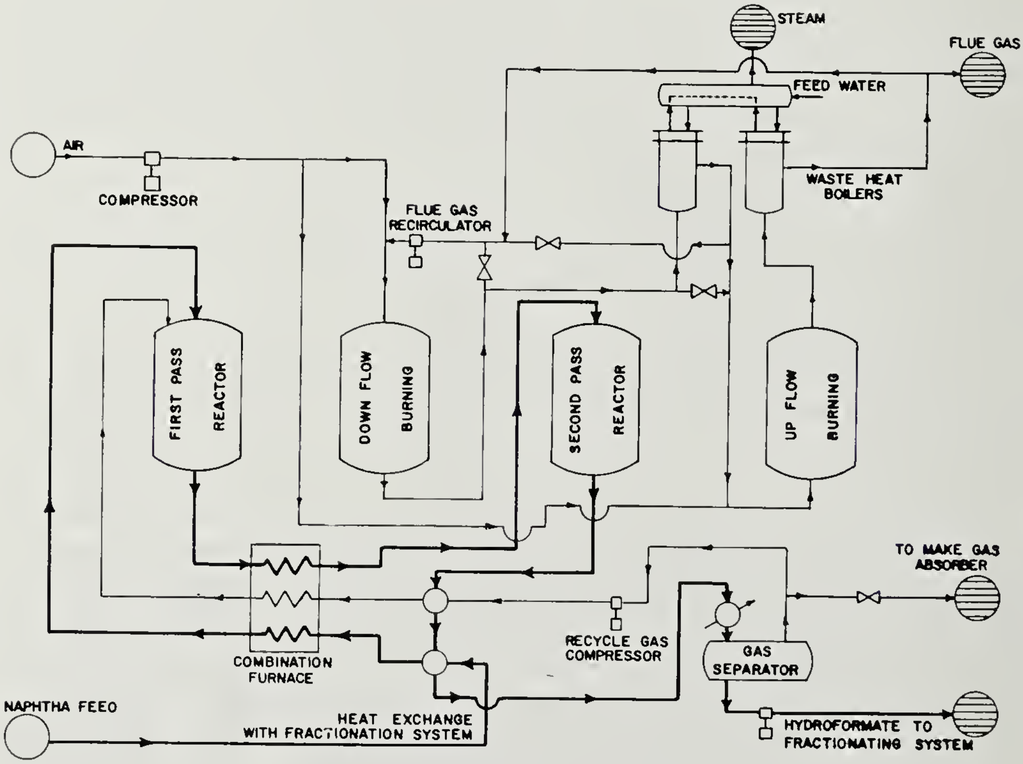


Figure 84. Fixed-Bed Hydroforming.

A comparison of the product distributions from (a) thermal reforming plus catalytic polymerization and (b) Hydroforming of an East Texas heavy naphtha is given in Table 71. These runs were carried out in pilot plants to about 80 octane number (CFRM, clear). The Hydroforming process shows a very definite yield advantage over the thermal process. At higher octane numbers, the spread between these would be much greater.

In addition, the gasoline quality from Hydroforming was much better than from the thermal process. Hydroformates were essentially sulfur-free (since most of the sulfur is removed by the catalyst) and contained only small amounts of olefins[105]. As a result they had much better TEL susceptibility. In addition, the Hydroformed gasolines had much better storage properties due to the absence of gum-forming diolefins.

While the yield from hydroforming was much better than from thermal reforming plus catalytic polymerization, the investment cost was about 50 to 60 per cent higher because of the more complex equipment. As a result, payouts were 3 to 7 years longer depending on the location[121]. However, where high octane gasolines or the production of aromatics were desired, this process was operable and thermal reforming was not.

A total of seven Fixed-Bed Hydroforming units with a designed capacity of about 70,000 bbl/day were built prior to and during World War II. These Hydroformers were a much needed solution to the production of wartime toluene and high octane aviation blending components, using a C_7 heart cut or a C_7–C_8 narrow boiling fraction. One plant alone produced more than 50 per cent of the toluene that went into TNT for the Armed Forces. Descriptions of the operation of the wartime hydroformers with emphasis on the production of toluene and other aromatics have been published[117, 121, 158]. Immediately following the war, most of the Fixed-Bed Hydroformers were shut down or were converted to the production of motor gasoline. In 1958 two units with a combined capacity of 19,000 bbl/day were listed as still operating. However, they were believed to be running for aromatics production.

A similar fixed-bed reforming process using a molybdena-alumina catalyst was also developed by Standard Oil of California for the production of toluene and high octane gasoline. Its principal difference was that each reactor contained a number of catalyst beds[33]. Feed entered at the center of the periphery of the reactor, traveled both up and down the annular space and entered the top of each bed from openings in this annular space, assuring a more even heat distribution through the entire bed. One unit of about 14,000 bbl/day capacity was built and was still operating for aromatics production in 1958.

Cycloversion. The Cycloversion process, developed by the Perco Division of the Phillips Petroleum Company, is capable of desulfurization, cracking of gas oils, or mild reforming of straight-run gasoline[60]. The process employed a naturally-occurring bauxite as the catalyst; no gas recycle to the reactors was used. Descriptions of units and of the processing schemes have been extensively reported[19, 77, 101]. The process was cyclic, one reactor being on the stream while the other was regenerated. When operated as a reformer or as a reformer-desulfurizer, operating pressures were 50 to 85 psig, temperatures about 1000°F, and space velocities of the order of 0.7 to 1.7 LHSV. In processing naphthas, the octane improvement was obtained principally from desulfurization and from the formation of light cracking products. These light products were rich in olefins and the propylenes and butylenes could be charged to catalytic polymerization units[19]. Only a small deposition of coke was reported to occur during a normal process cycle[60] and on-stream periods could vary between 12 and 72 hours.

An example of Cycloversion reforming is given below for upgrading an East Texas gasoline[60]. Operating conditions were: 1015°F; 50 psig; and space velocity = 1 LHSV.

	Raw Feed	*Reformate*
Boiling range, °F	170–475	117–427
Sulfur, wt. %	0.013	0.005
Gasoline		
Vol. % charge	—	83.5
RVP, lb	1.0	4.5
Octane No.		
F-1, clear	41.5	65.3
F-1 + 3 cc TEL	67.0	81.5

The first commercial Cycloversion unit went on stream in 1940. A total of 46 units with a capacity of about 155,000 bbl/day was constructed. However, Cycloversion cannot be considered as a reforming process suitable for present-day usage because of its very limited octane improvement potential. In 1957 no domestic units were reported being used as reformers[1]; most units still operating were being used for desulfurization of gasolines and kerosenes.

Modern Processes

In the four years following World War II, there was virtually no activity in catalytic reforming to produce motor gasoline beyond the use of several Fixed-Bed Hydroformers converted from the wartime production of aromatics and aviation blending stocks. No new catalytic reforming units were built, nor were any new processes announced. In this time, almost every refiner faced two problems (1) how to meet the challenge of competitors on motor fuel quality and (2) how to produce, in economic yields, fuels of sufficiently high octane numbers to meet the requirements of postwar automobiles.

In March, 1949, the Universal Oil Products Company announced the Platforming process. Its designated purpose was to upgrade straight-run or natural gasolines to high octane fuels with small volumetric losses and with attractive investment and operating costs. This was made possible through the use of a fixed-bed, continuous process employing a nonregenerative platinum catalyst. The first unit went on stream in October, 1949, at the Muskegon, Michigan, plant of the Old Dutch Refining Company (now Aurora Gasoline Company).

The successful operation of this process can truly be said to have started the reforming boom. Within the next two years four more processes were announced, and by 1955 another seven new processes or variations of old processes had been brought forth. Table 72 shows the chronology of the appearance of the various processes.

The growth of the catalytic reforming process can only be described as phenomenal. The last nine years have seen catalytic reforming capacity grow from seven fixed-bed reformers with a capacity of about 70,000 bbl/day to nearly 200 domestic units with a total capacity of about 1.53 million bbl/day, about 16 per cent of the total crude capacity of United States refineries. Units totaling 349,000 bbl of capacity are under construction or approved in this country. Canadian refineries have about 127,000 bbl/day of reforming capacity with another 38,000 bbl/day building or approved. Many more plants have been built abroad. Over 90 per cent of the total capacity employs processes using platinum catalysts. Table 73 lists the principal processes and their installed capacities.

TABLE 72. CATALYTIC REFORMING PROCESSES[52]

Process Name	Developed By	Date Process Announced
Fixed-Bed Hydroforming	Standard Oil Development Co.,[1] M. W. Kellogg Co. and Standard Oil Co. (Indiana)	1939
Platforming	Universal Oil Products Co.	Mar., 1949
Catforming	Atlantic Refining Co.	Feb., 1951
Houdriforming	Houdry Process Corp.	May, 1951
Thermofor Catalytic Reforming	Socony-Vacuum Oil Co., Inc.[2]	May, 1951
Fluid Hydroforming	Standard Oil Development Co.[1] and M. W. Kellogg Co.	May, 1951
Hyperforming	Union Oil Co., of Calif.	Feb., 1952
Sinclair-Baker RD-150	Baker & Co. with Sinclair Refining Co.	May, 1953
Orthoforming	M. W. Kellogg Co.	July, 1953
Ultraforming	Standard Oil Co. (Indiana)	Nov., 1953
Sovaforming	Socony-Vacuum Oil Co., Inc.[2]	Jan., 1954
Rexforming	Universal Oil Products Co.	Mar., 1955
Iso-plus	Houdry Process Corp.	Mar., 1955
Powerforming	Esso Research and Engineering Co.	Mar., 1956

[1] Now Esso Research and Engineering Co.

[2] Now Socony Mobil Oil Co., Inc.

The demand for increased reforming capacity is continuing, driven on by fierce intra-industry competition and by the increased fuel quality demands of present and future high-power, high-compression engines. By

Table 73. Catalytic Reforming Processes[1]
United States and Canada (Jan. 1, 1958)

Process	Number of Installations*	Capacity (BPSD)	Licensor	Catalyst manufacturer
Fixed-Bed Platinum				
Platforming	106	755,500	Universal Oil Products	Universal Oil Products
Rexforming	4	30,500	Universal Oil Products	Universal Oil Products
Catforming	16	92,000	Atlantic Refining Co.	Davison Chem. Co. (Div. of W. R. Grace & Co.)
Sinclair-Baker	8	94,500	Baker & Co.; M. W. Kellog	Baker & Co.
Houdriforming	11	78,000	Houdry Process Corp.	Houdry Process Corp.
Iso-Plus Houdriforming	1	45,000	Houdry Process Corp.	Houdry Process Corp.
Sovaforming	10	119,500	†Socony Mobil Oil Co., Inc.	Baker & Co.
Ultraforming	18	205,000	Std. Oil Co. (Indiana)	American Cyanamid Co.
Powerforming	10	77,000	Esso Research & Engineering Co.	Davison Chem. Co. (Div. of W. R. Grace & Co.)
Fixed-Bed Hydroforming	3	33,000	M. W. Kellog Co.	Harshaw Chem. Co. Oronite Chem. Co. National Aluminate Co.
Fluid-Bed Hydroforming	4	62,000	Esso Research & Engineering Co. M. W. Kellog Co.	National Aluminate Co.
Thermofor Catalytic Reforming	2	30,500	Socony Mobil Oil Co., Inc.	Socony Mobil Oil Co., Inc.
Undisclosed	6	34,500	—	—
Total	199	1,657,000		
Under construction or approved	28‡	387,500‡		

[1] *Oil & Gas J.* (March 24, 1958).

* Estimated—Some installations in larger refineries comprise more than one reforming unit of the same type.

† Unlicensed process.

‡ Estimated.

1960 catalytic reforming capacity will, according to some estimates, be 20 to 22 per cent of the total crude capacity, or more than 2 million bbl/day.

In this review a strict chronological sequence of processes will not be followed. Rather we have chosen to separate the contemporary processes into their three logical classes, treating each class separately. These are: (a) fixed-bed processes employing platinum catalysts (b) fluidized-bed processes employing molybdena-alumina catalysts and (c) moving-bed processes employing mixed oxide catalysts.

Fixed-Bed Processes Employing Platinum Catalysts—General Considerations. In the ten processes using platinum catalysts, there is considerable overlapping of the catalysts, process designs, and operating conditions. However, the processes fall into three general categories.

(A) Continuous, high-pressure reforming processes.
  (1) Non-regenerative reforming.
  (2) Processes equipped for intermittent regeneration.
(B) Cyclical regenerative, low-pressure reforming processes.
(C) Combination processes.

Catalysts. Catalysts containing platinum for use in fixed-bed reactors are dual-function catalysts—the platinum supplying the dehydrogenation function while the support provides the acid function necessary to catalyze the carbonium ion reactions involved in the hydrocracking and isomerization reactions. Platinum concentrations in commercial catalysts vary between 0.1 and 1 per cent with 0.3 to 0.7 per cent being the preferred range. The support materials, either alumina or silica-alumina, are usually pelleted, tableted or extruded to give granules of the order of ⅛ inch in diameter. Smaller particle sizes have been shown to increase catalyst activity and life[88, 104].

The acid function is provided by the mixed oxides in the case of silica-alumina. Issued patents indicate that halogens (either chloride or fluoride in quantities up to about 1 per cent) are added to aluminas for this purpose. These may be added either during preparation or by the direct addition of halogen compounds to the reformer feed stocks.

The balancing of the metal (platinum) and acid (support) functions to obtain most efficient reforming is very important as outlined earlier in this chapter. Any serious altering of the balance as a result of poisons in the feed or of operational upsets must be avoided for maximum operating efficiency.

Despite their general similarities, exact compositions and methods of manufacture of most commercial platinum catalysts are closely guarded company secrets. Many incorporate small variations designed to produce the optimum performance for their specific process. Catalysts costs are about $9.00 to $14.00 per pound for fresh catalysts including platinum.

At \$103.00 per troy ounce of platinum, the cost of the platinum alone in one pound of 0.5 per cent platinum catalyst is about \$7.50. Three to 5 pounds of fresh catalyst per barrel of designed daily charge are usually required for fresh fill plus about the same amount in reserve. This means that about 800,000 pounds of catalyst per 100,000 barrels of new capacity are required. Average catalyst life ranges from 50 to 100 barrels of charge per pound of catalyst. The spent catalyst is usually returned to the manufacturer where the platinum is recovered, deposited on fresh base, and then returned to the user at a cost of about \$4.00 per pound[110]. Table 73 lists the principal manufacturers of catalysts and the processes which they supply.

Feed Stocks. Straight-run naphthas provide the major feed stocks to platinum reforming processes although considerable interest has also been evidenced in the Southwest in reforming natural gasolines. Operations have also been reported using unsaturated stocks such as coker distillate[160], cracked gasolines[85, 136], and hydrocracked naphthas[96]. Successful operation with unsaturated charges, however, requires prehydrogenation or blending-in of straight-run stocks in order to maintain adequate hydrogen in the recycle stream.

While any straight-run naphtha can be considered as a potential charge stock, the reformability over platinum catalysts will be governed by the hydrocarbon composition, the initial and end boiling points of the feed, and the presence of potential catalyst poisons.

Effects of Hydrocarbon Composition. Only in reforming stocks having relatively high naphthene contents can the dehydrogenation and dehydroisomerization reactions alone produce very large octane improvements. In most stocks, conversion of paraffins to higher octane components is required to obtain the desired octane levels. At relatively high pressure operation (500 to 700 psig), much of the octane improvement is from hydrocracking with some contribution from isomerization in the intermediate severity ranges. As reforming severity increases with increased temperature of operation, aromatization of paraffins through dehydrocyclization of the straight-chain hydrocarbons becomes appreciable. While this reaction produces high octane components (i.e., n-heptane = 0 octane number; toluene = 124 blending octane number) it is accompanied by a large volumetric loss due to the density change. Further, dehydrocyclization is limited in once-through reforming processes, since, as the aromatics concentration increases, the rate of additional dehydrocyclization is drastically reduced[82, 130]. Hydrocracking, leading to yield losses through light gas formation, continues to occur, particularly at the temperatures necessary to produce significant dehydrocyclization at higher operating pressures. These limitations on octane number increases through dehydrocyclization at higher pressures form the basis for the use of the combination process (see p. 670) such as Rexforming and Iso-Plus reforming. For these reasons the more paraffinic stocks under the same conditions require higher operating temperatures and produce lower gasoline yields. Zielinski[164] has discussed the relationships between reformer feed composition and the properties of the products.

Low pressure operation favors the dehydrocyclization reaction while at the same time repressing hydrocracking. Improved yields of gasoline are obtained at the same octane level. Coke makes are increased, however, and low pressure operation is feasible only in units equipped for cyclical regeneration. A comparison of product yields from high and low pressure reforming for several naphthas of widely varying paraffin content is given in Table 78.

Effects of Boiling Range of Feeds. The distillation ranges of reformer feeds are set by considerations of the final product desired and by the necessity for obtaining optimum catalyst life and maximum efficiency from the reforming units. Most reformer feed stocks have an initial boiling point of at least 200°F. Materials boiling lower than this do not contribute greatly to increased octanes after reforming and take up reformer capacity which can be more efficiently used by the higher boiling components more susceptible to large octane improvements. Reformate end boiling points are normally about 15 to 25° higher than that of the charge owing to the formation of higher aromatics. As a result, end boiling points of reformer charges are limited to about 400°F or lower, in order to meet gasoline boiling point specifications. Further, higher boiling charges usually result in appreciably higher coke makes and more liquid losses to light gases. Frequently, units not equipped for regeneration limit the end point of the charge to 375°F.

Poisons (1) Sulfur. At the hydrogen-rich conditions employed in platinum reforming processes, sulfur-containing compounds in petroleum are readily converted to hydrogen sulfide[90, 112]. The hydrogen sulfide, unless removed, will build up in the recycle gas system to an amount equal to two to three times its equivalent concentration in the feed. This compound is a reversible poison for platinum and results in a decrease in the catalyst dehydrogenation and dehydrocyclization activities[98, 104] and in catalyst life[122]. Above 0.5 per cent sulfur in the feed, a significant drop in dehydrogenation activity is observed[98]. In commercial practice, sulfur is eliminated from catalytic reforming systems by desulfurizing the feed by one of the many available commercial hydrotreating processes[51], or by the removal of hydrogen sulfide from the recycle stream by a chemical agent (such as diethanolamine) whereby the sulfur in contact with the catalyst is limited to the sulfur concentration in the feed. Pilot plant studies made on a Platforming catalyst indicate that satisfactory catalyst life and yield relations may be obtained from naphthas containing up to 0.07 wt. per cent sulfur in the feed, provided recycle gas scrubbing facilities are included in the unit. Better yields and aging characteristics were obtained when the sulfur level was reduced to 0.01 wt. per cent prior to charging to the unit, and scrubbing was employed[122a].

(2) Nitrogen. Organic nitrogen compounds in the feed stocks are converted to ammonia under operating conditions. This ammonia, adsorbed on the acid sites, represses the hydrocracking, isomerization and the dehydrocyclization reactions[104]. More recent work[123] has indicated that the dehydrogenation function may also be affected. In commercial practice, nitrogen compounds are normally removed from the feed concurrently with sulfur by hydrotreating. Nitrogen levels of less than 2 ppm are usually sought.

(3) Water. The principal poisoning effect of water results from its action in poisoning the acid function of halogen-promoted catalysts by stripping out some of the halogen. The balance between the acid and metal functions of the catalyst is upset, and the selective hydrocracking and isomerization reactions are impaired. The required reforming severity for a given octane number becomes higher, and poorer yields and shorter catalyst life result. In commercial practice, the charge may be pretreated or dried to maintain water at the level of 5 to 10 ppm or lower. Alternately, the chloride level may be maintained through controlled additions of organic chlorides to the charge stock. The addition of 1 to 1.5 ppm of chloride to the feed for each 50 ppm water in the feed has been used.

(4) Chloride. Organic chlorides in reformer feeds, usually resulting from the use of chlorinated solvents in the oil fields, produce "poisoning" related, but opposite in effect, to water as discussed above. The organic chlorides, converted in the unit to hydrogen chloride, supply excess acid function to the catalyst and upset its balance. Excessive cracking to light gases, high coke formation, and losses in liquid yield result. The effects of excess chloride on yields, catalyst life, and equipment corrosion in a unit manufacturing aromatics has recently been reported[84].

(5) Metals. Arsenic, which forms an alloy with platinum, lead (frequently found in feeds thru TEL contamination from storage tanks), and copper are the most common metal poisons for platinum reforming catalysts. Concentrations of these metals in feed stocks must be kept at extremely low levels to insure satisfactory catalyst activity and life.

The poisons listed above can all be removed from feed stocks by catalytic treating of the stocks under hydrogen pressure using the commercially available hydrotreating processes. Many stocks formerly considered unsuitable for reforming have thus been made available to meet the needs of the tremendously expanded reformer capacity. At the present time, hydrotreating capacity is about 1.3 million bbl/day; by 1965 it is expected to be as much as 3.6 million bbl/day.

Process Variables. Temperature, pressure, space velocity, and hydrogen recycle rate are the principal operating variables in fixed-bed catalytic reforming. Table 74 summarizes their relationships with the principal reforming reactions.

Temperature increases are most effective in increasing the octane num- of the products through increasing both the aromatization and hydrocracking reactions. Too high temperatures cause serious losses in product yields through promoting excessive hydrocracking and, in very severe cases, thermal cracking in the preheaters, particularly at low space velocities[120]. Too low temperatures, on the other hand, give too little aromatization of naphthenes and paraffins to permit production of high octane gasolines. In practice, the effects of declining catalyst activity with time on stream are compensated for by gradual increases in the operating temperatures up to the limits described above. In general, reactor temperatures range from about 850 to 975°F.

The space velocity of the liquid can frequently be used to control reforming severity. Low space velocities increase hydrocracking (at constant temperature) but have little effect on the aromatization, since this reaction is quite rapid under normal operating conditions with platinum catalysts. Higher space velocities tend to inhibit hydrocracking. To make a high octane product, temperatures must be increased at the faster feed rates. This tends to cancel the beneficial effects on yield of the repressed hydrocracking. The relatively slow isomerization and cyclization reactions are likewise hindered by high space velocities. In general operation, space velocities range from 1 to 5 liquid hourly space velocity, with 2 to 3 being the preferred range.

The effects of the reactor pressure have been extensively discussed[68, 85, 89, 131]. High pressure operation tends to inhibit aromatization and to promote hydrocracking. A more volatile reformate is produced and hydrogen production is low. The upper limits of pressure for high severity reforming are limited by the effects of the required higher temperatures on the hydrocracking and thermal cracking of the feed stocks. Intermediate range (400 to 600 lb) reforming results in balanced operation, ideal for non-regenerative or intermittent regeneration processes. Good isomerization is obtained, hydrocracking is selective, and coke yields are low.

Low pressure operation, on the other hand, represses hydrocracking and significantly increases the amount of aromatics formed. Higher gasoline yields are obtained and the hydrogen production is maximized. However,

TABLE 74. BASIC RELATIONSHIPS IN CATALYTIC REFORMING

Reaction Involved	Reaction Rate	Heat Effect	Effect of High Pressure	Effect of High Temperatures	Effect of High Space Velocities	Effect on Product Vapor Pressure	Effect on Product Density	Effect on Volume Yield
Hydrocracking	Slowest	Quite exothermic	Aids	Aids	Hinders	Increase	Decrease	Decrease
Isomerization of paraffins to isoparaffins	Rapid	Mildly exothermic	None	Aids	Hinders	Increase	Slight decrease	Slight increase
Dehydrocyclization	Slow	Endothermic	Hinders	Aids	Hinders	Decrease	Increase	Decrease
Naphthene isomerization	Rapid	Mildly exothermic (76 Btu/lb naphthenes converted)	None	Aids	Hinders	Decrease	Slight increase	Slight decrease
Naphthene dehydrogenation	Very fast	Quite endothermic (1000 Btu/lb naphthenes converted)	Hinders	Aids	Hinders (Effect not too marked since reaction very rapid)	Decrease	Increase	Decrease

coking of the catalyst is increased owing to the lower hydrogen partial pressures, and the processes which employ low pressures (200 to 300 psig) are equipped with facilities for regular regeneration of the deactivated catalyst.

The hydrogen recycle rate, i.e., the partial pressure of hydrogen over the catalyst, is related in a gross sense to the total pressure of the operation. Recycle gas in these processes contains between 80 and 95 mole per cent hydrogen.

Hydrogen/fresh feed mole ratios of 3 to 10 are most frequently used, with 5 to 8 being the preferred range. High partial pressures of hydrogen increase hydrocracking and lessen coke laydown on the catalyst. There is an "equilibrium" established between hydrogen recycle and carbon deposited on the catalyst in the reactors. Coke is being continuously laid down on the catalyst and removed by the hydrogen in the recycle gas[85]. In practice, with higher boiling stocks, it is often desirable to increase the partial pressure of hydrogen. High pressures, however, tend to repress aromatization at constant conditions. Low partial pressures of hydrogen usually lead to too rapid deactivation of the catalyst through increased coke deposition and lower limits of pressure are governed by the desired amount of hydrocracking and the maximum allowable laydown of coke on the catalyst.

Reactor Systems and Heat Effects. A major consideration in all catalytic processes is to approach isothermal reaction temperatures. The major reaction in reforming, the dehydrogenation reaction, makes the over-all process endothermic. Large amounts of heat must therefore be supplied to the process in order to hold the reactants as close as possible to the optimum temperatures for conversion. A portion of the heat is supplied by preheating the naphtha feed stock and the hydrogen-rich recycle stream before they enter the reactor system. In the case of fixed-bed processes employing the very efficient platinum catalysts, this preheating cannot supply sufficient heat (without causing undesirable thermal reactions) to prevent a large drop in catalyst temperature. As a result, the extent of the dehydroisomerization, hydrocracking, and dehydrocyclization reactions is decreased.

Therefore, processes employing these catalysts approach isothermal operation by dividing the reaction system into separate reactors (normally three) and providing intermediate reheat furnaces before each reactor.

The following Table shows the type of heat relations existing in a typical three-reactor fixed-bed system, employing intermittent reheat, in reforming a commercial naphtha to 90 octane number (F-1, clear) over a platinum catalyst.

	Reactor 1	Reactor 2	Reactor 3
Inlet	935	935	935
Exit	815	880	925
Temperature drop, °F	120	55	10
Octane No. of charge (F-1, Clear) 38.5	65.5	79.5	90.0
Octane No. Increase	27	14	10.5
Principal Reactions	Dehydrogenation Dehydroisomerization	Dehydrogenation Dehydroisomerization Hydrocracking	Hydrocracking Dehydrocyclization

Process Descriptions

Continuous, High-Pressure Platinum Reforming Processes. The so-called continuous platinum reforming processes are characterized by employing three reactor systems and by the necessity of operating under conditions which minimize coke laydown. Feed stocks are normally in the boiling range 175 to 400°F; relatively high pressures are employed, approximately 500 psig; and high hydrogen to hydrocarbon mole ratios are used. In the Platforming process no regeneration facilities are provided. It is claimed that regeneration is possible but is not justified economically[59]. Facilities for in-situ regeneration under blocked out operation are provided in Catforming, Sinclair-Baker reforming, Houdriforming and Sovaforming, but regenerations are kept to a minimum since regeneration necessitates interrupting the production by shutting down the whole plant. Usually regeneration is carried out to remove deactivating coke resulting from long periods of severe operation or from process upsets.

Platforming. The Universal Oil Products Company's Platforming process was the pioneer reforming process to employ successfully a platinum catalyst for upgrading naphthas to high octane products. First announced in 1949, the process was an almost immediate success, coinciding as it did with the early stages of the present octane race. By the end of 1951 twenty-five units were operating, building, or under contract.

Patents issued to Haensel[86, 87] indicate that the Platforming catalyst comprises platinum (0.01 to 1 per cent), deposited on alumina with combined halogen (0.1 to 8 per cent fluoride and/or chloride) to provide the necessary acidity. In the first two runs in the first commercial unit using this catalyst. made at 92 to 94 octane number (F-1, leaded), catalyst lives of 45 and 42 bbl charge/lb catalyst were obtained. Catalyst costs were about 9¢/bbl of charge. Catalyst lives of over 200 bbl/lb of catalyst have been reported[2, 59]. Sulfur, arsenic, water, and heavy metals poison the catalyst and, if present in large amounts in the feed stock, must be removed by pretreating. An improved catalyst containing higher quantities of platinum which is specifically designed for use in producing gasolines of 98 octane number (F-1, leaded) and higher is now on the market[155].

The usual feed stocks for Platformers are naphthas with end points of about 375°F. These are normally obtained from a prefractionator. The design and operation of the Platforming units have been extensively described[27, 52, 59, 118]. A simplified flow diagram of the process is given in Figure 85. The unit may be divided into three sections: (1) the reactor-heater section where charge and recycle gas are heated and the reactions take place; (2) the separation and compression section where the reactor effluent is separated into gas and liquid streams, and the gas is compressed; and (3) the stabilization section where the separator liquid effluent is stabilized to the desired vapor pressure. Depending on the charge naphtha, a fourth section for hydrogen pretreatment of the feed may be required to remove undesirable constituents[59, 73]. In the case of some high-sulfur stocks, a scrubbing system may be employed to remove hydrogen sulfide from the recycle gas.

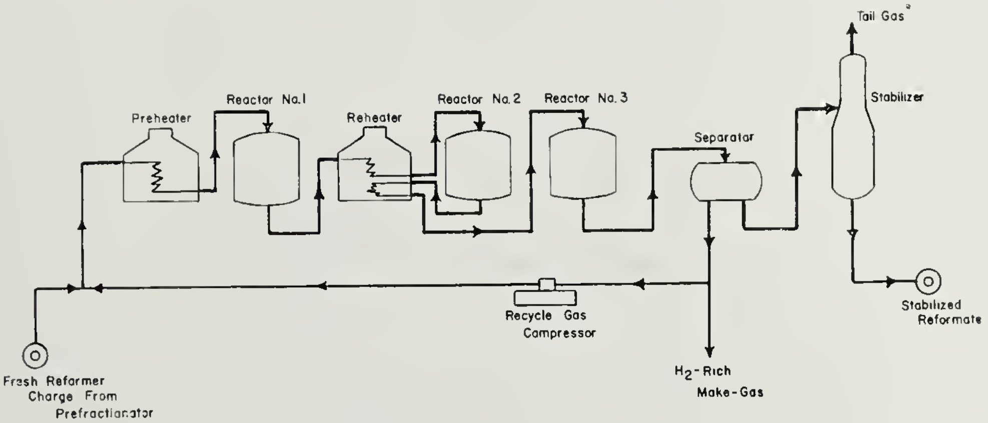


Figure 85. Non-regenerative platinum reforming.

Typical operating pressures are in the order of 500 to 700 psig; temperatures are 850 to 950°F. Space velocities and hydrogen/hydrocarbon mole ratios are said to be determined for each installation to obtain optimum results[59] but probably range between 1.5 and 3, and 4 and 8, respectively. In operation, incoming feed is mixed with recycle gas, preheated by heat exchange with the reactor effluent, heated to reaction temperature in the first heater and then passed into the first reactor. The predominant reaction here is dehydrogenation. This is endothermic and the heat is replaced by an interheater. The feed is then further reacted in the second reactor. The effluent is reheated to optimum reaction temperature (usually in the same range as for the first two stages) and passed into the third reactor. In some units, this reactor is made larger than the first two in order that the greater space and catalyst content can insure the longer contact time necessary for the slower hydrocracking and dehydrocyclization reactions. Products from the last reactor are cooled by heat exchange with fresh feed and passed into a separator. The separator gas required for recycle is compressed and returned to the feed system. The remainder may be used as raw material for a hydrogen pretreater or for other refinery uses. In the stabilizer, liquid from the separator is depropanized, and may be debutanized or depentanized, depending on the volatility requirements of the particular refinery. The overhead light hydrocarbons go either to refinery fuel or to a gas recovery system for feed for other processes. The stabilized reformate flows to finished gasoline storage for final blending. The product (as well as the products from other platinum reforming processes) is composed primarily of aromatics and isoparaffins; only small amounts of straight-chain paraffins and naphthenes are present. The product is essentially olefin-free (in contrast to catalytically cracked or thermally processed gasolines) and is very low in sulfur. The combination of the low olefin and low sulfur concentrations makes for very efficient utilization of and

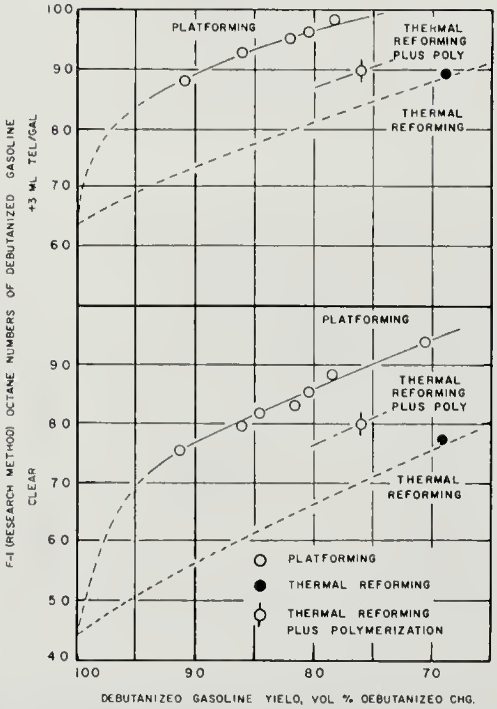


Figure 86. Comparison of F-1 (research method) octane numbers of debutanized gasolines from platforming and thermal reforming of Pennsylvania straight-run naphtha.

good susceptibility to tetraethyl lead. The low olefin content has an additional advantage in providing good storage stability, compared to cracked gasolines[27, 29].

The advantages of Platforming over thermal reforming have been discussed by Haensel and Sterba[90]. Figure 86 shows the yield-octane advantage of platinum reforming over thermal reforming or thermal reforming plus catalytic polymerization in processing a full boiling range Pennsylvania straight-run gasoline. In Figure 87 the hydrocarbon-type contents of the Pennsylvania naphtha feed stock, a 93 octane number (F-1 + 3 ml. TEL) Platformate, and an 89 octane number (F-1 + 3 ml. TEL) thermal reformate from this feed are shown. The significant points are the higher aromaticity and the absence of significant quantities of olefins in the Platformate, and the presence of the major amount of the paraffins in the lower boiling fractions, indicating hydrocracking and isomerization.

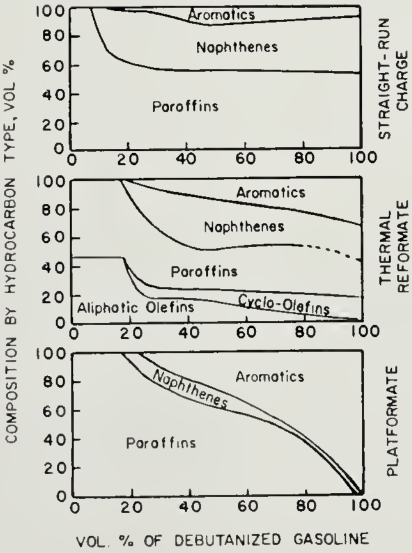


Figure 87. Hydrocarbon-type content of debutanized Pennsylvania straight-run gasoline, platformate and thermal reformate.

Typical Platforming yields from reforming a high and a low paraffin content feed stock are given in Table 75 at both high and low severities. These pilot plant data illustrate the advantages in higher yields of liquid product and lower production of butanes obtained in reforming lower paraffin content feeds. Haensel and Donaldson[89] have further discussed the effects of paraffin contents of feed stocks in Platforming, pointing out that, with high paraffin stocks at high severity, there is a yield loss inherent from the dehydrocyclization of paraffins plus the greater extent of hydrocracking accompanying dehydrocyclization.

Data from the commercial Platforming of Kuwait naphtha in a unit of the British Petroleum Company is given in Table 76. This run was reported to have lasted over 200 days (about 41 bbl charge/lb catalyst) before lack of charge stock forced the unit to shut down. It was claimed that there was no evidence of catalyst fouling or excessive hydrocracking[3].

Table 75. Laboratory Platforming of Naphthas[52]

Feed Stock	*Venezuela*		*Middle East*	
Gravity, °API	48.6		54.5	
ASTM distillation, °F				
IBP	272		272	
10%	284		282	
50	302		300	
90	338		342	
EP	378		378	
F-1 clear octane	52.2		32.4	
F-1 + 3 cc TEL	73.6		55.2	
Sulfur wt. %	0.022		0.03	
Naphthenes, vol. %	40		20	
Aromatics, vol. %	21		14	
Paraffins, vol. %	39		66	
Reforming severity	*Low*	*High*	*Low*	*High*
Reformate yields, charge basis				
Debut. reformate, vol. %	91.5	85.2	84.0	79.0
Total butanes, vol. %	3.0	6.4	8.4	11.1
Debutanized Reformate				
Gravity, °API @ 60°F	44.0	42.5	51.0	49.0
ASTM distillation, °F				
IBP	175	130	130	120
10%	260	225	185	165
50	300	300	280	275
90	345	345	340	340
EP	410	415	410	415
F-1 clear octane	85.0	95.0	85.0	92.0
F-1 + 3 cc TEL	94.5	99.5	96.0	99.5
RVP, psi	1.4	2.3	3.2	4.0
10 lb RVP reformate				
F-1 clear octane	86.0	95.0	86.0	92.2
F-1 + 3 cc TEL	95.5	99.8	96.5	99.7
Vol. % of charge	104.7	96.4	93.1	86.9
Outside n-C_4 required, LV % charge	11.6	6.5	2.1	−1.6

Platforming has been used in the Southwest to upgrade natural gasoline to octane levels which permit its use as a high octane blending stock[4, 49]. Data on Platforming cracked naphtha and blends of cracked naphtha with straight run gasoline[85, 136], a coker distillate—straight-run blend[160] and a hydrogenated Fischer-Tropsch naphtha[56] have also been published.

At the present time, there are approximately 110 Platformers in operation, under construction, or in the planning stages in the United States and Canada. Total operating capacity is about 755,000 bbl/day. Platformer construction costs are about $150 to $350/bbl of charge depending on the unit size. Operating costs, including catalyst and royalty, are in the range of 20¢ to 35¢/bbl of fresh feed stock.

Table 76. Commercial Platforming of Kuwait Naphtha[3]

	Charge*	Product†
Gravity, °API	58.2	51.3
ASTM distillation, °F		
IBP	215	100
10%	232	138
30%	248	188
50%	264	238
70%	291	283
90%	318	327
End point	349	390
Reid vapor pressure, psi		6.4
Sulfur, wt. %	0.04	Nil
Hydrocarbon type analysis, LV %		
Paraffins	64	—
Olefins	Trace	—
Naphthenes	23	—
Aromatics	13	49
Average yield of 95 octane no. (F-1, clear) reformate, 6-lb RVP, LV % on charge	—	75.0
Research octane ratings:		
Clear	—	95.3
With 3 ml TEL per gal.	—	102

* Depentanized

† Stabilized

Catforming. The Catforming process for upgrading low octane naphthas was developed by the Atlantic Refining Company and first announced to the petroleum industry in 1951. The major differences between this process and Platforming are in the catalyst composition and in the facilities for regeneration on a blocked-out basis provided in Catforming. The Catforming catalyst, as described by Ciapetta[36], consists of platinum deposited on a silica-alumina carrier of controlled activity which provides the acid function. The development of the catalyst was made possible by modifying the surface area of the silica-alumina base in order to provide the proper balance among the principal reforming reactions[71].

Since the Catforming catalyst contains no halogen it has a good tolerance to water in the feed stock[72]. It is not necessary to dry most charges or the recycle gas following the amine unit used for hydrogen sulfide removal. The low yields of methane and ethane resulting from the use of silica-alumina as a support produce a recycle stream of very high hydrogen purity. Catalyst lives in excess of 70 bbl/lb of catalyst have been reported from several units[20] and one unit was reported to be continuing operation after a life history of 136 bbl/lb of catalyst[76]. The catalyst is manufactured by the Davison Chemical Company (Div. of W. R. Grace & Co.) under license from the Atlantic Refining Company. Catalyst replacement cost, including platinum credit, is approximately $4.00 per pound[52].

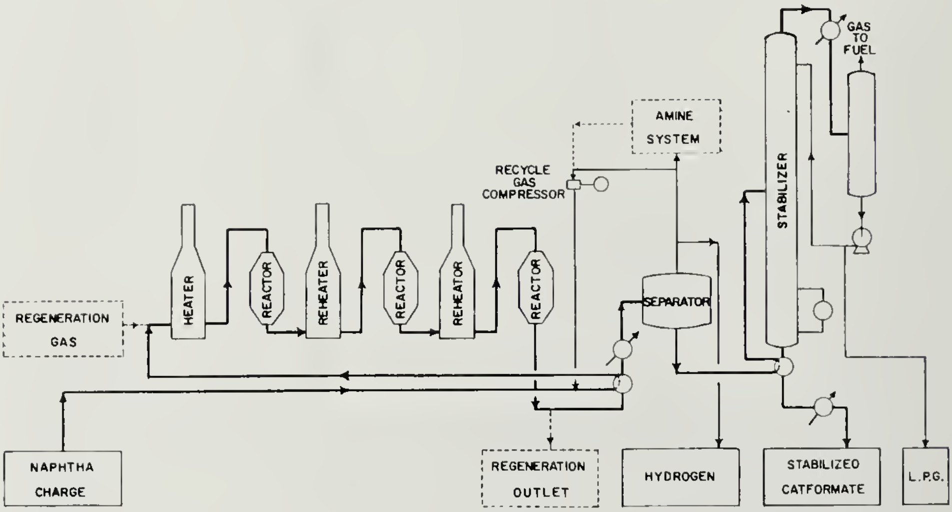


Figure 88. Platinum reforming with facilities for blocked-out regeneration.

Naphthas with end points up to 400°F serve as the charge stocks for Catforming. Catalyst poisons such as tetraethyl lead, copper, and sodium hydroxide must be excluded from the feed. While no pretreatment is said to be necessary to remove sulfur, nitrogen, and arsenic as they exist in normal feed stocks[20], there are upper tolerance limits for these components beyond which their removal is necessary. For example, sulfur contents above about 0.05 wt. per cent cause a temporary depression of catalyst activity large enough to justify sulfur removal. Usually this is done by desulfurization of the recycle gas using conventional amine scrubbers.

The operation and design of Catforming units, including the first commercial unit of the McBride Refining Company in La Blanca, Texas, have been extensively described[20, 52, 70, 125]. A flow diagram of the process including the regeneration facilities is given in Figure 88.

Naphtha feed from the crude units is preheated with hydrogen-rich recycle gas in a preheater, passed into the first reactor, and then through the two interheaters and the other two reactors. The effluent from the third reactor is cooled and passed into the gas separator, still under pressure. The separated hydrogen-rich recycle stream is passed, if necessary, through an amine scrubber to remove hydrogen sulfide and is then returned to the reactor system. Excess hydrogen-rich gas is used as a refinery fuel, in pretreating, or, in the case of Atlantic's Philadelphia refinery, is used together with atmospheric nitrogen to make ammonia. The liquid stream then passes through a stabilizer. The stabilized material, in common with other platinum reformates, is essentially free of sulfur. The reformate from a unit charging a feed containing 0.14 per cent sulfur contained less than 0.001 per cent sulfur[70]. Typical operating conditions are given in the following table[72].

Naphtha feed: Boiling range 175 to 375°F
Space velocity, lb naphtha/hr/lb of catalyst: 3
Reactor pressure: 500 psig.
Recycle, moles of recycle gas/mole of naphtha charge: 10
Recycle gas, mole % hydrogen: 95%

Reactor inlet temperatures may vary from 850 to 975°F depending on the severity of reforming and the feed stock.

As the catalyst slowly deactivates due to the build-up of coke during use, the activity loss is compensated for by increasing the inlet temperatures up to about 950 to 975°F. At this point yield losses due to catalytic hydrocracking and thermal reactions in the preheaters force the regeneration of the catalyst. For this reason, and to counteract major upsets, the Catforming units are equipped with facilities for blocked-out regeneration (Figure 88). This procedure requires no special equipment. The carbon is burned from the catalyst by admitting a dilute air-steam mixture to the first reactor and venting the waste gases following the last reactor[72]. Catalysts have reportedly been regenerated three to four times with somewhat shorter catalyst life between successive regenerations[52].

Typical product yields in reforming naphthas of varying paraffin contents and reformabilities are given in Table 77. These data also illustrate the very low ethane and methane yields, but relatively high butane yields, resulting from the use of silica-alumina as the catalyst support. The use of Catforming in conjunction with light hydrocarbon isomerization to upgrade natural gasolines has also been discussed[163].

Catformer investment costs are reported to be in the range $150 to $300/bbl of charge, depending on the unit size and the specific requirements. At the present time there are about 16 Catformers (Table 73) in service in the United States and Canada with a total design capacity of about 92,000 bbl/day.

Sinclair-Baker Reforming. The Sinclair-Baker reforming process was announced in May, 1953, with the first commercial unit, a 3000 bbl/day unit built by M. W. Kellogg Co., going on stream at the Heath, Ohio, refinery of the Pure Oil Company in September, 1954. The process was designed to provide a wide range in operating conditions to permit re-

TABLE 77. CATFORMING OF DIFFERENT NAPHTHA TYPES[52]

Feed Stock Source	*East Texas*		*Kuwait*	
Gravity, °API	51.4		54.3	
ASTM, distillation, °F				
IBP	248		228	
10%	270		253	
50%	299		285	
90%	250		338	
EP	393		370	
F-1 clear octane	45.0		38.0	
F-1 + 3 cc TEL	68.5		63.2	
Sulfur, wt. %	0.001		0.08	
Bromine No.	0		0.6	
Paraffins, vol. %	44.6		55.2	
Naphthenes, vol. %	42.6		28.4	
Aromatics, vol. %	12.8		16.4	
Reforming Severity	*Low*	*High*	*Low*	*High*
Reformate				
Yields, charge basis				
C_5 + reformate, vol. %	91.0	83.0	91.0	83.0
Butanes, vol. %	4.6	10.0	5.4	11.9
Propane, wt. %	1.9	3.6	2.4	4.6
Ethane, wt. %	0.22	0.49	0.29	0.68
Methane, wt. %	0.10	0.24	0.14	0.34
Hydrogen, wt. %	1.2	1.3	0.9	0.9
C_5 + Reformate				
Gravity, °API	46.9	43.0	51.8	50.6
ASTM distillation, °F				
IBP	145	133	105	98
10%	209	176	155	143
50%	288	284	262	255
90%	350	357	335	340
EP	395	408	371	378
Sulfur, wt. %	0.001	0.001	0.001	0.001
F-1, clear octane no.	80.2	94.4	72.4	87.1
F-1 + 3 cc TEL	92.6	99.8	88.7	97.0
RVP, psi	2.0	3.5	2.2	3.9
10 lb RVP Reformate				
F-1, clear octane no.	82.3	94.7	75.2	87.9
F-1 + 3 cc TEL	93.8	100.1	90.3	97.4
Yield, vol. % on charge	104.3	92.6	104.1	92.0

finers to obtain optimum economic operation with a wide range of feed stocks.

The process was built around the use of a new reforming catalyst, RD-150, which was claimed to have two major advantages: (1) a high ratio of paraffin cyclization activity to hydrocracking activity, and (2) the ability to be easily and repeatedly regenerated using dilute air[151]. This catalyst, developed jointly by the Sinclair Research Laboratories, Inc., and Baker and Co., contains about 0.6 wt. per cent platinum deposited on a special alumina base[18]. The reactions of the catalyst with various pure hydrocarbons and poisoning studies made on the catalyst have been discussed by Hettinger *et al.*[104] The life of the catalyst has been estimated at 40 to 200 bbl/lb depending on the charge stock and the severity of the operating conditions[53, 151].

While the regenerable feature of the catalyst widens the range of permissible charge stocks and operating levels, it has frequently proved more economical to remove excessive amounts of common poisons such as water, nitrogen, sulfur or arsenic by pretreating the charge or by scrubbing and drying the recycle gas stream. When cracked gasolines are used as reformer stocks, the olefins should be saturated by hydrotreating in order to maintain a favorable hydrogen balance in the units and to lessen coke formation[52].

According to Teter *et al.*[151], processing over this catalyst with ordinary stocks up to levels of 90 octane number (F-1, clear) can be carried out under continuous conditions with only intermittent regeneration. Above this octane level, particularly with paraffinic stocks, it may be economically desirable to use low pressure, regenerative type operation, despite the increased cost of additional equipment. Comparison of yields from high and low pressure operation with this catalyst are given in Table 78. The units built to date, however, have been equipped only with facilities for intermittent regeneration, although M. W. Kellogg Co. offers a modification of the process using a swing reactor for low pressure operation with continuous regeneration (see page 659).

Pilot-plant operation and data from the Sinclair-Baker Process have been discussed by Decker[53] and by Teter *et al.*[151]. A description of the operation of a 16,000 bbl/day commercial unit has been given by Decker and Stewart[54]. A flow diagram of the process including the regeneration facilities is given in Figure 88. Typical operating conditions are given in Table 79.

Operation is essentially the same as for the other platinum processes. Straight-run naphthas from a prefractionator-absorber are combined with hydrogen-rich recycle gases and, after being heated, flow in series through three reactors and two interheaters. The effluent from the third reactor is exchanged against incoming reactor feed, cooled to atmospheric temperature, and passed into the flash drum where the product is split into two streams.

Table 78. Pilot-Plant Reforming Data; Baker-Sinclair rd-150 Catalyst[151]

Feed Stock	*Mid-Continent*		*Kuwait*	
Gravity, °API	54.1		54.0	
ASTM Distillation, °F				
IBP	236		240	
10%	257		283	
50%	291		310	
90%	341		337	
EP	373		355	
Sulfur, wt. %	0.021		0.087	
F-1 clear octane	36.5		29.6	
F-1 + 3 cc TEL	61.0		52.5	
Naphthenes	43.2		19.4	
Aromatics	7.7		14.7	
Paraffins	48.8		65.1	
Operation	*500 psig Continuous*	*200 psig Regenerative*	*500 psig Continuous*	*200 psig Regenerative*
Products, Charge Basis				
C_5^+, vol. %	79.0	83.3	75.6	81.2
Butanes, vol. %	6.4	4.2	8.5	4.9
Propane, wt. %	6.5	3.6	7.2	3.4
Ethane, wt. %	3.0	2.1	4.5	2.4
Methane, wt. %	1.5	0.9	2.2	1.1
Hydrogen, SCF/bbl	740	1150	470	875
C_5^+ Reformate				
Gravity, °API	46.7	42.3	45.5	—
ASTM Distillation, °F				
IBP	138	126	—	—
10%	210	207	—	—
50%	281	288	—	—
90%	352	363	—	—
EP	420	457	—	—
Sulfur, wt. %	0.004	0.005	0.006	0.004
F-1 clear octane	95.0	95.0	95.0	95.0
F-1 + 3 cc TEL	99.6	99.7	99.7	99.2
10 lb RVP Gasoline				
F-1 clear octane	94.6	94.6	94.3	94.7
F-1 + 3 cc TEL	99.8	99.9	99.9	99.4
Vol. % Charge	89.4	94.8	84.4	92.8
Outside C_4's, vol. %	4.0	7.9	0.3	6.7

The released hydrogen-rich gas is compressed and recycled to the inlet naphtha system with the net gas make being released through the absorber to a fuel system or to hydrogen recovery. Liquid product from the flash

TABLE 79. COMMERCIAL OPERATION; BAKER-SINCLAIR RD-150 CATALYST[54]

A. *Comparison of Average Operating Conditions for the First and Second Processing Cycles*

	First Cycle*	Second Cycle
Operating conditions		
Feed rate, bbl/day	11,400	11,290
Space velocity, w.h.s.v.	1.42	1.56
Pressure, psig	500	500
Recycle ratio, moles gas/mole HC	8.1	8.0
Recycle ratio, moles H_2/mole HC	6.6	6.6
Reformate octane, research clear	85.5	88.2
Reactor temperature, °F		
No. 1 inlet	924	928
No. 2 inlet	914	914
No. 3 inlet	888	898
No. 1 outlet	824	829
No. 2 outlet	877	879
No. 3 outlet	890	902
Feed stock inspections:		
Gravity, °API	56.5	56.8
IBP, °F	214	210
10% °F	230	224
50% °F	249	247
90% °F	289	293
EP, °F	346	350
PONA analysis:		
P, vol. %	48.9	46.4
N, vol. %	37.3	39.9
A, vol. %	13.8	13.7
Octanes:		
Research method, clear	51.3	52.6
Research method + 3 cc	72.0	75.2

* 4 months; about 15 bbl charge/lb catalyst

B. *Comparison of Typical Yield Data for the First and Second Operating Cycles*

	First Cycle	Second Cycle
Yields*		
H_2, wt. %	1.0	0.9
C_1, wt. %	1.3	1.2
C_2, wt. %	1.9	1.8
C_3, wt. %	2.4	2.2
iC_4, vol. %	1.6	1.5
nC_4, vol. %	3.3	3.2
C_4-e.p. gasoline, vol. %	91.5	92.0
10-lb RVP gasoline, vol. %	101.0	101.7
Octanes, 10-lb RVP gasoline:		
Motor method, clear	80.2	80.2
Motor method + 3 cc TEL	89.7	89.7
Research method, clear	86.1	86.1
Research method + 3 cc TEL	96.6	96.6

* Yields adjusted to the same base octane level for comparison purposes.

drum flows to a stabilizer where it is stabilized to obtain the desired Reid vapor pressure.

To maintain octane level during the oil processing cycle, the reactor temperatures are raised to compensate for the gradual reduction in activity owing to coke on the catalyst. In order to restore maximum catalyst activity and productivity, facilities are provided for blocked-out regeration as shown in Figure 88. Decker and Stewart[54] have published an excellent description of the regeneration of a commercial reformer catalyst containing an average of 6 wt. per cent coke. Naphtha feed to the unit is stopped and the unit is cooled to 500°F catalyst temperature. The unit is then depressured and purged with inert gas from a small generator. After purging, the unit is pressured to 30 psig with inert gas. Circulation of this gas is started using the recycle compressor, and the heaters are fired to maintain a 500°F catalyst temperature. Regeneration is then started by admitting controlled amounts of air from an air compressor to the catalyst beds. The regeneration is then carried out in three steps as follows (for removing 6 wt. per cent coke in the catalyst).

(1) A low temperature burn (preburn at 500°F); 0.5 to 0.7 mole per cent oxygen.

(2) The main burn at 750°F; 0.5 to 0.7 mole per cent oxygen for 11 hr.

(3) Final burn at 920 to 940°F; final oxygen concentration 15 to 18 per cent (by addition of air from the compressor) for 14 hr.

The final carbon level on the catalyst was less than 0.2 wt. per cent. After the regeneration the units are cooled, purged and repressured with hydrogen or with stored recycle gas. The heaters are fired and at the set temperature the naphtha can be readmitted. Between 7 and 20 regenerations have been reported to be feasible[52].

Yields and product distributions from reforming a naphthenic and a paraffinic stock over the RD-150 catalyst are given in Table 78[151]. Data are shown at high pressure (500 psig, normal for continuous reforming with intermittent regeneration) and at low pressure (200 psig, normally associated with regenerative reforming). These results point out the advantages in higher gasoline and hydrogen yields and in lower C_1–C_3 yields characteristic of low pressure operation. In Table 79, yields and operating data for two cycles (separated by a regeneration) from a commercial unit operating at 500 psig are shown. These results are from the paper by Decker and Stewart[54] and are remarkable for their completeness. The data indicate that the regeneration apparently had no serious effects on the catalyst either as to activity (Table 79A) or selectivity (Table 79B).

Catalyst and operating costs for this process have been estimated at 24¢ to 31¢/bbl of reformate, exclusive of royalty[151]. At the present time, units, operating or under construction, using the RD-150 catalyst have a total capacity of about 300,000 bbl/day. Licensing arrangements for use of the catalyst can be made through Baker and Co. or the M. W. Kellogg Company.

Sinclair-Baker-Kellogg Process. This process, designed and licensed by M. W. Kellogg Co., is an extension of the Sinclair-Baker reforming process just described. Its features include a hydrotreater, utilizing make hydrogen from reforming, and a common furnace providing reheat for the last two reactors. Two reactor systems are available; the three-reactor system with conventional facilities for blocked-out operation may be employed[5] or alternately a second system, employing four reactors, may be used. The third and fourth reactors in this system are run in parallel—either can be shut down or regenerated without materially disturbing operations[52]. This system is designed to compensate for the higher coke lay-down in the last reactor where the average catalyst temperatures are higher and where the principal coke-making reactions take place. The first two reactors, if regeneration is required, must be regenerated in normal blocked-out operation.

Houdriforming. The Houdriforming process, a development of the Houdry Process Corp., was first announced in May, 1951. The first Houdriformer, a 12,000 bbl/day unit to produce aromatics from special straight-run gasoline fractions, went on stream at the Sun Oil Company's Marcus Hook, Pennsylvania, refinery in November, 1953[24].

The catalyst consists of platinum on an alumina support and is designated as Houdry Type 3D. This material is manufactured by Houdry at its plant in Paulsboro, New Jersey. Metals such as lead, copper, nickel, and arsenic are said to impair the catalyst activity permanently[26]. Protection against excessive amounts of water, oxygen, oxygenated compounds, nitrogen, and sulfur must be provided. The catalyst, however, is stated to be an excellent desulfurization catalyst and, in pure hydrocarbon studies, no effects of deactivation of the dehydrogenation function were observed in once-through operation up to about 0.2 wt. per cent sulfur in the feed with fresh catalyst over short run periods[98]. However, removal of sulfur by pretreatment or by recycle gas scrubbing may be required for the commercial operation at sulfur levels above 0.02 wt. per cent. While designed for continuous operation, the catalyst may be regenerated. The initial activity and selectivity are said to be restored.

The Houdriforming process is designed to handle the normal range of reformer feed stocks. Where pretreating is required for removal of excessive amounts of catalyst poisons from the feed, a "guard case" catalytic hydrogenation pretreater, using the same catalyst as used in the reactors, can be employed[15]. Much milder operating conditions are used to prevent any reforming in the "guard case". Besides removing catalyst poisons, this "guard case" will hydrogenate olefin-containing stocks, widening the range of possible charges.

The Houdriforming processing design and operating features are generally similar to the other intermittent-regeneration processes described previously in this section. The conventional three-reactor system with interheating is employed. Specific descriptions have been given by several authors of the processing scheme and operating conditions[15, 24, 26]. Typical operating conditions are: temperatures—875 to 950°F; pressures—250 to 600 psig; space velocities—1.5 to 5 volumes of liquid/hr/vol. of catalyst and hydrogen/oil mole recycle ratios—4 to 10. A flow diagram of the process is given in Figure 88.

Pilot-plant results from Houdriforming for motor gasoline are given in Table 80, using feed stocks varying from 31 per cent to 64 wt. per cent paraffin content[26]. Data are shown for both mild and severe operating conditions. The results illustrate the decreasing gasoline yields and hydrogen makes and the higher yields of light cracked products resulting from increasing paraffinicity of the feed. In the case of the Kuwait naphtha, the desulfurizing activity of the catalyst is indicated by the low sulfur content of the reformate. Pilot-plant data from Houdriforming of other straight-run naphthas[129], from reforming at low pressures[50], and from reforming naphthas produced by hydrocracking a 56 to 77 per cent fraction of an East Texas crude[96] have been published. A detailed economic study of the use of a Houdriformer in various refinery processing combinations has been reported[129].

In January, 1958, eleven Houdriforming units were on stream with a total designed capacity of 78,000 bbl/stream day.

Sovaforming. The Sovaforming process, developed and used by the Socony Mobil Oil Co., Inc., was announced in January, 1954. This is a three-reactor, fixed-bed system using the Sinclair-Baker RD-150 catalyst[153]. The process is designed for high-pressure, continuous operation. The process is not available for licensing and few process details have been published. The first commercial installation went on stream in November, 1954, at the General Petroleum Corporation's Ferndale, Washington, refinery. At the present time there are eleven units with a total capacity of about 150,000 bbl/day operating or under construction at the refineries of Socony Mobil and its subsidiaries.

Cyclical Regenerative, Low-Pressure Platinum Reforming Processes. Cyclical regenerative, fixed-bed reforming, using platinum catalysts, is basically a low pressure process—200 to 350 psig. The use of lower pressures offers several advantages: (1) higher gasoline yields resulting from decreased hydrocracking; (2) better product octanes from a given naphtha charge due to the increased dehydrocyclization of paraffins; and (3) higher

TABLE 80. PILOT-PLANT HOUDRIFORMING OF DIFFERENT NAPHTHA TYPES[26]

	Low Paraffin Naphtha		Intermediate Paraffin Content Naphtha		High Paraffin Naphtha	
Feed Stock Source	Mixed Crudes		East Texas		Kuwait	
Gravity, °API	45.8		55.3		52.9	
ASTM distillation, °F						
IBP	255		188		244	
10%	285		2.5		289	
50%	316		252		320	
90%	361		317		366	
EP	401		368		398	
F-1 clear octane	61.3		55.6		23.5	
F-1 + 3 cc TEL	79.0		76.3		46.1	
RVP, psi	0.6		0.7		0.6	
Sulfur, wt. %	0.012		0.006		0.10	
Naphthenes, vol. %	46		42		20	
Aromatics, vol. %	23		14		15	
Paraffins, vol. %	31		44		64	
Olefins, vol. %	0		0		1	
Reforming severity	*Low*	*High*	*Low*	*High*	*Low*	*High*
Reformate†						
Debutanized reformate						
Gravity, °API	39.7	36.5	52.7	45.8	50.7	47.7
ASTM distillation, °F						
IBP	170	148	173	149	141	130
10%	248	230	212	196	216	195
50%	306	306	260	248	284	283
90%	378	375	323	325	340	349
EP	460	465	379	392	413	426
Sulfur, wt. %	0.002	0.002	0.001	0.002	0.001	0.001
RVP, psi	1.0	1.9	1.0	3.0	2.1	3.6
Debutanized reformate, vol. %	88.3	80.6	91.0	83.5	87.4	80.4
Butanes, vol. %	3.9	7.0	2.7	6.2	6.1	9.3
Propane, wt. %	2.0	5.0	1.2	3.8	2.8	4.7
Ethane, wt. %	1.0	2.9	0.8	2.4	1.5	2.8
Methane, wt. %	0.6	1.8	0.5	1.0	1.1	2.2
Hydrogen, wt. %	2.0	1.8	1.6	1.3	0.7	0.7
Debutanized reformate						
F-1, clear octane no.	92.0	101.0*	80.0	92.0	76.8	90.0
F-1 + 3 cc TEL	99.2	104.2*	92.5	99.5	91.0	98.3

* Octanes above 100 extrapolated by method of Deters, J. F., *Petroleum Refiner*, June, 1951

† Yields on charge basis.

Table 81. Comparison of Regenerative Platinum, Non-Regenerative[146] Platinum and Fluid Molybdena Reforming Yields and Costs

Feed Stock	*Mid-Continent*			*Gulf Coast*		*Mixed*[1]		
Gravity, °API	55.5			48.1		52.2		
Sulfur, wt. %	0.03			0.02		0.20		
ASTM distillation, °F								
IBP	206			202		202		
10%	237			250		244		
50%	274			305		287		
90%	324			356		363		
EP	361			394		400		
F-1 clear octane no.	44.5			59.4		46.1		
Composition, vol. %								
Paraffins	50.0			26.0		44.5		
Olefins	0.0			0.0		4.0		
Naphthenes	41.5			55.5		37.5		
Aromatics	8.5			18.5		14.0		
	Nonregenerative Platinum	Fluid Molybdena	Regenerative Platinum	Fluid Molybdena	Regenerative Platinum	Nonregenerative Platinum	Fluid Molybdena	Regenerative Platinum
Reforming yields								
Dry gas, wt. %	11.4	11.7	7.5	10.7	6.1	12.6	12.3	8.7
Butanes, Vol. %	5.6	6.2	4.5	5.6	5.2	5.5	6.1	4.4
C_5^+ *Reformate*								
RVP increase, pounds[2]	2.0	2.4	16	3.3	2.2	1.1	1.6	0.7
Vol. % Chg.	80.2	79.0	84.7	80.5	86.0	79.6	78.4	84.1
Octane No. (F-1, clear)	93	93	93	98	98	93	93	93

	Reforming 5,000 B/CD of Mid-Continent Feed to 93 Octane No. (F-1, Clear)			Reforming 10,000 B/CD Gulf Coast Feed to 98 Octane No. (F-1, Clear)		Reforming 20,000 B/CD of Mixed Feed to 93 Octane No. (F-1, Clear)		
Economics[3]								
Total Annual Operating Cost[4]	2,970	2,730	2,160	4,530	3,410	10,370	9,210	7,690
Investment Cost[5]	1,700	2,100	1,900	3,500	3,600	5,400	4,500	6,100

[1] Mid-Continent virgin, high-sulfur virgin, and coke-still naphthas.

[2] RVP of C_5^+ reformate minus RVP of feed.

[3] Thousands of dollars.

[4] Includes materials, processing, catalyst make-up, etc.

[5] Includes equipment costs and initial catalyst fill.

hydrogen yields resulting from the decreased hydrocracking and the increased dehydrogenation and dehydrocyclization reactions. In low pressure operation, coke yields, with the attendant catalyst deactivation, increase rapidly. However, with catalysts resistant to activity and selectivity losses on cyclic regeneration, these processes afford the operating flexibility necessary to secure the advantages of low pressure operation, while compensating for the effects of the higher coke yields.

Investment costs for these processes are higher than in the intermittent-regeneration, high-pressure platinum reforming techniques described previously (pp. 651–660). This is primarily due to the need for an extra or "swing" reactor (plus its catalyst charge) and more elaborate controls. Use of this swing reactor permits, with suitable design, regeneration of one reactor at a time while processing continues in the others.

A very good comparison of regenerative reforming at low (300 psig) pressures, as represented by the Ultraforming process (see below), with nonregenerative reforming at high pressures (500 psig), and with fluid-bed molybdena-alumina reforming has been published by Steel, Bock, Hertwig, and Russum[146]. Yield-octane data and product distributions from three different naphthas of varying paraffin and sulfur contents were obtained, as shown in Table 81. Regenerative platinum showed a 4 to 6 per cent advantage in yield of C_5^+ gasoline in each case over the other catalysts, according to these results. Butane yields were lower, as were the C_1–C_3 light gas yields.

The lower section of Table 81 includes the economics of reforming using these processes, as derived by these authors. For this economic survey, catalyst lives of 20 bbl/lb of catalyst were assumed for nonregenerative platinum and 40 bbl/lb for regenerative platinum at 93 octane number, clear. At 98 octane number, non-regenerative platinum was assigned a catalyst life of 35 bbl/lb. The makeup rate for the fluid molybdena-alumina catalyst was assumed to be 0.2 lb/bbl. Replacement costs were cited at 60¢/lb for molybdena-alumina and $4.00/lb for the platinum catalysts. Annual operating costs included materials, processing and catalyst makeup costs. Investment costs included processing equipment and initial catalyst fills.

According to these authors, direct operating costs, labor, materials, and utilities are lowest for the non-regenerative platinum process because of its simpler equipment. However, over-all annual operating costs for this process are higher because of the poorer yield structure. As to investment, regenerative platinum reforming is 10 to 25 per cent more expensive. Fluid molybdena-alumina reforming is high in total investment, but the per cent difference is lower for larger units. The authors indicate that, while the regenerative platinum process is more expensive from an investment standpoint, it has an over-all economic advantage in the cases cited due to the higher yields of gasoline and lower Reid vapor pressures of the products.

Ultraforming. The Ultraforming process is a development of the Standard Oil Company of Indiana and was first announced in November, 1953. The first unit, designed for 6200 bbl of feed/day, went on stream at the El Dorado, Arkansas, refinery of the Pan-American Southern Corporation in May, 1954.

This process is designed for low-pressure operation in order to obtain the advantages of the higher gasoline yields, higher product octane levels, and better hydrogen yields at these conditions with platinum catalysts (Figures 89A and 89B). These advantages accrue principally from the lower amounts of hydrocracking and the increased extent of the dehydrogenation and dehydrocyclization reactions taking place at constant temperature and space velocity. At lower operating pressures, catalysts coke up faster and so deactivate more rapidly. As a result, the yields and octane numbers likewise drop faster (Figures 89C and 89D). For successful operation in such a process, frequent regeneration is required. This was for some time a detriment to the commercialization of low-pressure reforming. The Ultraforming process is claimed to overcome this restriction through the use of a new catalyst and a novel regeneration technique[25, 68].

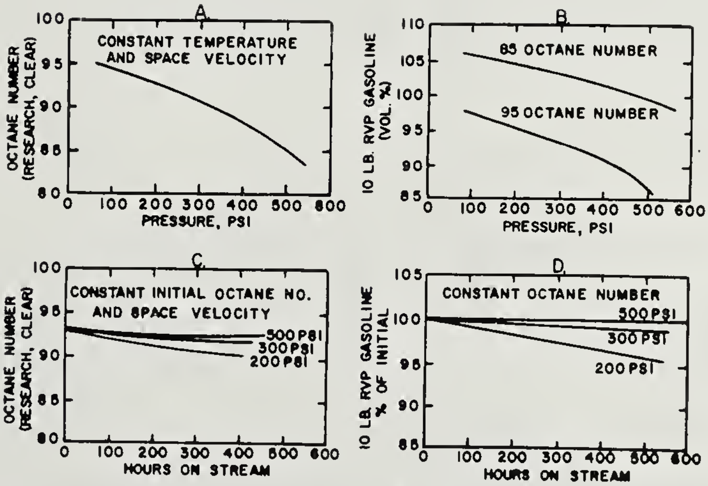


Figure 89. Effects of pressure in reforming Mid-Continent naphtha over a platinum catalyst.

The Ultraforming catalyst comprises 0.6 per cent platinum on an alumina support. A life of over 150 bbl/lb of catalyst at 300 psig, or well beyond 40 bbl at 200 psig has been predicted from pilot-plant data[68]. Lives of up to 100 bbl/lb have been reported from commercial operation[2]. Including a credit for platinum contained in the spent catalyst, replacement cost for the material is about \$4.00/lb[52]. The catalyst is manufactured by the American Cyanamid Company. The regeneration is claimed to go beyond coke removal—to restore the catalyst completely to the fresh condition[25, 68]. On this basis, the regeneration could possibly include rehalogenation of the catalyst to replace any chloride lost during the previous on-stream period.

Fresh feed stocks for Ultraformers can vary widely due to the regenerative nature of the process. Removal of sulfur (and other catalyst poisons) is necessary for optimum catalyst performance, and charges containing excessive amounts of these materials must be pretreated. However, in regenerative operation, lowering the sulfur concentration significantly below that required for good catalytic reaction (approximately 200 ppm) has been found necessary in at least one case[128] in order to control corrosion and scale formation in the unit. Higher end-point feeds and cracked stocks will require more frequent regeneration because of the higher coke makes.

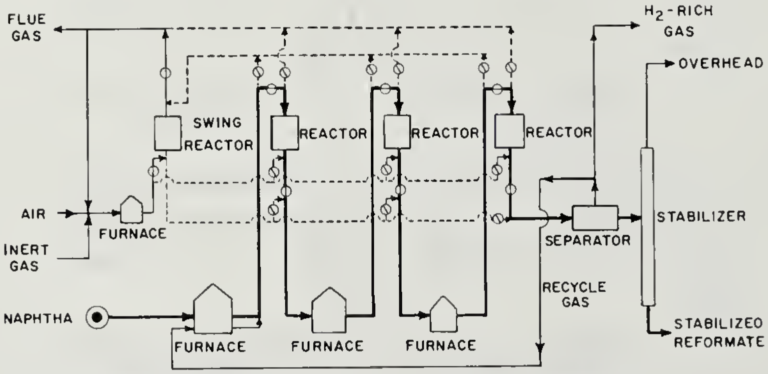


Figure 90. Regenerative platinum reforming using a swing reactor.

The operation of the Ultraforming process has been discussed by several authors[25, 68, 83, 111, 138]. A flow diagram of the process is shown in Figure 90. The principal difference between this operating scheme and the platinum processes previously described is the presence of a fourth or "swing" reactor which permits regeneration of any one reactor at a time without interrupting the processing scheme. Some units have also been designed for five and six reactors including the swing reactor[111, 128]. General process conditions are usually in the range 200 to 300 psig, temperatures of 900 to 970°F, liquid hourly space velocities of 1 to 4, and hydrogen/hydrocarbon mole ratios of 4 to 8.

Feed stocks and hydrogen-rich recycle gas are heated to reaction temperatures and passed through the three on-stream reactors and the two interheaters. Separation of the liquid and the recycle gas as well as stabilization of the liquid product are carried out by conventional means.

Catalyst activity is maintained by cyclic regeneration of the reactors. As a catalyst in any reactor becomes deactivated, the reactor is isolated from the system and replaced by the swing reactor which contains active catalyst. The deactivated reactor is purged with inert gas and an inert gas-air mixture containing about 2 per cent oxygen is passed over the catalyst at 800 to 1050°F[128]. When the burning is complete, the unit is purged with inert gas and recycle gas and then put back on-stream. The swing reactor is then available until another reactor requires regeneration. The regeneration operation is automatically controlled and takes about 20 hours to complete[111]. The frequency of regenerations depends largely on the severity of operation and on the feed stock. For example, one unit, reforming a paraffinic stock to 85 clear octane number, required an average of 10 regenerations/reactor to process 40 bbl of feed/lb of catalyst[83]. Another unit, reforming a naphthenic stock to 100 clear octane number, required an average of 65 regenerations/reactor to process 22 bbl/lb of catalyst[111].

Table 82. Commercial Ultraforming[83, 111]

Charge Stock	*Arkansas*	*Mixed Naphthas*[1]
ASTM Distillation, °F		
IBP	132	200
10%	178	—
50%	240	—
90%	298	—
EP	358	400
Composition, vol %		
Paraffins	71	33
Naphthenes	20	53
Aromatics	9	14
Octane No., F-1, clear	—	51
Yields, charge basis		
Hydrogen	690 s.c.f./bbl	2.1 wt. %
Dry gas, wt. %	—	10.3
Butane, vol. %	—	7.5
C_5^+ Reformate		
Octane No., F-1 clear	85.0	100.0
RVP, psi	6.1	—
Vol. %	84.2	77.7
10-lb. RVP Gasoline		
Octane No., F-1, clear	85.0	—
F-1 + 3 cc TEL	96.5	—
Yield, vol. %	91.2	—

[1] Mixture of virgin naphthas from Gulf Coast, East Texas, and West Texas sweet crudes.

Pilot-plant data from Ultraforming of selected feed stocks are given in Table 81[146], and by Forrester, Conn, and Malloy[68]. Data from operation of the first Ultraformer at the Pan-American Southern refinery have been given by Gumaer and Raiford[83]. Results from reforming a very paraffinic Arkansas feed in this unit are shown in Table 82. Some of the catalyst in this unit has obtained a life of 100 bbl/lb of catalyst over a period of nearly two years of operation[2].

Results from the American Oil Company's Texas City Ultraformer have been given by Johnston, Montgomery, and White[111]. Data from reforming a naphthenic mixed feed at high severities in this unit are shown in Table 82. A catalyst life of at least 60 bbl/lb is expected. Nix[128] has reported results of reforming three narrow-cut fractions produced from a mixture of naphthas boiling from 200 to 370°F in a unit of the Humble Oil Co. The catalyst in one reactor of this unit attained a life of 60 bbl/lb with no indication of any permanent activity decline. The oldest catalyst in the unit had been on stream for 450 days. An ultimate life of at least two years was expected.

Direct operating costs for Ultraforming have been reported to be in the range 18¢ to 25¢/bbl of feed, exclusive of return on investment[83, 111]. At the present time there are about 20 Ultraforming units operating, under construction, or in the design stage with a combined capacity of approximately 240,000 bbl/day. The process is licensed by the Standard Oil Company of Indiana.

Powerforming. Powerforming, a low-pressure, cyclic regenerative process developed by the Esso Research and Engineering Company, was announced in March, 1956. However, two units, both of the non-regenerative type, have been in operation since mid-1955[106]. The process employs four to six reactors (usually five), any one of which may serve as a swing reactor in place of one of the primary reactors during the regeneration cycle. With favorable feed stocks or where only moderate octane improvement is required, the swing reactor can be deleted and an intermittent regeneration system employed.

The catalyst used for the Powerforming process consists of platinum in combination with an alumina support prepared by a special process. The platinum level is said to be relatively low[6]. When a reactor requires regeneration it is replaced on the line by the swing reactor. The deactivated catalyst is then regenerated by an improved technique which is said to contribute significantly to the higher activity and long life of the catalyst. Besides removing carbon, this new technique compensates for more permanent deactivation which may occur and restores the catalyst to essentially its original activity and selectivity[106]. The catalyst is manufactured by the Davison Chemical Company (Div. of W. R. Grace & Co.).

Typical feed stocks consist of virgin naphthas in the boiling range of 160 to 400°F, cracked naphtha-virgin naphtha blends, or fluid coking naphtha-virgin naphtha blends. Hydrogen pretreating is necessary when processing these blends but may be omitted when charging saturated, sweet straight-run stocks[7].

The process operating scheme has been described by Holt and Haig[106] and is similar to that used for the other low-pressure platinum reforming process described above. A flow diagram of the process is given in Figure 90. Typical operating conditions are: pressure, 300 to 450 psig; reactor inlet temperature, 900 to 1000°F; recycle gas rate, 4000 to 6000 s.c.f./bbl; space velocity, 1 to 4 wt feed/hr/wt catalyst. In a typical unit the catalyst in a reactor can be regenerated in 16 to 24 hours so that the entire charge (including the swing reactor) in a five-reactor system can, if necessary, be completely regenerated every 80 to 120 hours.

TABLE 83. POWERFORMING OF NAPHTHAS[106]

	Case 1	Case 2[1]	Case 3[1]	Case 4	Case 5	Case 6
Feed Sources	*Arabian*	*Arabian*	*Arabian*	*Red-water*	*Mixed La.*	*West Texas*
Nominal cut range, °F	160/260	150/300	300/385	170/310	200/330	200/300
Feed Properties						
Gravity, °API	64.7	61.6	49.6	57.2	55.0	53.0
ASTM 5% point, °F	199	190	310	220	223	235
ASTM 50% point, °F	217	236	342	241	253	260
ASTM 95% point, °F	249	294	380	288	304	291
Watson K Factor	12.2	12.1	11.9	11.9	11.8	11.7
Research O.N. clear	44	42	26	58	58	56
Yields, Per cent on feed						
H_2 wt. %	1.6	1.3	1.3	2.4	2.1	2.0
C_1, wt. %	2.9	2.3	1.3	2.1	1.7	1.5
C_2, wt. %	7.0	5.9	2.8	3.7	2.9	2.5
C_3, wt. %	11.1	10.0	5.7	8.2	5.1	4.4
C_4, vol. %	17.0	15.0	8.4	10.7	8.8	7.8
C_5^+ *Powerformate*						
Vol. %	60.1	64.3	78.3	73.5	77.5	81.0
ASTM Final B. Pt, °F	381	392	444[2]	396	402	385
Gravity, °API	53.0	49.0	40.0	47.5	45.9	44.3
RVP, psi	7.6	7.5	2.7	4.5	4.0	3.5
Octane Numbers						
F-1 clear	100	100	100	100	100	100
F-1 + 3 cc TEL	105.6	105.6	105.6	105.6	105.6	105.6

[1] An Arabian 160°/385° stock split into two fractions for running in blocked operation in Cases 2 and 3.

[2] Before rerunning

Powerforming yield data at 100 octane number (F-1, clear) from a series of naphthas varying from a paraffinic Arabian stock to a highly naphthenic West Texas stock are given in Table 83[106].

In January, 1958, there were eleven units with a total capacity of approximately 105,000 bbl/day operating, building, or approved for construction in the United States and Canada. The process is licensed by the Esso Research & Engineering Co.

Combination Processes. In once-through processing, particularly at continuous, high-pressure operation, the presence of small, but significant, amounts of low-octane paraffins is a real barrier to the production of super-octane fuels. Paraffins are normally upgraded by isomerization, hydrocracking, and dehydrocyclization. Isomerization, as a part of the over-all reforming process, produces only moderate octane improvement because of the fact that the equilibrium mixture contains appreciable amounts of low-octane *n*-paraffins at the reaction conditions. Hydrocracking is a good method for improving octane number, but the extent of the reaction must be limited because of the liquid yield losses and volatility specifications. Dehydrocyclization of paraffins to form aromatics and hydrogen is a very excellent means of upgrading octane ratings, despite the inherent volumetric losses due to density changes. However, as the concentration of aromatics in a charge increases as it passes through the successive reactors of a platinum reformer, the rate of the dehydrocyclization reaction is slowed down by equilibrium considerations despite the fact that significant quantities of paraffins may remain. As a result of these factors, all once-through reformates contain some paraffins boiling in the upper part of the feed stock range and having very low octane numbers (40 and below).

The aim of the combination processes is to produce very high octane gasolines in good yields through selective treatment of these low octane paraffins. This is done by reforming the total feed under relatively mild conditions so as to obtain a partial conversion of paraffins without excessive gas or coke makes and then either (1) extracting the aromatics from the reformate and subjecting the paraffinic raffinate to further catalytic reforming (Rexforming and Iso-Plus Houdriforming) or (2) running the depentanized reformate through a thermal reformer to obtain further upgrading of the *n*-paraffin fraction (Iso-Plus Houdriforming). While the severe reforming, together with the increased coke make and catalyst deactivation, necessary to produce very high octanes under continuous operation at high pressures can thus be avoided, some of the advantage is offset by the increased investment and operating costs required by the combination processes.

Rexforming. The Rexforming process was developed by the Universal Oil Products Co. and was announced in March, 1955. It combines elements of both the Platforming process and the Udex solvent extraction process to produce very high octane gasolines from straight-run naphthas. The low octane number paraffinic raffinate from the solvent extraction is continuously recycled with fresh feed.

Processing is said to be of moderate severity. Very high concentrations of aromatics are unnecessary since there are only small concentrations of low octane number *n*-paraffins in the product. Reactor inlet temperatures in Rexforming may be as much as 50°F lower than for once-through Platforming[82]. Space velocities are claimed to be somewhat higher. At these milder conditions, higher over-all yields are possible and longer catalyst life may be obtained.

The liquid-liquid extraction system of the Rexformer is similar in many respects to the Udex process used for the extraction of pure aromatics[159]. However, in Rexforming a cheaper system can be used since high-efficiency, high-purity extraction is not necessary. Any aromatics getting into the raffinate stream are not lost to a low value stream, but are recycled to the unit. Further, in Rexforming, solvent extraction conditions can be adjusted to include a desirable amount of low boiling paraffins and naphthenes along with aromatics in order to produce a better balanced fuel.

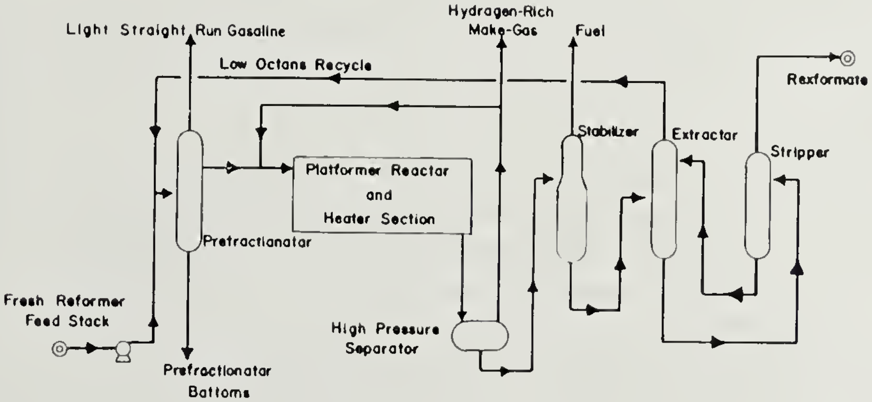


Figure 91. Rexforming.

Feed stocks for the process are normally straight-run naphthas. A pretreater may be added to remove any catalyst poisons. The operation of the process has been described[82]. A flow diagram of the system is given in Figure 91.

The Rexformer consists of several integral parts; a feed fractionator, a reaction system, a stabilizer section, and an extraction section. Full boiling range naphtha and recycled paraffinic raffinate are fed to the prefractionator. The side cut from this column together with recycled hydrogen passes through a Platforming unit. Reactor effluent passes to a separator from which recycle gas is recirculated to the reactors and hydrogen-rich make-gas is taken off. The separator liquid passes to a stabilizer where the product is debutanized. The stabilized stream, having an octane number of 75 to 85 (F-1, clear) and containing 35 to 45 per cent aromatics, is then charged to an extraction column containing a diethylene glycol-water solvent. The separation in the extractor is adjusted to be selective in that the high boiling non-aromatics (the lowest octane number materials) are least soluble in the solvent. These components are continuously rejected from the top of the column and are returned to be combined with fresh feed. The more soluble aromatics and the lower boiling, high octane non-aromatics are removed from the extractor with the rich solvent. The hydrocarbons are stripped from the solvent which is then returned to the extractor. The gasoline from the stripper, the Rexformate, will have a much higher octane number than the primary reformate, and, when of about 100 octane number, will contain approximately 60 to 65 per cent aromatics[8]. The properties of the various process streams from reforming a Mid-Continent naphtha are given in Table 84A[82].

Operating data from the first Rexformers at the Aurora Gasoline Company and at the Cosden Petroleum Corporation have been reported[10, 11]. Data from the Cosden commercial unit for reforming a West Texas naphtha are shown in Table 84B. Pilot-plant results from processing a very paraffinic Middle Eastern stock are also given in this Table.

Estimated installation costs for a Rexforming unit are about $400/bbl for a 5000 bbl/day unit. Total operating costs, excluding return on investment, are estimated at 60¢ to 90¢/bbl[153]. Four commercial Rexformers are now in operation with a total capacity of about 30,500 bbl/day.

Iso-Plus Houdriforming. The Iso-Plus Houdriforming process, developed by the Houdry Process Corp., was announced in March, 1955[130]. This is a combination process using a conventional Houdriformer operating at moderate severity followed by (1) aromatics extraction with either separate or recycle reforming of the paraffinic raffinate, or (2) thermal reforming of the depentanized catalytic reformate. In the cases of Houdriforming where aromatics extraction is used, an Arosorb unit (separating aromatics by a cyclic selective adsorption-desorption process in fixed silica gel beds)[95] or other suitable aromatics recovery unit may be employed.

Feed stocks to this type of unit consist of conventional naphtha charges. Use of a Houdry "guard case" (see Houdriforming, p. 659) permits charging of stocks of relatively high sulfur contents.

Operating conditions for the first stage Houdriformer are generally in the range common to platinum reforming process under continuous operation, except for somewhat milder temperatures; the reformate from this step being of relatively low octane. Process operation has been described by several authors[97, 130, 153]. A flow diagram of the various processing schemes of Iso-Plus Houdriforming is given in Figure 92. Typical operations, using these schemes, to produce 100 clear octane number gasoline from a 200 to 394°F virgin naphtha (51°API; 46 per cent paraffins; 0.125

TABLE 84. REXFORMING

A. *Pilot Plant Rexforming Data; Mid-Continent Feed Stock*[82]

Inspection Data	Fresh Charge	Rerun Bottoms	Combined Feed	Stabilized Reactor Effluent	Low Octane recycle	Debutanized Rexformate
Gravity, °API	52.3	29.5	56.1	52.4	63.4	47.0
100 Ml. distillation						
IBP, °F	242	417	168	133	114	93
5%	259	431	227	172	148	109
10%	264	436	241	194	165	121
30%	292	—	271	245	225	173
50%	316	—	298	280	266	262
70%	346	—	332	313	300	309
90%	374	—	367	366	355	367
95%	384	—	376	387	378	393
EP, °F	415	—	395	424	420	424
F-1, clear octane	33.0	—	—	76.3	41.0	97.2
Aromatics, vol. %	9	—	—	37.5	8.5	53.5
Quantities, vol. per 100 vol. net feed	101.4	1.4	144.6	125.1	44.6	80.5

B. *Commercial and Pilot-Plant Rexforming of Naphthas*

	West Texas*		Middle Eastern†	
	Reactor Charge	Reformate‡	Reactor Charge	Reformate‡
Gravity, °API	56.4	—	57.4	45.4
100 ml. dist., °F:				
IBP	168	149	204	121
10%	184	184	236	163
30%	214	—	259	230
50%	244	258	282	275
70%	286	—	304	304
90%	328	338	334	345
End point	390	394	386	418
Research, clear octane	52.5	§98.2	—	98.0
Aromatics, vol. %	9.7	64.2	12	58.8
Naphthenes, vol. %	36.1	—	19	—
Yields, debutanized reformate, vol. % charge	—	79.0	—	75.6

* Commercial operation. † Pilot plant. ‡ Properties and yields are for debutanized reformate. § Wiese octane scale extension; 103.4 with 3 ml. TEL/gal.

per cent sulfur; 54.1 clear octane number) may be summarized as follows:

Type 1. Moderate Houdriforming followed by aromatics extraction and separate Houdriforming of the paraffinic raffinate (Figure 92-1).

After being pretreated and stripped, the feed naphtha is Houdriformed at moderate conditions to produce a reformate of about 87 clear octane number. After flashing and recycle gas removal, the liquid product is first depropanized and depentanized. The C_6^+ liquid is charged to an Arosorb unit where an aromatic concentrate containing about 91 per cent aromatics is separated as the product. The raffinate, containing about 81 per cent paraffins, is charged to a second Houdriforming unit and reformed to approximately 81 clear octane number. After being flashed and depropanized, this C_4^+ reformate is blended with the aromatic concentrate and with butanes and pentanes from the first step to produce the 100 octane number (F-1, clear) final product.

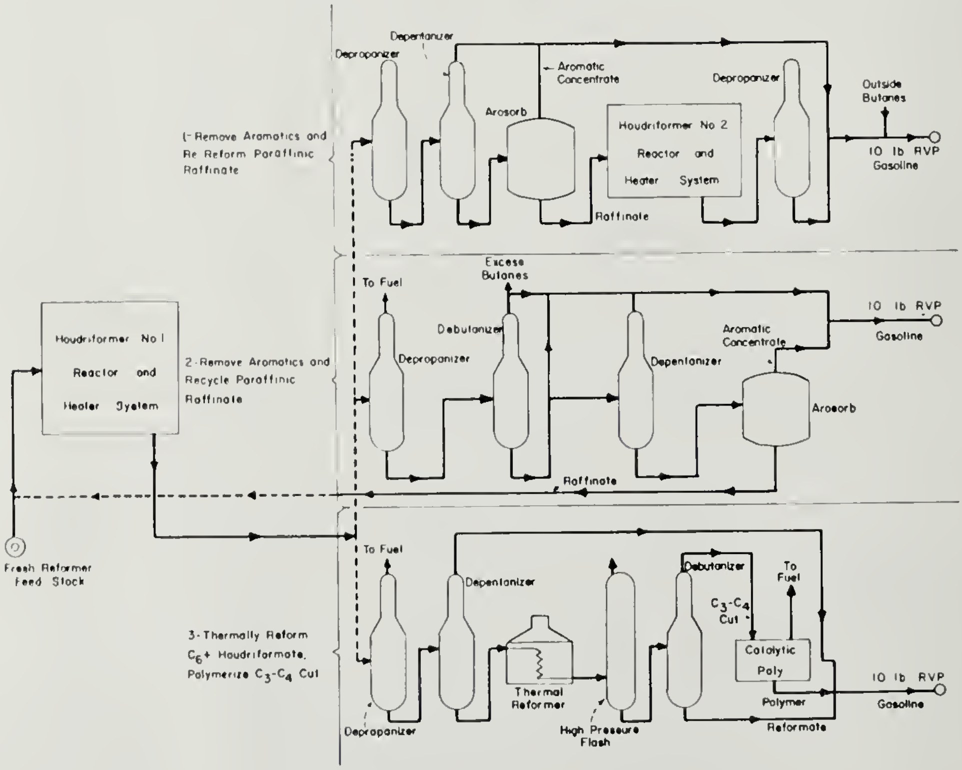


Figure 92. Iso-plus Houdriforming.

Type 2. Moderate Houdriforming followed by aromatics extraction and recycle reforming of the paraffinic raffinate (Figure 92-2).

In this case, pretreated virgin naphtha and paraffinic raffinate from the Arosorb unit are combined and processed in a single Houdriformer to produce an 83 octane number (F-1, clear) gasoline. After debutanization, most of the butane and a calculated portion of the debutanized reformate go directly to the final product. The remainder of this C_5^+ liquid is depentanized and the C_6^+ material is charged to the Arosorb unit. The resulting aromatic concentrate is blended with the butane and debutanized reformate from above, and the paraffinic raffinate is recycled to the Houdriformer.

Type 3. Moderate Houdriforming followed by thermal reforming (Figure 92-3).

The pretreated virgin naphtha in this case is Houdriformed to about 87 octane number (F-1, clear). The depentanized reformate is then thermally reformed to produce a high octane product. Recovered propylene and butenes from thermal reforming are converted to polymer gasoline and blended with products from the earlier steps to produce a 100 octane number (F-1, clear) product. Heinemann *et al.*[97] have described the process operation and product distributions from the thermal reforming of several Houdriformates in a 5000 bbl/day commercial unit. They found essentially no destruction of aromatics in thermal reforming up to 100 octane number (F-1, clear).

In Table 85A, product yields and the volumes of the process streams in using these three process variations are given for producing 100 octane number (F-1, clear) gasoline using the charge stock as described above. Data are included for producing a 100 octane number (F-1, clear) product from this same feed stock by severe one-pass Houdriforming[130].

The best yield of 10 lb RVP gasoline is obtained from Type 1, where the yield losses to hydrocracking are minimized by moderate first-stage reforming, followed by processing the paraffin stream in a second reformer where quite selective aromatization can be obtained. Type 2 operation gives the next best yield, but is not as selective as Type 1 since the reforming of the paraffinic concentrate is done in conjunction with fresh feed reforming. Type 3, designed to take advantage of the thermal stability of aromatics and the ability of thermal reforming to produce high octane olefins from low octane paraffins, has the poorest yield of the combination processes. However, use of catalytic polymerization of the butenes and propene results in a rather good overall yield of 10 lb RVP gasoline. The poorest yield picture is obtained from once-through, conventional reforming. Here, to produce 100 octane number (F-1, clear) gasoline, the maximum yield of aromatics is necessary. At the severe conditions which are required, paraffins are cracked to lower molecular weight liquid and gaseous products. This produces the required octane number improvement, but at a high cost in 10 lb RVP gasoline yield.

Economic appraisals of these four processing schemes are given in Table 85B. The combination processes show a definite advantage over severe reforming, based on their higher yields. This spread would probably increase

TABLE 85. ISO-PLUS REFORMING TO 100 OCTANE NO. (F-1, CLEAR) 10 LB RVP GASOLINE[130]

A. Yields and Process Streams

	Severe Houdriforming	Iso-Plus		
		Type 1	Type 2	Type 3
Total Houdriformer feed	6,600	6,600	10,131[1]	6,600
C_5^+ reformate yield	5,003	5,900	8,753	5,900
Butane Yield	653	271	574	271
Fuel Gas (F.O.E.), yield	938	422	818	422
Arosorb aromatic conc.	—	3,174	3,014	—
C_5^+ F-1, clear, octane no.	100.4	87.0	83.0	87.0
Second pass reforming	—	Catalytic	None	Thermal
C_5^+ Reformate		1,932	—	4,807
Heavy Polymer	—	—	—	33
Butanes	—	246	—	143
Butenes and propenes for catalytic polymerization	—	—	—	456
Fuel Gas (F.O.E.)		293		491
Catalytic polymer gasoline	—	—	—	328
Reformate, F-1 clear octane	—	81.0	—	99.6
Over-all yields				
C_5^+ Gasoline	5,003	5,403	5,222	5,135
Butanes for 10-lb RVP	501	590	529	536
Total 10-lb RVP Gasoline	5,504	5,993	5,751	5,671
Excess Butanes	152	−73	45	−122
10-lb RVP gasoline				
Vol % fresh feed	83.6	90.9	87.1	86.0
F-1 clear octane	100.0	100.0	100.0	100.0

Note: All quantities in B/SD for a service factor of 0.909.

[1] Includes 3,531 B/SD paraffin recycle from "Arosorb".

B. Iso-Plus Economics for 6000 B/SD Unit

	Severe Houdriforming	Type 1	Type 2	Type 3
Investment, process equipment ($)	2,205,000	3,183,000	3,065,000	2,680,000
Catalyst Inventory at $9/lb ($)	1,062,000	322,000	362,000	236,000
SiO_2 gel Inventory at 30¢/lb ($)	—	93,000	109,000	—
Total	$3,267,000	$3,598,000	$3,536,000	$2,916,000
Gasoline		—		
10-lb RVP at 100 F-1, clear, octane	5,004	5,447	5,228	5,155
Cost, $/SD*	22,100	22,900	22,700	21,700

* Assuming credits for fuel gas (F.O.E.) at $1.80/bbl. and excess butane at $2.10/bbl., and charges for feed stock at $3.36/bbl.

at higher octane levels. Type 3 has the lowest investment and operating costs and could be attractive, particularly if the refiner had idle thermal equipment available. However, the cases involving aromatic separation have the highest potential for both octane improvement and yield. In Type 2, for this stock, the octane level can be increased to 105 octane number (F-1, clear) by reforming a larger recycle paraffin stream. In Type 1, recycling the second-pass reformate to the Arosorb unit to an ultimate conversion of 91 per cent aromatic concentrate, pentanes and lighter, makes it possible to produce 4950 bbl/CD of 108 F-1, clear octane number 10 lb RVP gasoline from 6000 bbl/CD of this standard charge[130]. With rising octane levels, the higher octane number ceilings of the Type 1 and Type 2 processes, plus their yield advantages, would probably outweigh their increased investment costs in comparison with the Type 3 processing scheme.

As indicated above, unit installation costs for the Iso-Plus process vary between $450 and $530/bbl of charge. Total operating costs (excluding investment return) have been estimated at 70 to 90¢/bbl[153]. Two of these combination units are on stream. One, a 4000 bbl/day unit in Italy, uses thermal reforming in conjunction with a Houdriformer. The other, at the Tidewater Oil Company's Delaware City, Delaware, refinery, uses an aromatics extraction unit coupled to the 45,000 bbl/day reforming unit.

Fluidized Bed Reforming Processes Using Molybdena-Alumina Catalysts

Fluid Hydroforming. Fluidized-bed reforming using molybdena-alumina catalysts was a natural outgrowth of the Fixed-Bed Hydroforming process already described. The basic work on adapting the fluid technique to the Hydroforming process was done by the M. W. Kellogg Company and Esso Research & Engineering Company[121, 126].

By use of the fluidization technique, the entire catalyst bed can be maintained in a narrow constant temperature range, making for more efficient reforming. Eliminating the necessity for reheating between the reactors prevents over-reforming in some portions of the bed and under-reforming in others. For the same octane level, the inlet vapor temperature can be lower than in Fixed-Bed Hydroforming with molybdena-alumina catalysts. Lower average catalyst temperatures result in higher liquid yields due to the smaller losses to light cracked products. More efficient utilization of the catalyst can be obtained through intimate contact of the feed and the catalyst and through the elimination of channeling[121].

The heat transfer advantages attained by the fluidized technique are also very useful in regenerating the coked catalyst. Burn-off is faster due to the lessening of diffusion limitations and better control of the maximum burning temperature; it also entails less damage to the catalyst. Full air can be used rather than the 2 to 3 per cent air used in Fixed-Bed Hydroforming and the regenerator can be relatively small. The effects of these advantages are illustrated by pilot-plant data as given by Murphree[127] for reforming a Mixed-Base naphtha. These results are included in Table 86.

Fluid Hydroforming, as it is now practiced commercially, converts petroleum naphthas to high-octane gasolines in a single fluidized bed with continuous regeneration in a separate vessel. The catalyst comprises 10 wt. per cent molybdena deposited on or coprecipitated with alumina. Typical Roller analysis shows less than 3 per cent of the catalyst in the 0 to 20 micron particle size range and about 45 per cent greater than 80 micron size. The bulk density of the catalyst is about 55 lb/cu ft. Catalyst replacement costs are of the order of 60¢/lb and the average catalyst make-up to maintain the required catalyst activity is about 0.1 to 0.2 lb/bbl of charge.

TABLE 86. FLUID VS. FIXED-BED HYDROFORMING[127]

Feed Stock	*200–400°F Mixed-Base Naphtha*			
Gravity, °API	53.3			
Sulfur, wt. %	0.113			
Octane No.; CFRR, Clear	43.0			
Aromatics, vol. %	8.2			
Naphthenes, vol. %	42.6			
Paraffins, vol %	49.2			
Process	*Fixed Bed*	*Fluid*	*Fixed Bed*	*Fluid*
Operating pressure, psig	200		200	
Octane level; CFRR, Clear	85	85	95	95
Yields, charge basis				
C_4-400°F E.P. Gasoline, vol. %	89.5	90	81.1	83.6
Total C_4 , vol. %	6.3	5.8	9.2	8.4
Polymer, vol. %	1.0	1.7	1.6	2.4
Dry Gas, wt. %	8.1	6.5	15.0	10.3
Hydrogen, SCF/bbl	580	450	580	450
Carbon, wt. %	0.4	1.4	1.2	1.8
10-lb. RVP gasoline				
Sulfur, wt. %	—	—	0.002	0.002
Octane Numbers				
CFRR, clear	85	85	95	95
CFRR + 3 cc TEL	96.1	96.1	101	101
Yield, vol. %	96.1	97.2	79.0	84.5
Outside C_4's added, vol. %	6.6	7.2	−2.1	0.9

Feed stocks for Fluid Hydroforming may be sweet or sour straight-run gasolines, cracked naphtha, coker naphtha, or blends of these materials with straight-run gasolines. The catalyst is sufficiently resistant to normal amounts of feed stock impurities that feed stock preparation, except for tailoring the boiling range for specific products, is normally not practiced. Stocks containing up to 0.5 wt. per cent sulfur have been processed, as have high-sulfur blends containing 60 per cent cracked naphthas. Molybdenum sulfide formed on the catalyst is reoxidized to molybdenum oxide with the release of SO_2 on regeneration. Prehydrogenation of olefinic stocks is not necessary since the higher coke lay-down can be compensated for by adjusting the amount of catalyst withdrawn from the reactor for regeneration.

Operation of Fluid Hydroformers has been described by several authors[12, 137, 144]. A Fluid Hydroformer flow diagram is shown in Figure 93. Typical operating conditions are: temperatures—900 to 940°F; pressures—200 to 250 psig; recycle gas rates—4000 to 6000 SCF/bbl. Naphtha feed stock is heated to about 1000°F maximum (to minimize thermal cracking) before entering the reactor, thus furnishing about 25 per cent of the heat of reaction. Recycle gas, heated separately to 1200°F, furnishes another 55 per cent of the heat. The remaining 20 per cent is carried into the reactor by the freshly regenerated catalyst. The rate of circulation of the catalyst must be limited since it would tend to increase coke formation with possible overloading of the regenerator[52].

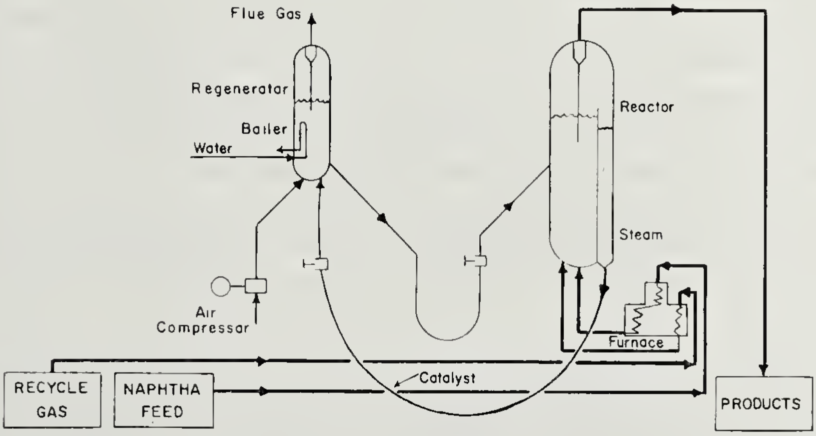


Figure 93. Fluid hydroforming.

In operation, the fluidized catalyst circulates continuously between reactor and regenerator. The preheated liquid feed and recycle hydrogen enter the bottom of the reactor as super-heated vapors, meeting the isothermal bed of fluidized catalyst. The reformed products leave the top of the catalyst bed and pass through separators where entrained catalyst is removed. The overhead vapors are heat exchanged, cooled, and separated into gaseous and liquid products. After being stripped and stabilized, the liquid is removed as high octane gasoline. A hydrogen-rich portion of the gaseous product is compressed, reheated and returned to the reactor.

Since the over-all effect in reforming is endothermic, perhaps the major advantage of fluidized operation is its ability to supply large quantities of heat over a narrow temperature range. The average bed temperature can be held within about 5°F of the exit temperature, maximizing the yield of the desired products.

Catalyst regeneration is accomplished in the same general way as in catalytic cracking—through direct combustion of the coke with full air. The good heat transfer characteristics of the fluidized bed are also utilized in the regeneration cycle. A portion of the catalyst in the reactor is constantly being withdrawn and cycled through the regenerator. The regeneration is carried out at about 1100 to 1150°F and at reaction pressure; 200–250 psig. Heat produced in the combustion can be used to generate steam or to help preheat reactor feed. The operating cycle is completed by returning the hot regenerated catalyst to the reactor as a fluidized stream.

The process can produce good yields of 90 to 100 octane (F-1, clear) gasolines from a wide variety of stocks. Reformates are essentially sulfur-free, aiding their lead response. As in other reforming processes, highly paraffinic stocks are the most difficult to reform. This effect and the results from reforming high-sulfur stocks in a commercial unit are illustrated in Table 87.

The first commercial Fluid Hydroformer, a 2,000 bbl/day unit designed and engineered by M. W. Kellogg Co., was put on stream at the Destrahan, Louisiana, refinery of the Pan-American Southern Co. in June, 1953[67, 144]. At present there are four units operating with a total capacity of about 62,000 bbl/day. These units, generally referred to as Model I units, are licensed by Esso Research & Engineering Co. and by M. W. Kellogg Company. They still employ the side-by-side reactor-regenerator arrangement as shown in Figure 93. A modification, developed by Esso Research & Engineering Co., employs a relatively coarse, inert solid which is circulated along with the catalyst to improve the heat transfer between the reactor and the regenerator[152]. This design, the Model II, is claimed to have lower investment and operating costs. No commercial units of this type have been built.

Economic comparisons of Fluid Hydroforming with thermal reforming plus catalytic polymerization[145], with Fixed-Bed Hydroforming[120, 157], and with regenerative and nonregenerative platinum reforming[146] have been published. At present, installation costs, depending on unit size, vary between $200 and $400/bbl of charge. Operating costs, excluding return on investment, vary between 45¢ and 60¢/bbl[153].

Orthoforming. The Orthoforming process, developed by the M. W. Kellogg Co., is primarily a variation in the basic Fluid Hydroforming unit design described above. The process uses a single structure comprising the reactor with an integrated regenerator above it, allowing in-line transfer of the catalyst[137]. This modification was designed to reduce construction costs, improve heat economy, and to increase the flexibility of operation. One commercial unit was built; a 25,000 bbl/day installation at the Whiting refinery of the Standard Oil Co. of Indiana[35]. The unit went on stream in April, 1955, and was destroyed by an explosion in August, 1955.

TABLE 87. FLUID HYDROFORMING OF VARIOUS NAPHTHAS[52]

Feed Stock	*Virgin Louisiana*	*Virgin Arabian*	*Mixed California*[1]
Initial ASTM boiling point, °F	205	220	240
End ASTM boiling point, °F	325	345	415
Sulfur, wt. %	0.005	0.025	0.51
Paraffins, vol. %	44	70	37
Bromine number	—	—	
Reformate			
Yields, charge basis:			
C_4's, vol. %	6.4	9.6	3.9
C_3 and lighter, vol. %	9.2	13.9	9.3
Carbon, wt. %	0.9	1.5	2.3
C_5^+ Gasoline			
Gravity, °API	45.2	49.0	39.4
Volatility, ASTM% at:			
212 °F	20	28	23.5
257 °F	58	59	53
302 °F	88	88	83
356 °F	98	98	—
Sulfur, wt. %	0.001	0.001	0.0014
Vol. % charge	80.5	73.0	83.5
RVP, psi	3.4	6.0	—
F-1, clear octane no.	95.0	95.0	95.0

[1] 38% virgin California naphtha, 19% low quality thermal cracked naphtha, and 43% heavy catalytic naphtha.

Moving-Bed Processes. The two moving-bed processes in use today employ single moving catalyst bed reactors with continuous catalyst regeneration in a separate vessel. The metal oxide catalysts, in bead or pellet form, are transported between the reactor and the regenerator by mechanical or air lifts.

Thermofor Catalytic Reforming. The Thermofor Catalytic Reforming process, a direct outgrowth of the well-known Thermofor Catalytic Cracking process, was developed by the Socony Mobil Oil Co., Inc., and was announced in May, 1951. The process is of the regenerative, moving-bed type, employing a single pressure reactor with no reheat furnaces and an atmospheric pressure kiln-type regenerator. The catalyst is used in the form of chromia-alumina beads made by a cogel technique developed at the Socony Mobil laboratories[149]. It contains about 32 wt. per cent chromia and 68 wt. per cent alumina. Good desulfurization characteristics are claimed for the catalyst, with the sulfur being removed mainly as H_2S[107]. Water, however, acts as a poison, and provisions must be made for drying the recycle gas stream[132]. An alternative catalyst which can be used in this process, comprising 10 per cent molybdena deposited on the regularly-produced, dried chromia-alumina hydrogel, has been described by Stover[148].

In operation, the catalyst is maintained at a high "equilibrium" activity by make-up of the normal attrition losses. This amounts to about 0.1 to 0.2 lb/bbl of fresh charge[13]. Catalyst life studies made on a 50 bbl/day pilot unit indicated the loss of as little as 2 to 3 vol. per cent in yield at 98 octane number (F-1 + 3 ml. TEL) after 18 months' operation on various process studies with different feeds[132].

Feed stocks can be straight-run gasolines or blends of straight-run with coker or cracked gasolines. Because of the resistance of the catalyst to poisons, no pretreating of the feed is employed.

The operation of commercial TCR reformers has been extensively described[13, 14, 52, 132]. Operating temperatures range from 950 to 1000°F, depending on the stock being processed. Space velocities of about 0.7 vol. of naphtha/hr/vol. of the reactor (vol. catalyst/vol. oil; about 0.3) are normally employed. Gas recycle rates are about 6 moles gas/mole of naphtha; the recycle gas contains approximately 50 per cent hydrogen. Unit operating pressure is about 175 psig. Changes in the catalyst: naphtha ratio are reported to have little effect on yields of product or on product quality, provided the coke deposition does not become excessive[107].

A flow diagram of the process is given in Figure 94. Since the regenerator operates at essentially atmospheric pressure and the reactor at about 175 psig, a pressure lock system is employed to inject catalyst into the reactor. The system operates on a batch principle and is controlled by a cycle timer[132]. The catalyst moves downward through the reactor section in a compact mass. From the reactor, it moves through a depressuring leg to a bucket elevator for transfer to the top of the kiln.

Charge stock and recycle gas are heated separately, and combined before entering the center section of the reactor. Vapor flow is both upward and downward to suitable vapor disengaging sections. The effluent streams are combined and passed through heat exchangers. The cooled product stream is separated into liquid and gas phases in a primary separator, recombined at higher pressure, and then separated into recycle gas and liquid condensate in the recycle separator. Since, on most reformed stocks, it is necessary to remove 1 to 2 per cent heavy polymer formed during the reaction, the condensate from the recycle separator is first stabilized to depropanized reformate and then this material is passed to two rerun towers to remove the polymer. The gas from the recycle separator is split into two streams, the smaller stream has its C_5's and most of the C_4's absorbed by fresh naphtha feed in an absorber; the larger stream is dried and reheated to 1100 to 1200°F before recombining with the heated absorber effluent prior to entering the reactor.

The relatively low coke makes in the reaction permit the use of bucket elevators for transferring the coked catalyst from the bottom of the reactor to the top of the regenerator and from the regenerator to the top of the reactor. The catalyst circulation rate for a 15,000 bbl/day unit amounts to about 25 tons/hour. The kiln is of the multizone "Thermofor" design; coke is burned off with air in several stages with intermittent cooling by water coils. Temperatures are in the range of 950 to 1050°F.

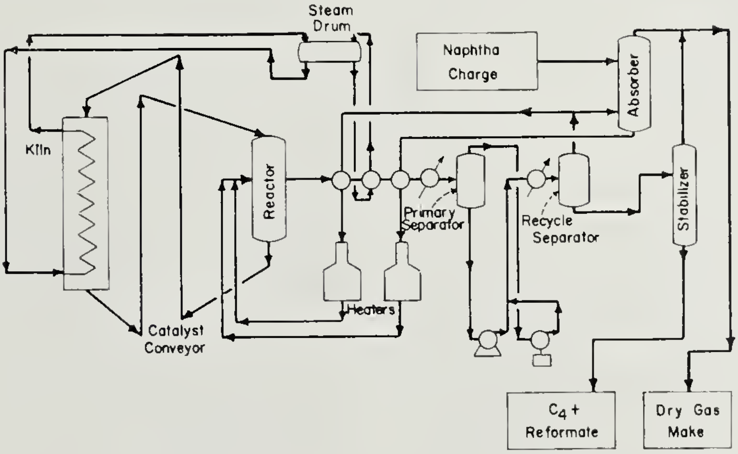


Figure 94. Thermofor catalytic reforming.

Product yields from a 50 bbl/day pilot plant for reforming a paraffinic naphtha, a naphthenic California stock, and a blend of straight-run and coker naphthas are given in Table 88. The effect of the paraffinicity of the feed is shown, for the same reactor temperature, by a comparison of data from stocks 1 and 2. The ability of the process to handle high-sulfur, unsaturated stocks containing nitrogen is given by the third column. The desulfurization of the two sour stocks is above 90 per cent. Even in cases of charging saturated feed, appreciable olefins are found in the product, as illustrated by the high Norwood bromine numbers. This is probably due to the poor hydrogenation-dehydrogenation activity of the chromia-alumina catalyst.

Two commercial TCR units, totaling about 30,500 bbl/day capacity (Table 73), have been built; one at the Beaumont, Texas, refinery of the

TABLE 88. THERMOFOR CATALYTIC REFORMING[132]
Yields and Operating Data—50 bbl/Day Pilot Plant

Charge Stock	*Tibu-Petrolea Paraffinic Naphtha*	*California Naphtha*	*California Straight-run and Coker Blend*[1]
Gravity, °API	54.6	45.9	46.3
Norwood Br No.	0.9	1.0	36.7
Olefins, vol. %	0.7	0.8	30.3
Aromatics, vol. %	11.3	16.0	14.7
Sulfur, wt. %	0.032	0.15	0.59
F-1 octane No.:			
Without TEL addition	33.0	55.0	65.2
With addition of 3 ml TEL per gal.	60.6	71.5	75.4
ASTM distillation, in °F			
Initial boiling point	177	166	225
10% point	265	264	266
50% point	298	338	314
90% point	337	380	368
End point	380	401	400
Reforming Conditions			
Pressure, psig	175	175	175
Space velocity, vol. of naphtha per hr per vol. of catalyst in the reactor	0.88	0.50	0.80
Average reactor temperature, °F	986	985	955
Recycle gas to naphtha, mole ratio	6.0	9.0	5.9
Hydrogen in recycle gas, mole per cent	50	49	50
Yields, charge basis			
Coke, wt. %	0.7	1.5	1.4
H_2, cu ft/bbl	376	430	247
C_3 and lighter, wt. %	16.1	14.5	10.0
C_4's, vol. %	8.4	6.5	4.7
C_5's, vol. %	8.6	4.8	3.6
C_4^+ Gasoline			
Vol. %	83.0	82.7	87.9
Gravity, °API	53.2	44.4	46.6
Norwood Br. No.	9.5	17.4	13.5
Aromatics, vol. %	44.0	45.5	33.1
Sulfur, wt. %	0.007	0.013	0.015
10-lb. RVP gasoline			
Oct. No., F-1, clear	91.1	94.9	89.3
F-1 + 3 cc TEL	99.1	101.4	97.9
Vol. %	82.0	85.4	94.0
Outside C_4's, vol. %	−1	2.7	6.1

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[1] 54% straight-run naphtha + 46% coker naphtha from Wilmington crude.

Magnolia Petroleum Co. and one at the Torrance, California, refinery of the General Petroleum Corporation. Both went on stream in 1955. Reactor equipment and product stabilization make the TCR process relatively expensive. In 1952 the estimated cost of a 3600 bbl/day unit, including royalty and off-site requirements, was $3,100,000 (about $860/bbl of charge)[132]. Larger units are somewhat less expensive. The operating costs in reforming a heavy virgin naphtha to 98 octane number (F-1 + 3 ml. TEL) have been given as approximately 39¢/bbl[52].

Hyperforming. The Hyperforming process, designed as a general-purpose reforming and refining operation, was developed by the Union Oil Co. of California and announced in 1952. The process uses a moving bed of cobalt molybdate catalyst in a single reactor with continuous regeneration. Directed to treatment of California stocks, the process is claimed to have the following advantages:

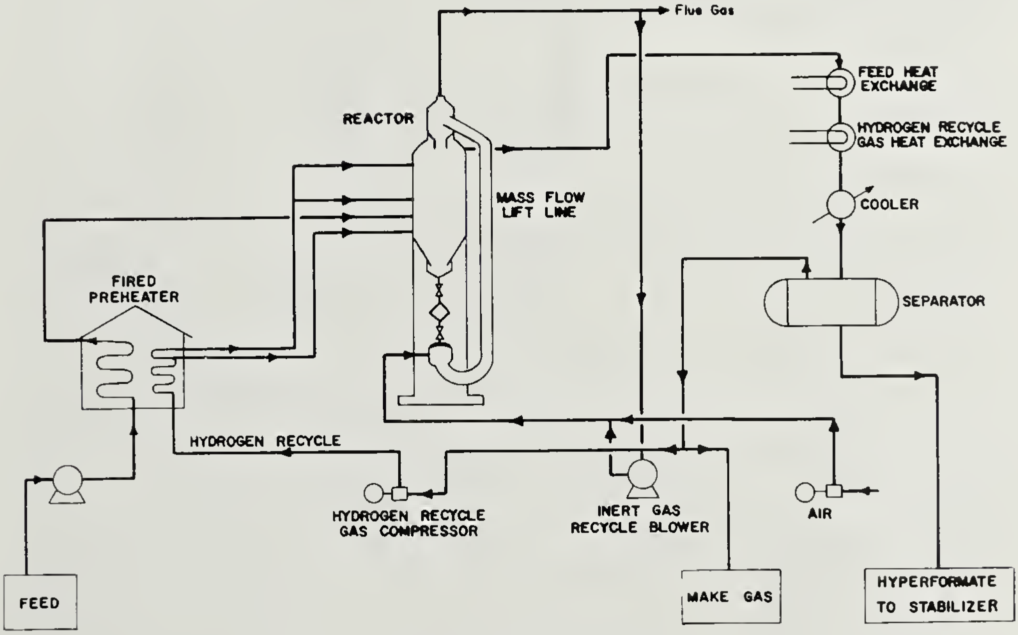

Figure 95. Hyperforming.

(1) Simultaneous octane improvement and desulfurization of straight-run naphthas, cracked stocks or blends.

(2) Use of a continuous moving-bed system to provide uninterrupted operation and maintenance of satisfactory catalyst activity.

(3) A low-cost catalyst, insensitive to poisoning by nitrogen, sulfur and olefinic compounds.

The catalyst employed is $\frac{3}{16}$ inch pelleted cobalt molybdate on a silica-stabilized alumina base. The catalyst is circulated by the hyperflow (mass flow) technique. The low velocity used in the system results in minimum attrition losses[21]. In the process, reactor pressures of the order of 400 psig have been found to be optimum for minimizing coke formation. Reactor temperatures range from 800 to 900°F (about 900°F for straight-run

TABLE 89. HYPERFORMING OF DIFFERENT NAPHTHA TYPES[52]

Feed Stock	*Mid-Continent*		*Coker Distillate**	*Straight-run Cracked Blend†*	
Gravity, °API	51.8		52.7	46.3	
Engler distillation, °F					
Initial	256		147	241	
10%	270		192	270	
50%	292		267	316	
90%	340		342	381	
Maximum	382		390	418	
F-1, clear octane	40		—	61.8	
F-1 + 3 cc TEL	63		80	73.0	
Sulfur, wt. %	0.05		3.47	0.579	
Nitrogen, wt. %	0.01		0.020	0.020	
Naphthenes, vol. %	27		—	—	
Aromatics, vol. %	19		—	—	
Paraffins, vol %	53		—	—	
Olefins, vol. %	1		—	—	
Reforming severity	*Low*	*High*	—	—	—
Reformate					
Yields, charge basis					
C_4^+, vol. %	93.9	88.4	—	91.3	104.4[2] 91.7[1]
Butanes, vol %	4.6	8.3	—	—	3.7
Dry gas, SCF/bbl	300	423	—	—	564
Reformate	C_4^+	C_4^+	not given	C_4^+	10-lb RVP
Gravity, °API	52.2	52.8	60.0	—	52.8
Engler dist., °F					
Initial	—	—	87	—	97
10%	209	158	131	—	168
50%	280	270	205	—	280
90%	335	349	328	—	380
Maximum	—	—	429	—	427
Sulfur, wt. %	—	—	0.035	—	0.007
Nitrogen, wt. %	—	—	0.002	—	—
F-1, clear octane no.	84.2	96.1	—	91.5	83.0
F-1 + 3 cc TEL	94.9	101.7	94.5	98.9	93.7

[1] C_5^+ reformate

[2] 10 lb RVP with addition of 9% outside butanes to C_5^+ reformate

* Santa Maria light coker distillate

† Cracked and straight-run blend from Los Angeles basin crude

stocks); hydrogen recycle is about 3000 cu ft/bbl of charge; catalyst to oil volume ratio is about 0.05.

The Hyperforming process operating scheme has been described by Berg[21, 22, 23]. A flow diagram of the process is shown in Figure 95. Hot feed naphtha enters at the bottom of the reactor section and the vapor, together with recycle gas, flows upward countercurrent to the descending catalyst. Hot hydrogen-rich recycle gas is also injected at several points further up the reactor to help supply the heat of reaction. Reaction products exit near the reactor top. After heat exchange with fresh feed, the reformate passes through a polymer knockout drum. The reaction products are then cooled, hydrogen-rich recycle gas split out, and the liquid product stabilized and sent to the blending tanks.

Used catalyst from the bottom of the reactor enters the lift device through a lock system. It is returned to the top of the reactor by mass conveyance in a transfer line. Regeneration is carried out simultaneously in the lift line using a recycle of flue gas containing less than 2 per cent oxygen—allowing precise control and moderate regeneration temperatures (about 950°F)[52]. Catalyst fines are elutriated at the flue gas disengaging point and the catalyst returned to the reactor.

During operation, in addition to the normal reforming reactions, hydrogen released by the dehydrogenation of naphthenes is used for the saturation of olefins and for the elimination of sulfur, nitrogen and oxygen compounds in the feed. By using outside hydrogen, or blending with straight-run naphthas, cracked stocks containing up to 3.5 per cent sulfur have been refined.

Table 89 illustrates the performance of the process in reforming a straight-run stock, a coker distillate, and a high-sulfur blend of cracked and straight-run California stocks.

Investment costs for a Hyperforming unit have been estimated at $150 to $300/bbl of capacity, depending on unit size. The initial catalyst cost amounts to about $20/bbl of capacity. Direct operating costs for an 1100 bbl/day unit have been estimated at 18¢/bbl of charge[23]. The only commercial Hyperformer built was placed on stream at the Signal Hill, California, refinery of the Cal-State Refining Company in 1955.

Acknowledgment

The unpublished work of reference 55 reported here for the first time was done in the Research and Development Laboratory of the Socony Mobil Oil Company, Inc., by R. M. Dobres, D. S. Henderson, S. J. Lucki and B. W. Rope. Permission to publish these data is gratefully acknowledged.

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