CATALYSIS

VOLUME V

Hydrogenation, Oxo-Synthesis, Hydrocracking, Hydrodesulfurization, Hydrogen Isotope Exchange and Related Catalytic Reactions

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PREFACE

As explained in the Preface to Volume IV of this series, Volumes III, IV, and V are intended to cover most of the work on catalytic hydrogenation. Volume III included principally simple hydrogenation and dehydrogenation reactions in which hydrogen molecules are added to unsaturated bonds or are removed from saturated to form unsaturated molecules. Volume IV was devoted almost exclusively to reactions that involved the reduction of carbon monoxide or other carbonaceous material such as coal or tar to form hydrocarbons. Volume V, the last of the volumes dealing with hydrogenation, includes chapters of both types, those concerned with the simple addition of hydrogen and those in which destructive hydrogenation or hydrogenolysis occurs.

Chapters 1 and 2 cover high-pressure catalytic reactions of carbon monoxide. Some topics in these chapters such as oxo synthesis clearly include hydrogen as one of the reactants; other portions are concerned mostly with the catalytic reaction of carbon monoxide directly with other molecules in the absence of molecular hydrogen. Chapter 3 deals with the synthesis of higher alcohols from carbon monoxide and hydrogen. The other three chapters of Volume V comprise a treatment of hydrogenation reactions in which carbon monoxide is not one of the reactants. The enormous amount of work that has been reported on the catalytic hydrogenation of aromatic compounds is summarized in Chapter 4. Chapter 5 analyzes critically the tracer work that has been done using deuterium or tritium to ascertain more about the mechanism of catalytic hydrogenation. Finally, Chapter 6 contains an authoritative summary of recent work on the catalytic hydrocracking and hydrodesulfurization of petroleum fractions.

The editor wishes to express his appreciation to all of the authors who have contributed to this volume. He would like also to thank the U.S. Bureau of Mines for permitting some of its workers to report their work on oxo synthesis and to summarize critically this important field of catalysis. Again, as in preceding volumes, a special vote of thanks is due our friends from other nations who have contributed sections of the book covering work in their special fields. The assistance of Professor G. Natta, and Dr. I. Pasquon of the Polytechnic of Milan, and Dr. Umberto Colombo of the "G. Donegani" Research Institute at Novara, Italy is gratefully acknowledged.

In this, as in all volumes of the series, an attempt is being made to blend discussions of the fundamentals of catalysis with a presentation of a summary of the factual matter in the various catalytic fields. It is hoped that the subject matter presented in this way will be of interest to those working primarily with industrial applications of catalysis as well as to those who are trying to elucidate the mechanisms by which catalysts are able to function.

Paul H. Emmett

August 1, 1957
Baltimore, Md.

CONTENTS

CHAPTER 1

REACTIONS OF CARBON MONOXIDE[*]

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The Structure of Carbon Monoxide

Proposals purporting to explain the structure of carbon monoxide are almost as old as organic chemistry itself. As a matter of fact, the arguments which these proposals engendered reflect the stages in the development of the ideas regarding the nature of bonding of atoms, from Nef's[99] "conclusive proof" of divalent carbon to Pauling's criticism[105] of Coulson's molecular orbital proposals.

Some time ago, Pauling[106] suggested that carbon monoxide could be represented by three important resonance forms each of which made an approximately equal contribution to the normal state of the molecule. These forms were:

$$:\overset{+}{C}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\overset{-}{:} \qquad :C::\overset{\cdot\cdot}{O}: \qquad :\overset{-}{C}:::\overset{+}{O}:$$

(a) (b) (c)

At the present time, the triply bonded structure (c) is thought to be the most important structure and the one best describing carbon monoxide. Accordingly, the evidence for this structure will be discussed first.

The carbon monoxide molecule contains 14 electrons; six contributed by carbon and eight by oxygen. In the ground state, the electron distribution in carbon is $1s^2 2s^2 2p^2$, and the eight electrons of oxygen are distributed as follows: $1s^2 2s^2 2p^4$. A triple bond may be formed between carbon and oxygen by the transfer of one p electron from the oxygen atom in which it is paired, to the vacant p orbital in carbon. The transfer produces two ions with

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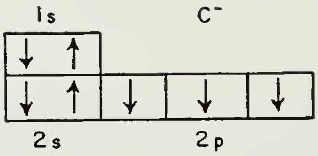
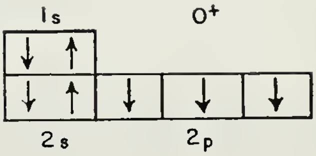
[*] This is not an official publication of the Bureau of Mines.

identical electronic structures:





This structure may be represented as $:\overset{-}{\mathrm{C}}:::\overset{+}{\mathrm{O}}:$ in which only the valence (L shell) electrons are shown, or by the equivalent formulation $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$, in which the formal charges are not shown and the coordinate bond (formed by a transfer of one electron from oxygen to carbon and giving rise to a shared pair in which both electrons are contributed by oxygen) is shown by the familiar arrow. The transfer of the electron produces a structure with three covalent bonds; additional stability is provided by the coulombic interaction of the oppositely charged atoms.

TABLE 1. COMPARISON OF PROPERTIES OF NITROGEN AND CARBON MONOXIDE

	Molecule	
	N_2	CO
Ionization potential (kcals)	359	324
Dissociation energy (kcals)	225.1	256.1
Melting point (°K)	63	66
Boiling point (°K)	78	81.5
Critical temperature (°K)	127	134
Critical pressure (atm.)	33	35
Density in liquid state	0.796	0.793
Force constant (dynes/cm $\times 10^{-5}$)	22	19

TABLE 2. BOND LENGTHS, Å[104]

Linked Atoms	Single	Double	Triple
C—C	1.54	1.33	1.20
C—N	1.47	—	1.15
C—O	1.42	1.20	1.13 (CO)
N—N	1.47	1.21	1.09

One of the principal arguments cited[104] in favor of the above triple bond structure is its analogy with the nitrogen molecule which also contains 14 electrons and to which a triple bond structure can unequivocally be assigned. There is a striking similarity in the physical properties of nitrogen and carbon monoxide as Table 1 shows. A comparison of the bond lengths of various atoms linked by single, double, and triple bonds (Table 2) also argues for a triple bond in carbon monoxide. Tables of bond energies, Table 3, and force constants, Table 4, have been compiled[104] for atoms linked by single and multiple bonds. The relative increase in these values with multiple bond formation is in reasonable agreement with the postulated triple bond linkage for carbon monoxide.

In the above discussion, the arguments for the triple bond structure are based on (1) the isoelectronic principle and the physical and chemical similarities of nitrogen and carbon monoxide and (2) the comparison of interatomic distances, force constants, and energies of the C—O bond in carbonyl groups and in carbon monoxide. In arguing that some consideration be given the double bond structure of carbon monoxide, $:C::\ddot{O}:$, Long and Walsh[92] point out that the physical property similarities are owing to similar molecular volumes, molecular weights, and external force fields rather than to similar electronic arrangements. Similar molecular volumes for nitrogen and carbon monoxide are expected from the location of carbon, nitrogen, and oxygen in the periodic chart. Similar external force fields are also expected because at distances which are large compared with internuclear distances, both nitrogen and carbon monoxide may be considered as approximately single nuclei of positive charge 14 screened by 14 electrons. Similar molecular volumes mean similar *b* values and similar force fields mean similar *a* values in the van der Waals equation of state.

TABLE 3. BOND ENERGIES[104]

(Heats of formation of bonds from atoms—kcal/bond)

Linked Atoms	Single	Double	Triple
C—C	83 (C_2H_6)	139 (C_2H_4)	186 (C_2H_2)
C—O	82.6 ($(CH_3)_2O$)	175 (CH_3COCH_3)	254 (CO-spectroscopic)
	81 (C_2H_5OH)	173 (CH_3CHO)	
C—N	58 (CH_3NH_2)	132 (CH_3NCO)	178 (CH_3CN)
	59 ($(CH_3)_2NH$)	132 (C_2H_5NCO)	
	59 ($(CH_3)_3N$)		

TABLE 4. FORCE CONSTANTS[104]

(dynes/cm × 10^{-5})

Linked Atoms	Single	Double	Triple
C—C	5.0 (C_2H_6)	9.8 (C_2H_4)	15.7 (C_2H_2)
C—O	4.5 (C_2H_5OH)	13.4 (H_2CO)	19.0 (CO)
C—N	5.0 (CH_3NH_2)	(12.1)	17.9 (HCN)
N—N	3.6 (N_2H_4)	—	22.0 (N_2)

As regards C—O distances, force constants, and bond energies, Long and Walsh[92] show that these properties can vary greatly with the polarity of the C—O bond; the greater the polarity, the weaker the bond, that is, the greater the interatomic distance and the less the force constant. The C—O bond in carbon monoxide should more properly be compared with a non-polar carbonyl group than one in an aldehyde or ketone which is highly polarized. Long and Walsh further suggest that the difficulty in describing the bond structure is partly a semantic one, and while they inferentially concede the major role of the triply-bonded structure, they prefer to describe the coordinate bond in carbon monoxide as an "incipient coordinate link."

The very low dipole moment of carbon monoxide (0.12 e.s.u.) presents a problem in all formulations of the molecule. Pauling proposed[106] that the resonance forms (a) and (c)

$$\underset{(a)}{:\overset{+}{\mathrm{C}}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{\mathrm{O}}}:} \quad \leftrightarrow \quad \underset{(c)}{:\overset{-}{\mathrm{C}}:::\overset{+}{\mathrm{O}}:}$$

made approximately equal contributions to the normal state of the molecule and since the polarities are opposed, the net result was an essentially zero dipole moment.

The molecular orbital treatment of the carbon monoxide molecule as developed by Mulliken[98], Moffitt[96], and Sahni[119] indicates the following orbital assignment of the ten electrons in the L or valence shell of the carbon and oxygen atoms: two electrons in the sigma bond formed between the carbon *sp* hybrid orbital and the oxygen *p* (with possibly some *s* character) orbital, two electrons in each of two pi bonds from *p* orbitals of carbon and *p* orbitals of oxygen, two electrons in an atomic s orbital (possibly with some *p* character) of oxygen, and finally two electrons in the other *sp* hybrid orbital of carbon. The three bonds between carbon and oxygen would result in a polarity $\overset{+}{\mathrm{C}}—\overset{-}{\mathrm{O}}$ but the lone pair of electrons on carbon provide an atomic dipole which practically cancels this $\overset{+}{\mathrm{C}}—\overset{-}{\mathrm{O}}$ dipole, the net result being a dipole very close to zero. The linkage between carbon and oxygen in carbon monoxide is thus most properly described as a triple bond in the ground state. In terms of a resonance structure, the form $:\overset{-}{\mathrm{C}}:::\overset{+}{\mathrm{O}}:$ can then be said to make the principal contribution to the carbon monoxide molecule.

The molecular orbital treatment helps in an understanding of the chemical differences between the carbon monoxide molecule and the nitrogen molecule, the similarity between which was explored above. In contrast to the lone pair of electrons in the nitrogen molecule which are in an unhybridized *s* orbital close to the nitrogen nuclei, the lone pair of electrons on the carbon of carbon monoxide are in the *sp* orbital[33] which is directed away from the C—O bond. The greater reactivity of carbon monoxide as compared to nitrogen and the electron-donor properties of CO can be understood in terms of the molecular orbital representation. It is reasonable to expect that electrophilic groups such as carbonium ions would react with the carbon monoxide molecule. Since carbonium-ion formation is catalyzed by acids it is not unexpected that under acid conditions, carbon monoxide will react with a variety of substrates and some such reactions are discussed below.

In the resonance picture, the uncharged form of carbon monoxide is written $:C::\underset{\cdot\cdot}{O}:$. Some of the chemistry of the molecule is conveniently explained by this representation, the molecular orbital equivalent of which will not be discussed here. In this structure, carbon is shown as having a lone pair of electrons and an empty orbital since there are only a sextet of electrons around carbon instead of the usual octet. From this consideration it may be expected that carbon monoxide could also react with nucleophilic groups such as bases which can contribute electrons to fill out the octet. Indeed such reactions are known and these also will be discussed below.

It is of interest to point out here that the C═O structure was responsible for years of polemics centered around the "divalent" character of carbon. Although the advocates of divalent carbon were successfully routed, the ghost is not completely laid. Very strong evidence is currently accumulating to support the intermediacy of a dichlorocarbene[39a], CCl_2, in base-catalyzed reactions involving chloroform[63a]. A possible structure for the dichlorocarbene is one in which carbon is shown with a lone pair of electrons and an empty orbital, similar in these two respects to the carbon of carbon monoxide. As a matter of fact, such a structure would be stabilized by contributions from a charged double bond structure, analogous to stabilization provided in carbon monoxide by charged structures:

$$:C{=}\underset{\cdot\cdot}{O}: \quad \leftrightarrow \quad :\overset{-}{C}{\equiv}\overset{+}{O}:$$

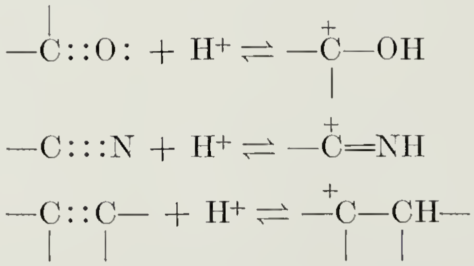
$$Cl{-}\overset{\cdot\cdot}{C}{-}Cl \quad \leftrightarrow \quad \overset{+}{Cl}{=}\underset{\cdot\cdot}{\overset{-}{C}}{-}Cl \quad \leftrightarrow \quad Cl{-}\underset{\cdot\cdot}{\overset{-}{C}}{=}\overset{+}{Cl}$$

The electronic similarity between carbon monoxide and dichlorocarbene should, conceivably, be reflected in similar chemical behavior and indeed such similarities can be found. The Reimer-Tieman reaction involving the base-catalyzed attack of chloroform on certain activated aromatic nuclei is best rationalized on the basis of a CCl_2 intermediate[140a]. Indole has been found to undergo the Reimer-Tieman reaction, leading to 3-indolecarboxaldehyde. Treatment of the indole anion with high pressure carbon monoxide gives the same aldehyde (vide infra). Chloroform reacts with alkali metal alkoxides to give orthoformates; alkoxides with carbon monoxide give formate esters. Future work will certainly turn up many more interesting analogies.

REACTIONS OF CARBON MONOXIDE CATALYZED BY ACIDS

Formation of Carbonium Ions

When a compound containing atoms joined by multiple bonds is dissolved in a proton donating solvent (protonic acid), the following equilibria are established:



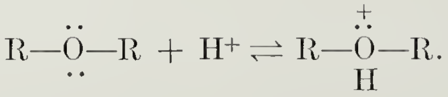
$$—\overset{|}{C}::O: + H^+ \rightleftharpoons —\overset{+}{\underset{|}{C}}—OH$$

$$—C:::N + H^+ \rightleftharpoons —\overset{+}{C}=NH$$

$$—\underset{|}{C}::\underset{|}{C}— + H^+ \rightleftharpoons —\overset{+}{\underset{|}{C}}—\underset{|}{C}H—$$

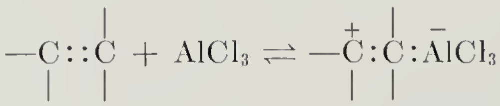
The positively charged ions formed in these reactions are called carbonium ions; they possess a carbon atom with only six valence electrons.

The proton acceptors in the above reactions are bases in terms of the definition of acids and bases proposed by G. N. Lewis, that is, they act as electron donors. Compounds which do not contain multiple bonds but which do have atoms possessing a lone pair of electrons also may function as bases. A common example is an ether, which in the presence of an acid is converted to an oxonium ion:



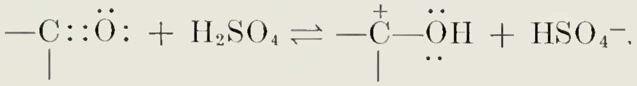
$$R—\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}—R + H^+ \rightleftharpoons R—\overset{+}{\overset{\cdot\cdot}{\underset{H}{O}}}—R.$$

In Lewis' generalized concept of acids and bases, acids are substances which can accept electrons; accordingly, atoms with incomplete octets such as aluminum in aluminum chloride and boron in boron trifluoride are responsible for the acid character of these compounds. For example, an olefin may form a carbonium ion in the presence of aluminum chloride in the following manner:



$$—\underset{|}{C}::\overset{|}{\underset{|}{C}} + AlCl_3 \rightleftharpoons —\overset{+}{\underset{|}{C}}:\overset{|}{\underset{|}{C}}:\overset{-}{Al}Cl_3$$

The existence of carbonium ions (at least in solvated form) is now well accepted. Most esters, ketones, aldehydes, acids, and nitriles give a molar freezing point depression twice that produced by a nonelectrolyte when they are dissolved in 100 per cent sulfuric acid. The reaction is almost certainly:



$$-\underset{|}{C}::\ddot{O}: + H_2SO_4 \rightleftharpoons -\overset{+}{\underset{|}{C}}-\underset{..}{\ddot{O}}H + HSO_4^-.$$

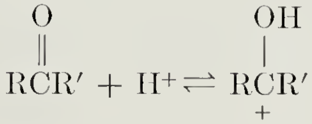
The starting materials can be recovered unchanged by the addition of water to the sulfuric acid solution.

For purposes of the present discussion, the formation of carbonium ions by addition of acids (a) to unsaturated compounds, (b) to compounds containing an oxygen atom of the type $-\underset{..}{\ddot{O}}-$, and (c) to organic halides, is of principal importance. Examples of addition of protonic acids to these three types of compounds are as follows:

(a) Carbonium ions from unsaturated compounds

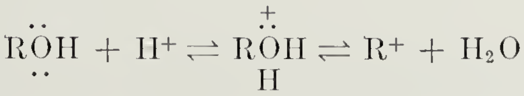
$$1.\ RCH{=}CH_2 + H^+ \rightleftharpoons R\overset{+}{C}HCH_3$$

$$2.\ RCH_2CHO + H^+ \rightleftharpoons RCH_2\overset{+}{C}HOH$$

3. 

$$3.\ R\overset{\overset{O}{\|}}{C}R' + H^+ \rightleftharpoons R\overset{\overset{OH}{|}}{\underset{+}{C}}R'$$

(b) Carbonium ions from compounds containing oxygen atoms of the type $-\underset{..}{\ddot{O}}-$

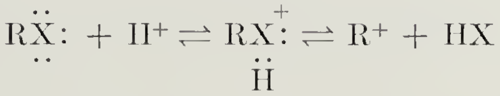
1. 

$$1.\ R\underset{..}{\ddot{O}}H + H^+ \rightleftharpoons R\underset{H}{\overset{+}{\ddot{O}}}H \rightleftharpoons R^+ + H_2O$$

2. 

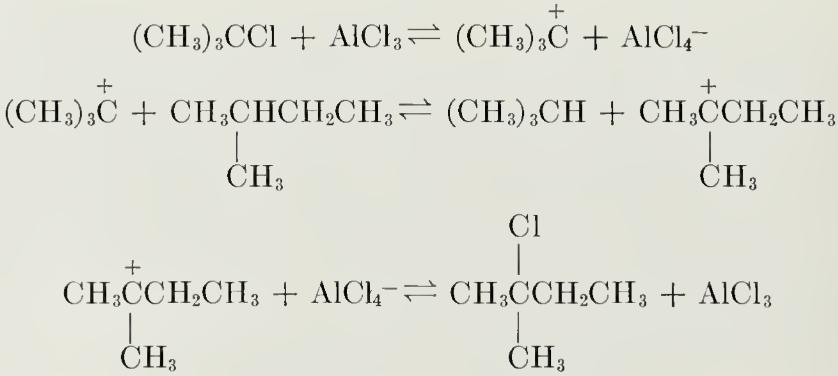
$$2.\ R\underset{..}{\ddot{O}}R + H^+ \rightleftharpoons R\underset{H}{\overset{+}{\ddot{O}}}R \rightleftharpoons R^+ + ROH$$

(c) Carbonium ions from alkyl halides

1. 

$$1.\ R\underset{..}{\ddot{X}}: + H^+ \rightleftharpoons R\underset{\underset{H}{..}}{\overset{+}{X}}: \rightleftharpoons R^+ + HX$$

Before completing this short discussion of the formation of carbonium ions, it is important to discuss one other means of securing these reactive intermediates. This method involves the attack of another carbonium ion upon a saturated hydrocarbon. The classical example of such a process is the "hydrogen-halogen exchange" reaction, demonstrated to occur in less than 0.001 second. In one such experiment[6], *tert*-butyl chloride reacted with isopentane in the presence of aluminum chloride to give isobutane and *tert*-amyl chloride. The steps in this remarkably fast reaction may be expressed as follows:



$$(CH_3)_3CCl + AlCl_3 \rightleftharpoons (CH_3)_3\overset{+}{C} + AlCl_4^-$$

$$(CH_3)_3\overset{+}{C} + CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3 \rightleftharpoons (CH_3)_3CH + CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{C}}CH_2CH_3$$

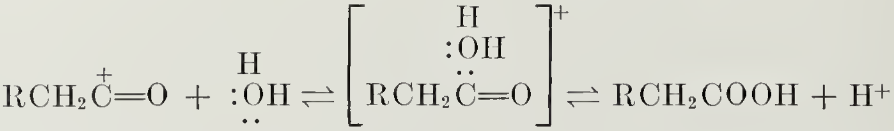
$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{C}}CH_2CH_3 + AlCl_4^- \rightleftharpoons CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}CH_2CH_3 + AlCl_3$$

This mechanism involves the removal of a hydride ion from isopentane by the *tert*-butyl carbonium ion. This hydrogen-halogen exchange is a key reaction in the postulated mechanism which Schmerling[68] employed in his series of articles elucidating the alkylation reaction.

Carbonium ions are reactive intermediates and once formed proceed to react by one or more of several different routes, depending on the environment and the nature of the reactants. The combination of a carbonium ion with carbon monoxide provides a new carbonium ion in which the electron deficiency is probably on the carbon contributed by the carbon monoxide:

$$RCH_2^+ + :\overset{-}{C}:::\overset{+}{O}: \rightleftharpoons RCH_2:C:::\overset{+}{O}: \leftrightarrow RCH_2:\overset{+}{C}::\underset{\cdot\cdot}{O}:$$

The new carbonium ion, among other things, can react with a nucleophilic reagent to terminate the reaction; with water the steps may be written:



$$RCH_2\overset{+}{C}{=}O + \overset{H}{:\underset{\cdot\cdot}{O}H} \rightleftharpoons \left[RCH_2\overset{\overset{\displaystyle H}{:\underset{\cdot\cdot}{O}H}}{C}{=}O \right]^+ \rightleftharpoons RCH_2COOH + H^+$$

In the presence of alcohols, esters may be formed and the presence of acids can lead to anhydride formation:

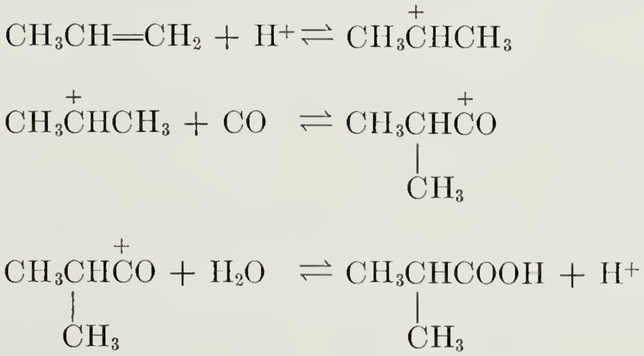
$$RCH_2\overset{+}{C}O + R'OH \rightleftharpoons RCH_2COOR' + H^+$$

$$RCH_2\overset{+}{C}O + R'COOH \rightleftharpoons RCH_2COOCOR' + H^+$$

The Synthesis of Acids and Esters

From Olefins. On August 29, 1933, seven patents were issued to the du Pont Company[26, 27, 28, 29, 80, 133, 140]. The processes described in all these patents are essentially the same; a mixture of carbon monoxide, ethylene, and steam was passed over a solid catalyst, usually carbon impregnated with phosphoric acid, at about 300°C and 200 to 300 atm. pressure. Propionic acid was claimed as the principal product. Silver-lined autoclaves were usually employed for the purpose. Apparently, the process has no appreciable commercial significance at the present time.

In one of the early systematic studies of this reaction[59], propylene, steam, and carbon monoxide were passed through phosphoric acid at 200°C and 200 atm. pressure. The liquid product contained hydrocarbons (from the polymerization of the olefin) as well as carboxylic acids. With propylene, the acid product was nearly all isobutyric acid; butyric acid was absent.



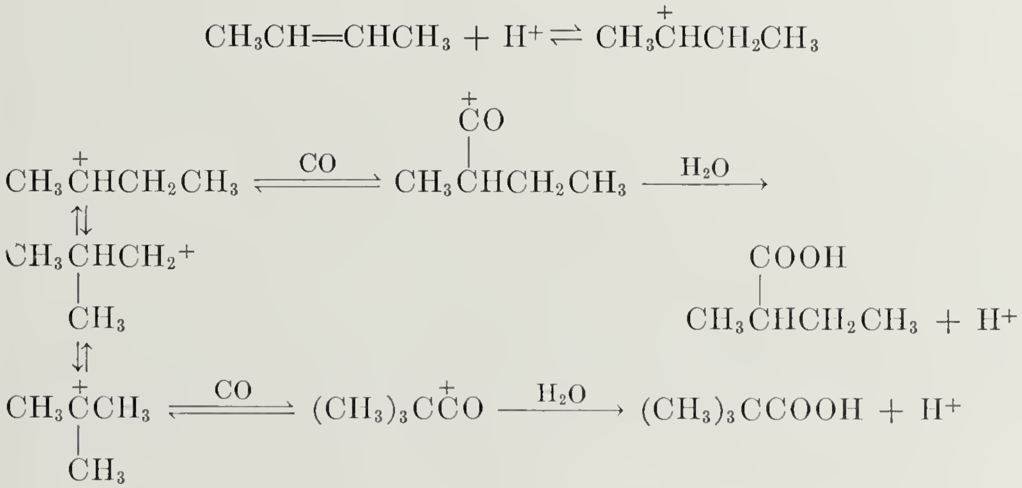
$$CH_3CH{=}CH_2 + H^+ \rightleftharpoons CH_3\overset{+}{C}HCH_3$$

$$CH_3\overset{+}{C}HCH_3 + CO \rightleftharpoons CH_3\underset{\substack{|\\ CH_3}}{C}H\overset{+}{C}O$$

$$CH_3\underset{\substack{|\\ CH_3}}{C}H\overset{+}{C}O + H_2O \rightleftharpoons CH_3\underset{\substack{|\\ CH_3}}{C}HCOOH + H^+$$

The branched-chain acid is always the expected product in an acid-catalyzed reaction since the proton would add to the carbon atom containing more hydrogen atoms (Markownikoff's rule) to form the secondary carbonium ion which is more stable than the primary.

Under the same conditions as employed with propylene, 2-butene gave 2-methylbutyric acid and trimethylacetic acid (pivalic acid). The formation of pivalic acid is the result of a series of rearrangements:

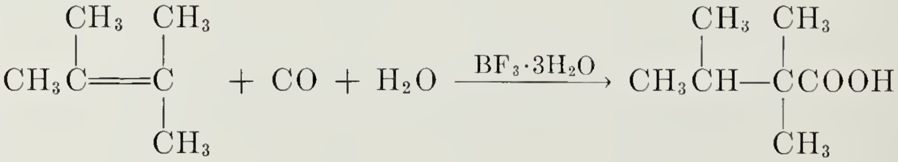


$$CH_3CH{=}CHCH_3 + H^+ \rightleftharpoons CH_3\overset{+}{C}HCH_2CH_3$$

$$\begin{tikzcd}
CH_3\overset{+}{C}HCH_2CH_3 \arrow[r, "CO", rightleftharpoons] \arrow[d, rightleftharpoons] & CH_3\overset{\substack{\overset{+}{C}O\\ |}}{C}HCH_2CH_3 \arrow[r, "H_2O"] & {} \\
CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2^+ \arrow[d, rightleftharpoons] & & CH_3\overset{\substack{COOH\\ |}}{C}HCH_2CH_3 + H^+ \\
CH_3\underset{\substack{|\\ CH_3}}{\overset{+}{C}}CH_3 \arrow[r, "CO", rightleftharpoons] & (CH_3)_3C\overset{+}{C}O \arrow[r, "H_2O"] & (CH_3)_3CCOOH + H^+
\end{tikzcd}$$

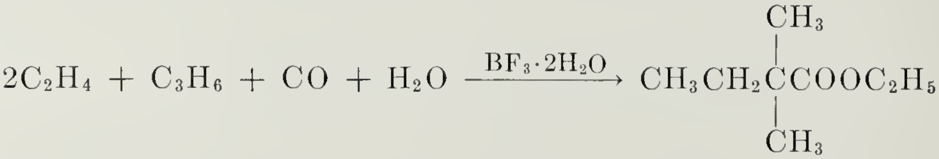
The first rearrangement involves the shift of a methyl group with its pair of electrons. The primary alkyl carbonium thus formed readily rearranges to the tertiary carbonium ion by migration of the hydride ion. These rearrangements use well-known reactions of carbonium ions and were first systematized by Whitmore[137]. It is interesting that no isovaleric acid was isolated; this acid would arise from the first rearranged ion shown.

As previously indicated, protonic acids are not essential for the conversion of olefins to acids by the above schemes. In a beautiful application of the procedure, 2,2,3-trimethylbutyric acid was prepared from tetramethylethylene as follows[45]: 121.8 grams of boron trifluoride trihydrate (1 mole) was treated with 400 atm. of carbon monoxide at 75°C (reaction pressure 600 atm.). Over a period of 2.5 hours, 73 grams of tetramethylethylene (0.87 mole) was injected and heating at 75 to 77°C was continued for a total of 9.5 hours. The product contained 113 grams (100 per cent yield) of 2,2,3-trimethylbutyric acid. The over-all reaction may be written:



$$CH_3\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} + CO + H_2O \xrightarrow{BF_3\cdot 3H_2O} CH_3\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}COOH$$

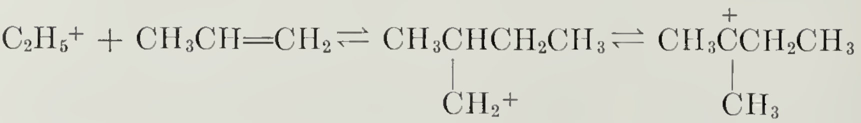
When an excess of olefin is used in the above reactions, a considerable amount of ester may be formed. Thus, by treating a mixture of 3 moles of ethylene and 2 moles of propylene with 500 atm. of carbon monoxide at 110°C in the presence of boron trifluoride dihydrate, Ford[46] obtained a 14 per cent yield (based on propylene) of ethyl 2,2-dimethylbutyrate. The over-all reaction may be written:



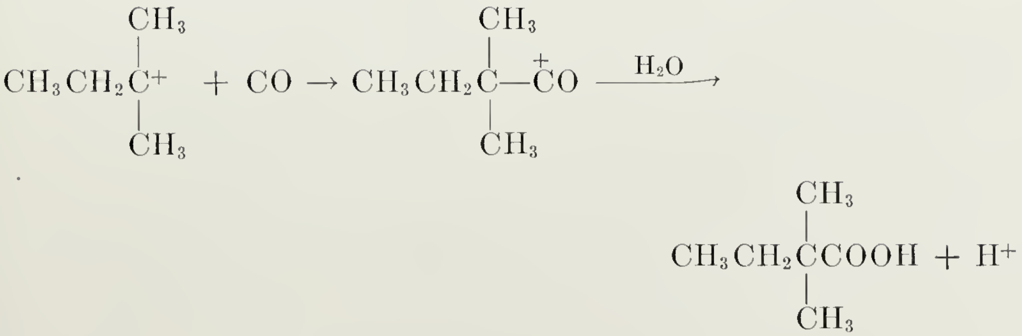
$$2C_2H_4 + C_3H_6 + CO + H_2O \xrightarrow{BF_3\cdot 2H_2O} CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}COOC_2H_5$$

A possible mechanism for the reaction is as follows:

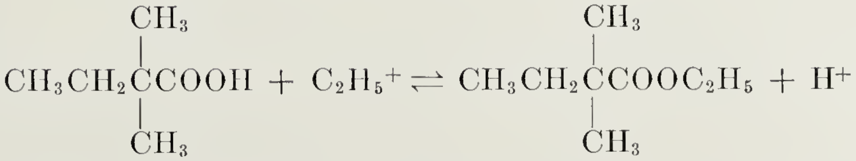
$$CH_2{=}CH_2 + H^+ \rightleftharpoons C_2H_5^+$$



$$C_2H_5^+ + CH_3CH{=}CH_2 \rightleftharpoons CH_3\underset{\underset{CH_2^+}{|}}{C}HCH_2CH_3 \rightleftharpoons CH_3\underset{\underset{CH_3}{|}}{\overset{+}{C}}CH_2CH_3$$



$$\mathrm{CH_3CH_2\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}^{+} + CO \rightarrow CH_3CH_2\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}\overset{+}{C}O \xrightarrow{H_2O} CH_3CH_2\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}COOH + H^{+}}$$



$$\mathrm{CH_3CH_2\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}COOH + C_2H_5^{+} \rightleftharpoons CH_3CH_2\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}COOC_2H_5 + H^{+}}$$

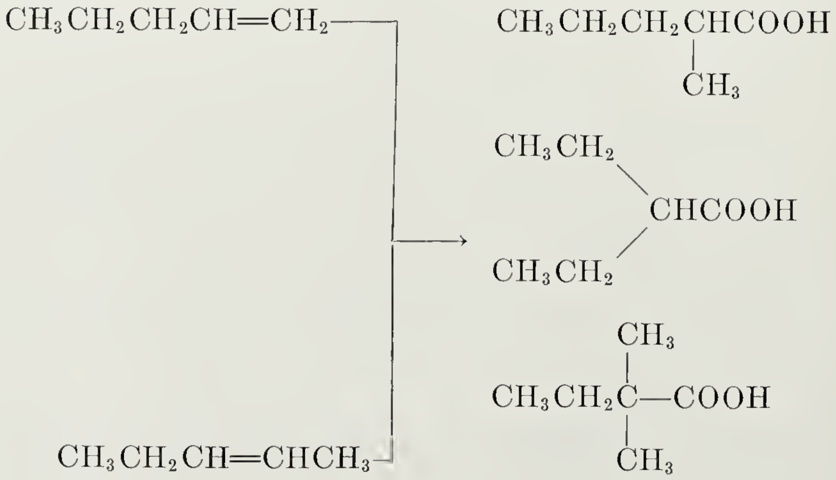
A new synthesis of aliphatic acids from olefins, carbon monoxide and water has recently been published by Koch[79]. The reaction takes place in two steps. The olefin is first mixed with an excess of concentrated sulfuric acid and treated with 20 to 100 atm. of carbon monoxide at between 0 and 50°C. The carboxylic acid is then obtained by treating this mixture with water. Yields as high as 90 to 95 per cent based on the olefin are often obtained. The first reaction must be carried out under anhydrous conditions; dilution of commercial 96 per cent sulfuric acid to 90 per cent acid reduces the yield of acid considerably.

The conditions for this synthesis are surprisingly mild. Thus, when isobutylene and carbon monoxide at atmospheric pressure are placed in a glass vessel with sulfuric acid, there is an appreciable reaction upon vigorous shaking even at 0°C. A 28 per cent yield of carboxylic acids is obtained on dilution of this mixture with water; trimethylacetic acid is the chief product.

In general, the products secured in this synthesis are those expected from a reaction involving acid catalysis. Thus, propylene gives only isobutyric acid, and 1-butene and 2-butene both yield 2-methylbutyric acid.

An increase in the carbon monoxide pressure results in an inhibition of both olefin polymerization and isomerization of the carbon chain. When 2-pentene is treated with 96 per cent sulfuric acid at a carbon monoxide pressure of 5 atm., approximately equal amounts of C_6, C_{11}, C_{16}, and C_{21} acids are obtained; the over-all yield is 59 per cent. The only C_6 acid formed at this low pressure is 2,2-dimethylbutyric acid. At 100 atm. of carbon monoxide, however, a mixture of 2-methylvaleric and 2-ethylbutyric acids is obtained in about 70 per cent yield. Only a small amount of 2,2-dimethylbutyric and essentially no higher acids are obtained at this pressure.

The three C_6 acids obtained from 1-pentene and 2-pentene are shown below:



$$\mathrm{CH_3CH_2CH_2CH{=}CH_2,\ CH_3CH_2CH{=}CHCH_3 \longrightarrow CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}COOH,\quad (CH_3CH_2)_2CHCOOH,\quad CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}COOH}$$

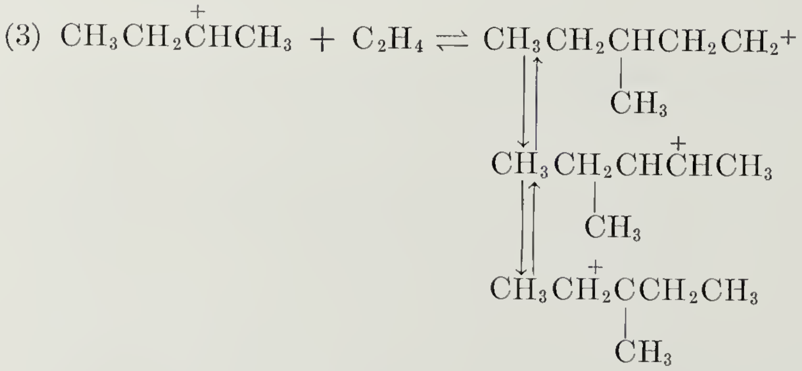
In another interesting reaction[118], ethyl 2-ethyl-2-methylbutyrate was the principal and unexpected product obtained when ethylene and carbon monoxide were heated to 115°C and 100 atm. in the presence of boron fluoride hydrate (1:1.7 mole ratio) catalyst. The authors offered evidence of the following mechanism:

(1) $\mathrm{C_2H_4 + H^+ \rightleftharpoons CH_3CH_2^+}$ I

(2) $\mathrm{CH_3CH_2^+ + C_2H_4 \rightleftharpoons CH_3CH_2CH_2CH_2^+}$ II

$$\mathrm{\Updownarrow}$$

$\mathrm{CH_3CH_2\overset{+}{C}HCH_3}$ III



(3) $\mathrm{CH_3CH_2\overset{+}{C}HCH_3 + C_2H_4 \rightleftharpoons CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2CH_2^+}$ IV

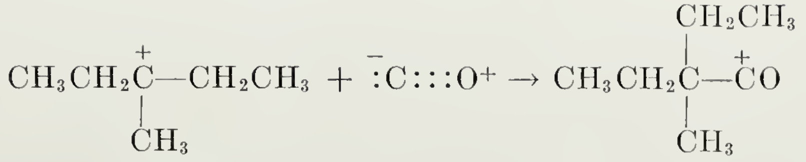
$$\Updownarrow$$

$\mathrm{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}\overset{+}{C}HCH_3}$ V

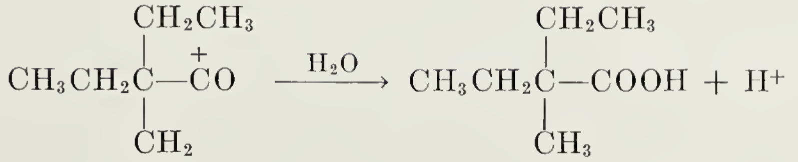
$$\Updownarrow$$

$\mathrm{CH_3CH_2\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}CH_2CH_3}$ VI

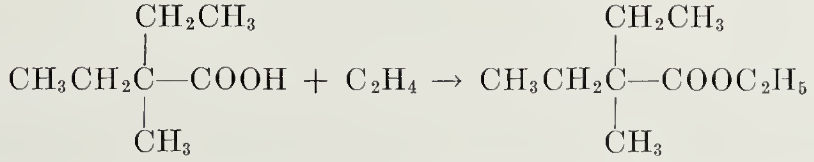
The relatively stable carbonium ion (VI) can react in turn with carbon monoxide, water, and finally with ethylene to form the ester (IX). (Equations 4, 5, and 6).



$$(4)\quad CH_3CH_2\underset{\displaystyle CH_3}{\overset{+}{C}}-CH_2CH_3 + \overset{-}{:}C:::O^+ \rightarrow CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_3}{C}}-\overset{+}{C}O \qquad \text{VII}$$



$$(5)\quad CH_3CH_2\underset{\displaystyle CH_2}{\overset{\displaystyle CH_2CH_3}{C}}-\overset{+}{C}O \xrightarrow{H_2O} CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_3}{C}}-COOH + H^+ \qquad \text{VIII}$$



$$(6)\quad CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_3}{C}}-COOH + C_2H_4 \rightarrow CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_3}{C}}-COOC_2H_5 \qquad \text{IX}$$

The tendency of the intermediate carbonium ions to satisfy the electron deficiencies of the carbon atoms by rearrangement to more stable forms, that is, from primary to secondary to tertiary, must be very large since products corresponding to intermediates (II), (IV), and (V) were not found. The distillation curve of the reaction mixture showed slight breaks at the boiling points of ethyl propionate and ethyl 2-methylbutyrate; these compounds would be obtained from (I) and (III), respectively, by carboxylation and esterification.

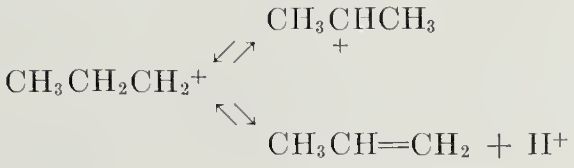
When the reaction between an olefin and carbon monoxide is carried out in the presence of an alcohol rather than with steam, there usually is secured a mixture of acids, esters, and ethers. In one example[134], methanol was injected into a gaseous mixture containing 32 per cent of carbon monoxide, 4.5 per cent of ethylene, and 63.5 per cent of hydrogen. The mixture was passed at 700 atm. and 325°C over charcoal impregnated with phosphoric acid. The condensate contained 5.8 per cent of propionic acid and 9.2 per cent of methyl propionate. About half of the methanol was converted to dimethyl ether.

From Alcohols. In the presence of acid catalysts, alcohols may form carbonium ions according to the following equation:

$$ROH + H^+ \rightleftharpoons R\overset{+}{O}H_2 \rightleftharpoons R^+ + H_2O$$

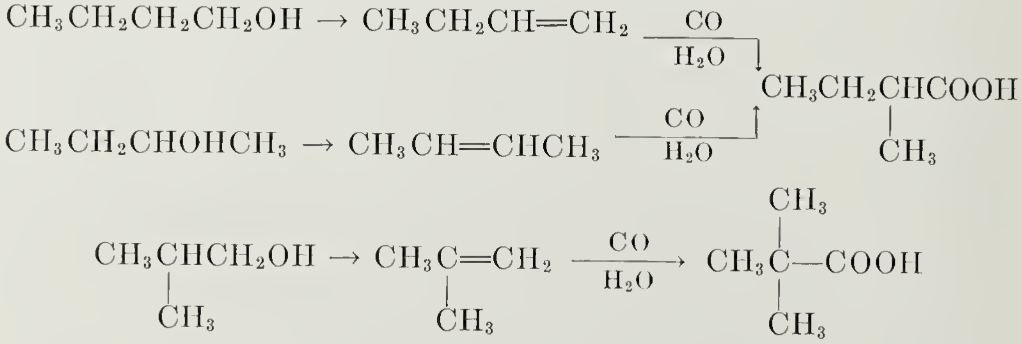
This ion may react as such, it may rearrange, or it may lose a proton to form an olefin. These possibilities are illustrated with propanol

$$CH_3CH_2CH_2OH + H^+ \rightarrow CH_3CH_2CH_2^+ + H_2O$$



Under acidic conditions, alcohols may therefore be regarded as potential olefins and should react with carbon monoxide. If steam is present, the product will be principally branched-chain acids; if water is absent, esters may predominate.

The behavior of various alcohols in the presence of steam, phosphoric acid, and carbon monoxide at elevated temperatures and pressures was reported in a series of articles by Hardy[60]. He passed mixtures of alcoholic vapor, steam, and carbon monoxide under a pressure of 200 atm. through phosphoric acid containing a small amount of copper phosphate. With ethanol, at 250 to 370°C, ethylenic polymers were formed at two to three times the rate at which propionic acid was produced. Both propanol and 2-propanol reacted readily with carbon monoxide at 150 to 250°C. Both alcohols gave isobutyric acid; no butyric acid was present. Substantial quantities of higher acids were also present. Hardy concluded that the alcohols were first dehydrated to propylene which then either (a) reacted to give isobutyric acid or (b) polymerized to a higher molecular weight olefin which then was carboxylated. The reactions of *n*-, *sec*-, and *iso*-butyl alcohols were also studied and in each case, the products were best explained by the assumption that a preliminary dehydration occurred followed by attack of the carbon monoxide on the olefin. Both *n*-, and *sec*-butyl alcohol gave 2-methylbutyric acid and pivalic acid with the latter predominating. Isobutyl alcohol gave principally pivalic acid with only a trace of 2-methylbutyric acid. The reactions may be summarized as follows:



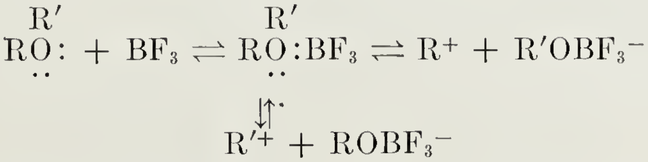
$$CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH{=}CH_2 \xrightarrow[H_2O]{CO} CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}COOH$$

$$CH_3CH_2CHOHCH_3 \rightarrow CH_3CH{=}CHCH_3 \xrightarrow[H_2O]{CO} CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}COOH$$

$$CH_3\underset{\substack{|\\ CH_3}}{CH}CH_2OH \rightarrow CH_3\underset{\substack{|\\ CH_3}}{C}{=}CH_2 \xrightarrow[H_2O]{CO} CH_3\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}{-}COOH$$

From Ethers. Inasmuch as ethers can form carbonium ions, it is reasonable to expect that treatment of ethers with acid in the presence of carbon monoxide will produce carboxylic acids and esters. There are many patents describing this reaction. In a typical example[89] the authors prepared the catalyst by passing 46 parts by weight of dry methyl ether into a flask into which 67.8 parts of dry boron trifluoride was simultaneously admitted. A heavy liquid consisting of 1:1 $BF_3:(CH_3)_2O$ was formed. When 308 grams of this substance was treated with carbon monoxide at 900 atm. and 150 to 190°C for 2 hours and the product distilled, a weight of methyl acetate corresponding to a 65 per cent conversion of the methyl ether was secured.

It may be profitable to consider briefly the nature of the boron trifluoride catalysis. The alkylation of benzene by alcohols in the presence of boron trifluoride was first assumed to proceed via an olefin[95]. However, Price and Ciskowski[111] showed that the olefin mechanism was not necessary, and they proposed the following mechanism for alkylation with ethers catalyzed by boron trifluoride:

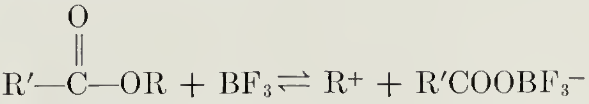


$$\underset{\cdot\cdot}{\overset{R'}{RO}}: + BF_3 \rightleftharpoons \underset{\cdot\cdot}{\overset{R'}{RO}}:BF_3 \rightleftharpoons R^+ + R'OBF_3^-$$

$$\downarrow\uparrow$$

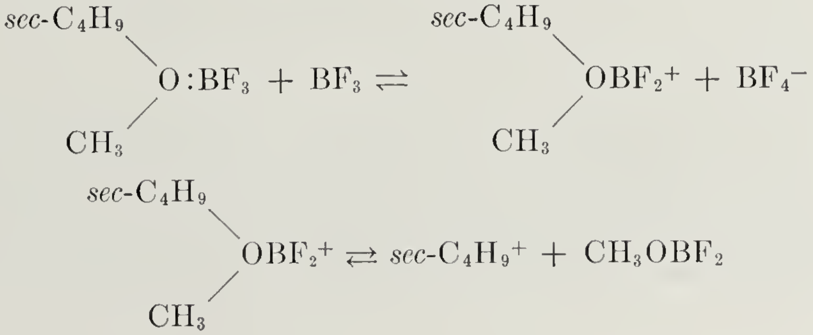
$$R'^+ + ROBF_3^-$$

With mixed ethers such as benzyl ethyl ether, $C_6H_5CH_2OC_2H_5$, the benzyl carbonium ion is formed preferentially. With aliphatic esters, the carbonium ion is usually formed from the alkyl group attached to the oxygen, resulting in alkylation rather than acylation:



$$R'\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OR + BF_3 \rightleftharpoons R^+ + R'COOBF_3^-$$

The results of the alkylation of aromatic hydrocarbons by *sec*-butyl methyl ether[23] make necessary some modifications of the above mechanism, at least for secondary ethers. With mole ratios of boron trifluoride to ether of about 0.9 and aromatic hydrocarbon-ether ratios of about 6, no alkylation could be observed after months at room temperature. It was found that reasonably rapid alkylation with *sec*-butyl methyl ether at room temperature required the presence of small additional quantities of boron trifluoride or of strong proton acids, or of substances that become strong proton acids when complexed with boron trifluoride. When benzene was alkylated with *sec*-butyl methyl ether, no toluene could be detected in the products; this is consistent with a carbonium ion reaction since one would expect the formation of *sec*-butyl carbonium ions enormously to outweigh that of methyl carbonium ions. Burwell, Elkins, and Shields[23] postulated that, with a mole ratio of boron trifluoride to ether in the vicinity of one or greater, carbonium ions may be formed in the following manner:



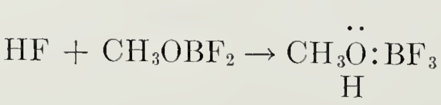
In the presence of strong acids, the reaction may proceed through the oxonium ion:

$$(sec\text{-}C_4H_9)(CH_3)OH^+ \rightleftarrows sec\text{-}C_4H_9^+ + CH_3OH.$$

Once the carbonium ion is formed, it attacks the benzene nucleus. The stoichiometry of the reaction may be satisfied by several alternate equations, one of which may be written as follows[24]:

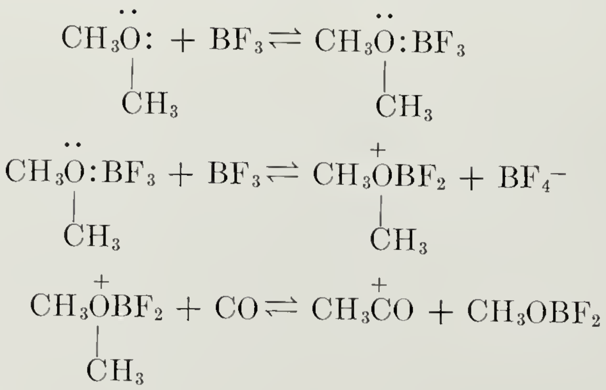
$$R^+ + C_6H_6 \rightleftharpoons RC_6H_6^+$$

$$RC_6H_6^+ + BF_4^- \rightarrow RC_6H_5 + HF + BF_3$$



$$HF + CH_3OBF_2 \rightarrow CH_3\underset{H}{\ddot{O}}:BF_3$$

The reaction mechanism by which dimethyl ether reacts with carbon monoxide in the presence of boron trifluoride may be written:



$$\underset{\substack{|\\ CH_3}}{CH_3\ddot{O}:} + BF_3 \rightleftharpoons \underset{\substack{|\\ CH_3}}{CH_3\ddot{O}}:BF_3$$

$$\underset{\substack{|\\ CH_3}}{CH_3\ddot{O}}:BF_3 + BF_3 \rightleftharpoons \underset{\substack{|\\ CH_3}}{CH_3\overset{+}{O}}BF_2 + BF_4^-$$

$$\underset{\substack{|\\ CH_3}}{CH_3\overset{+}{O}}BF_2 + CO \rightleftharpoons CH_3\overset{+}{C}O + CH_3OBF_2$$

$$CH_3\overset{+}{C}O + CH_3OBF_2 + BF_4^- \rightarrow CH_3COOCH_3 + 2BF_3$$

It is still an open question as to whether excess boron trifluoride is required for primary dialkyl ethers to function as alkylating reagents. The patent literature seems to indicate that dry boron trifluoride is frequently ineffective whereas the trihydrate is often a good catalyst in the same reaction.

The reaction of ethers with carbon monoxide can be applied to more complex substrates. Thus, dimethyl succinate has been synthesized[52] by the treatment of methyl 3-methoxypropionate, an ether, with carbon monoxide and boron trifluoride.

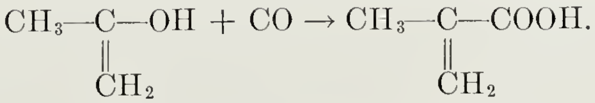
$$CH_3OCH_2CH_2COOCH_3 + CO \xrightarrow{800\text{–}900\ \text{atm.}} CH_3OOCCH_2CH_2COOCH_3$$

The highest yield (60 per cent) of dimethyl succinate was secured at 200°C with a boron trifluoride-ether ratio of 1.08.

From Ketones. In his experiments on the reaction of carbon monoxide with alcohols in the presence of steam and a phosphoric acid catalyst, Hardy found[60] that the over-all reaction which resulted in the formation of carboxylic acids could be represented by the following equation, with isopropyl alcohol as an example:

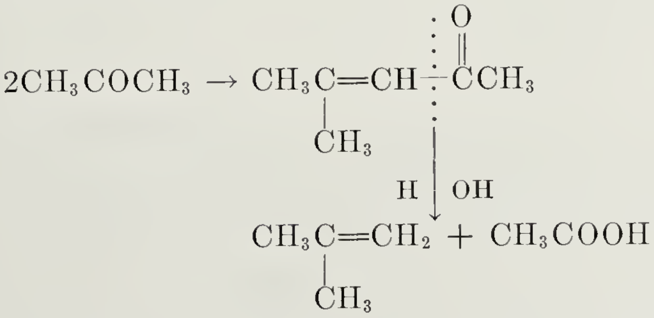
$$(CH_3)_2CHOH + CO \rightarrow (CH_3)_2CHCOOH.$$

With this in mind, he proposed to treat ketones under the same conditions in the hope that they would react in the enolic form to give unsaturated acids. Acetone, for example, might react in the following manner:



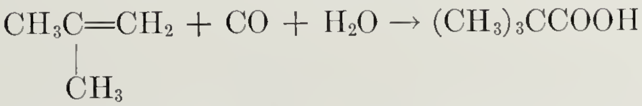
$$CH_3{-}\underset{\underset{CH_2}{\|}}{C}{-}OH + CO \rightarrow CH_3{-}\underset{\underset{CH_2}{\|}}{C}{-}COOH.$$

However, he found[61] that when a mixture of acetone and water vapor was led with carbon monoxide through liquid phosphoric acid at 200 to 210°C, a mixture of acetic and pivalic acids was formed in the molar ratio of 2:1. At the time Hardy did the work, he was unaware that essentially the same results had been reported earlier in the patent literature[81]. Hardy explained the reaction products as arising from the condensation of 2 moles of acetone to mesityl oxide, followed by hydrolytic fission of this compound to isobutylene and acetic acid.



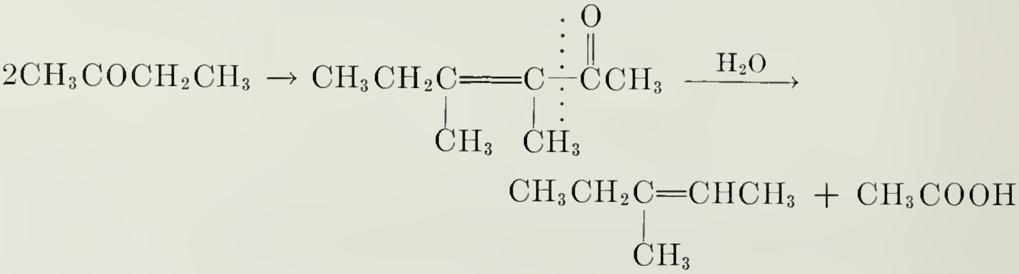
$$2CH_3COCH_3 \rightarrow CH_3\underset{\underset{CH_3}{|}}{C}{=}CH \vdots \overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{H\ |\ OH} CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2 + CH_3COOH$$

Part of the isobutylene polymerized to higher olefins and the remainder reacted with carbon monoxide and steam to give pivalic acid in the known fashion:



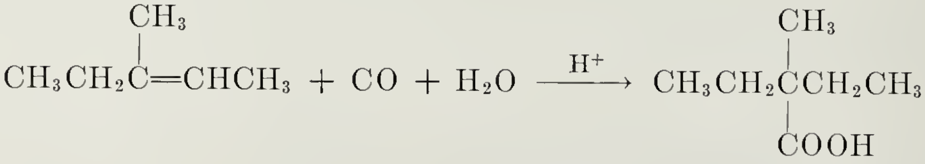
$$CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2 + CO + H_2O \rightarrow (CH_3)_3CCOOH$$

Confirmation of this mechanism was obtained by the treatment of mesityl oxide with carbon monoxide and steam in the presence of phosphoric acid; acetic and pivalic acids were readily obtained. Moreover, if hydrogen or nitrogen were employed in place of carbon monoxide, acetone yielded acetic acid together with an increased amount of neutral, unsaturated oil, this reaction being independent of pressure. In the absence of carbon monoxide, therefore, no pivalic acid could be formed. Attempts to isolate isobutylene failed; it evidently polymerizes under reaction conditions. When methyl ethyl ketone was treated similarly to acetone, a complex mixture of acids resulted. The following compounds were identified; acetic, propionic, 2,2-dimethylbutyric, 2,2-dimethylvaleric, and 2-ethyl-2-methylbutyric acids. Acetic acid and the two C_7 acids constituted the bulk of the mixture and could have been produced only by hydrolytic fission of 3,4-dimethyl-3-hexen-2-one obtained by loss of methylene hydrogen:



$$2CH_3COCH_2CH_3 \rightarrow CH_3CH_2\underset{\substack{|\\CH_3}}{C}{=}\underset{\substack{|\\CH_3}}{C}{-}\overset{\substack{O\\\|}}{C}CH_3 \xrightarrow{H_2O} CH_3CH_2\underset{\substack{|\\CH_3}}{C}{=}CHCH_3 + CH_3COOH$$

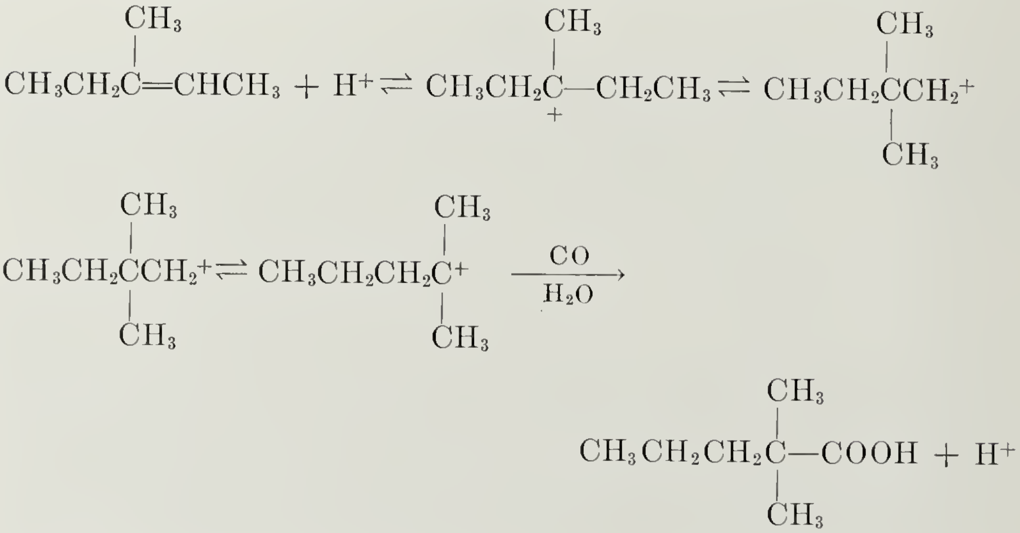
This reaction was apparently followed by the reaction of 3-methyl-2-pentene with carbon monoxide and water



$$CH_3CH_2\overset{\substack{CH_3\\|}}{C}{=}CHCH_3 + CO + H_2O \xrightarrow{H^+} CH_3CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\COOH}}{C}}CH_2CH_3$$

2-ethyl-2-methylbutyric acid

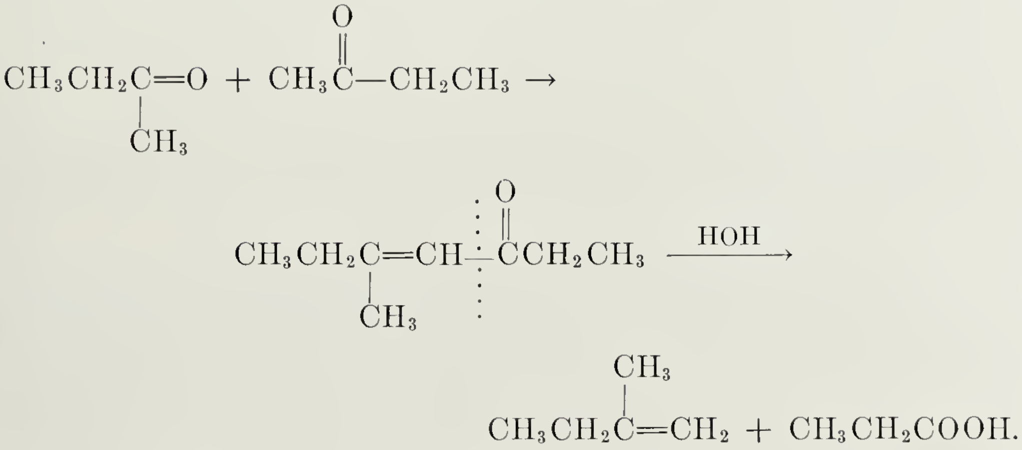
The compound, 2,2-dimethylvaleric acid, was probably secured as a result of the rearrangement of 3-methyl-2-pentene and subsequent reaction:



$$CH_3CH_2\overset{\substack{CH_3\\|}}{C}{=}CHCH_3 + H^+ \rightleftharpoons CH_3CH_2\overset{\substack{CH_3\\|}}{\underset{+}{C}}{-}CH_2CH_3 \rightleftharpoons CH_3CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}CH_2^+$$

$$CH_3CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}CH_2^+ \rightleftharpoons CH_3CH_2CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}{}^+ \xrightarrow[H_2O]{CO} CH_3CH_2CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}{-}COOH + H^+$$

The two remaining acids isolated from the mixture, namely, propionic and 2,2-dimethylbutyric acids, are derived from the other possible unsaturated ketone obtained by loss of methyl hydrogen:

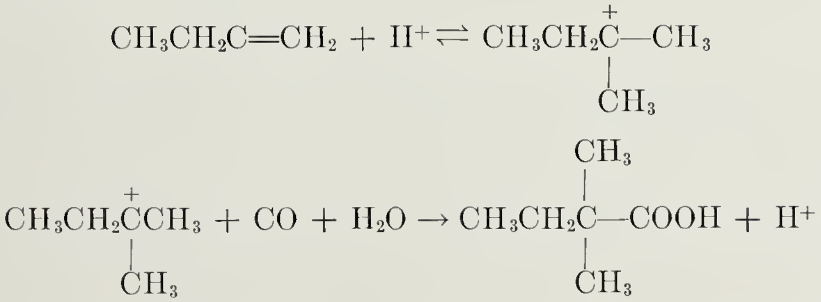


$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O + CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2CH_3 \rightarrow$$

$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH \vdots \overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{HOH}$$

$$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + CH_3CH_2COOH.$$

The 2-methyl-1-butene reacts with carbon monoxide and water as expected to give 2,2-dimethylbutyric acid:



$$CH_3CH_2C{=}CH_2 + H^+ \rightleftharpoons CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}{-}CH_3$$

$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}CH_3 + CO + H_2O \rightarrow CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}COOH + H^+$$

It is evident that in the presence of phosphoric acid under Hardy's experimental conditions, methyl ethyl ketone condenses with itself to give a mixture of a dimethylhexenone and a methylheptenone in which the former (methylene condensation) predominates. This is in agreement with the observations of Abbott, Kon, and Satchell[1] who found that acid catalysts favor the formation of dimethylhexenones whereas alkaline agents lead to methylheptenones.

Attempts by Hardy to apply this process to other ketones met with little success. No acid could be obtained from cyclohexanone, while diethyl ketone gave a very small amount of a mixture of propionic acid and an unidentified heptanoic acid instead of the anticipated octanoic acid. However, the patent literature contains references to the successful reaction of diethyl ketone and other ketones under somewhat different conditions[32].

From Aldehydes. One of the most important commercial processes in the United States utilizing carbon monoxide is its condensation with aqueous formaldehyde to produce glycollic acid:

$$HCHO + CO + H_2O \rightarrow HOCH_2COOH.$$

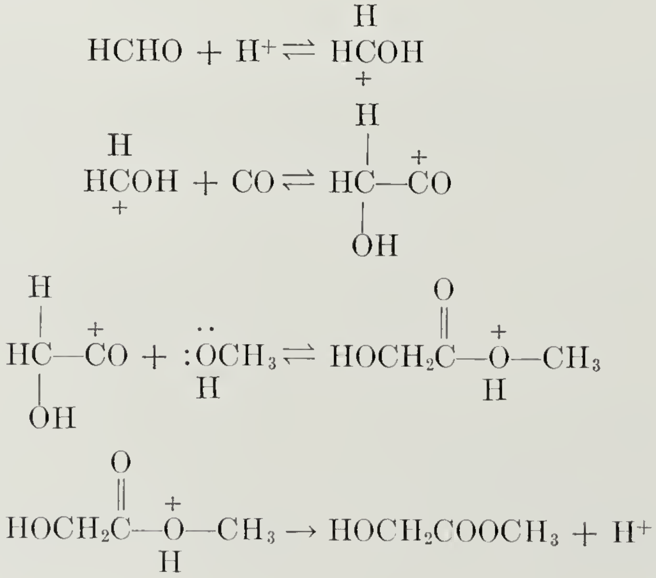
In a typical example from the patent literature[83], the reaction is described as follows: One mole of formaldehyde, 2 moles of water, 2 moles of glycollic acid, and 0.03 mole of sulfuric acid are heated at 200°C with 700 atm. of carbon monoxide for 5 minutes. The yield is 90 per cent based on the formaldehyde. The presence of glycollic acid as a solvent apparently is beneficial. The glycollic acid may be removed by crystallization or distillation.

The commercial importance of glycollic acid stems from the fact that it is the precursor of ethylene glycol. Conversion proceeds via esterification of the acid with methanol to yield methyl glycollate. This ester, on vapor-phase hydrogenation with copper chromite as catalyst at 200–225°C and 20 to 40 atm. pressure, gives ethylene glycol in high yield[84]. The methyl alcohol is recovered and recycled:

$$\begin{array}{l} HOCH_2COOH + CH_3OH \rightarrow HOCH_2COOCH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow + 2H_2 \\ \qquad\qquad\qquad\qquad\qquad\quad HOCH_2CH_2OH + CH_3OH \end{array}$$

When the condensation of formaldehyde is carried out in aqueous methanol, methyl glycollate is secured directly, but the yield is only 60 per cent compared to over 90 per cent by the two-stage process[90].

The steps in the formation of glycollic acid (or methyl glycollate) from formaldehyde and carbon monoxide in the presence of acids may be written in the following manner:



$$HCHO + H^+ \rightleftharpoons H\underset{+}{\overset{H}{C}}OH$$

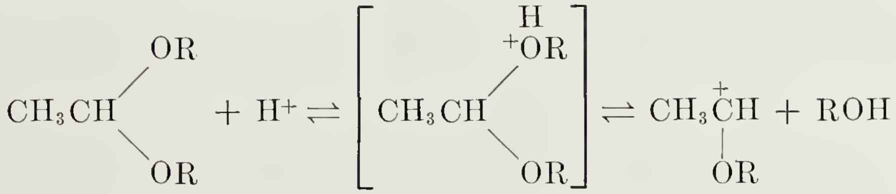
$$H\underset{+}{\overset{H}{C}}OH + CO \rightleftharpoons H\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{+}{C}O$$

$$H\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{+}{C}O + :\underset{H}{\ddot{O}}CH_3 \rightleftharpoons HOCH_2\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{+}{O}}-CH_3$$

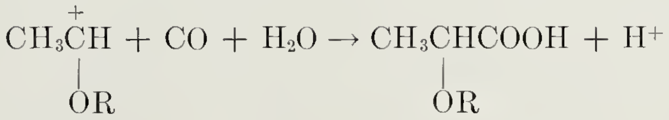
$$HOCH_2\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{+}{O}}-CH_3 \rightarrow HOCH_2COOCH_3 + H^+$$

Acetaldehyde has been reported to yield lactic acid by similar treatment[91].

From Acetals. It is well known that acetals are hydrolyzed to alcohols and aldehydes easily in the presence of acids; the reaction probably proceeds through an intermediate carbonium ion which conceivably could add carbon monoxide in the usual manner

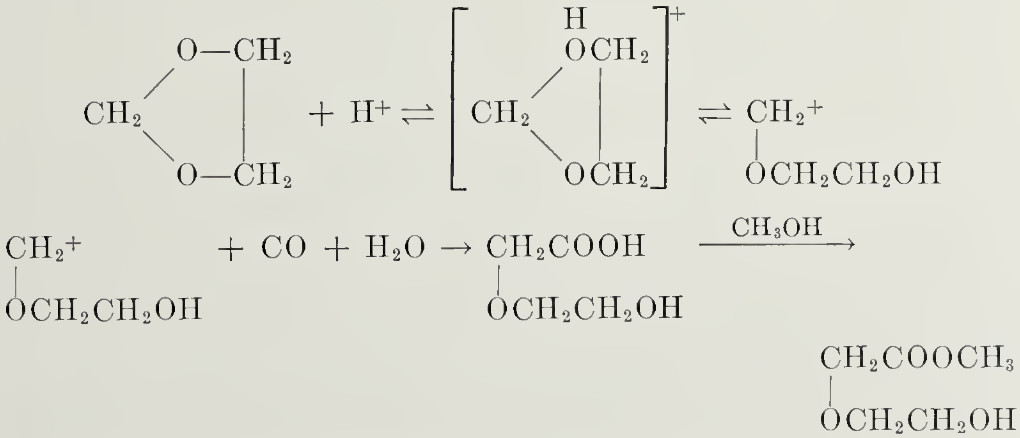


In the presence of water, ∝-alkoxy acids are formed:



$$\underset{\displaystyle OR}{\underset{|}{CH_3\overset{+}{C}H}} + CO + H_2O \rightarrow \underset{\displaystyle OR}{\underset{|}{CH_3CH}}COOH + H^+$$

Gresham[53] treated 1,3-dioxolane (the ethylene glycol acetal of formaldehyde) with 200 to 700 atm. of carbon monoxide at 90 to 120°C in the presence of boron trifluoride and sulfuric acid; he obtained a good yield of a polymeric ester. This polymeric material, when refluxed with methanol, yielded methyl 2-hydroxyethoxyglycollate whose formation can be explained as follows:



$$\underset{\displaystyle OCH_2CH_2OH}{\underset{|}{CH_2^+}} + CO + H_2O \rightarrow \underset{\displaystyle OCH_2CH_2OH}{\underset{|}{CH_2}}COOH \xrightarrow{CH_3OH} \underset{\displaystyle OCH_2CH_2OH}{\underset{|}{CH_2}}COOCH_3$$

From Water—the Synthesis of Formic Acid. Formic acid readily decomposes into carbon monoxide and water when heated with acid:

$$HCOOH \rightleftharpoons H_2O + CO$$

This is the method by which carbon monoxide is most conveniently prepared in the laboratory. Much work has been done in an effort to reverse the reaction and synthesize formic acid from carbon monoxide, but no such synthesis is in use today.

Branch[15] determined the equilibrium constant of the reaction.

$$HCOOH\ (aq.) \rightleftharpoons H_2O\ (l) + CO\quad (g)$$

He used $0.5M$ hydrochloric acid instead of pure water and obtained values for the equilibrium constant of 89.9 at 156.1°C and 310 at 217.9°C. Table 5 shows the calculated pressures that would be needed at a few selected temperatures to obtain various concentrations of formic acid.

Table 5. Pressures Required to Secure Various Concentrations of Formic Acid[a]

Concentration of HCOOH by Weight (%)	Pressure of CO (Atmospheres)			
	25°C	100°C	160°C	217.9°C
1	0.26	6.2	30	69
10	3	70.5	360	781
20	7.1	167.3	850	1850
50	36	847	4200	9380
90	1065	25,100	125,000	278,000

[a] From Reference 3.

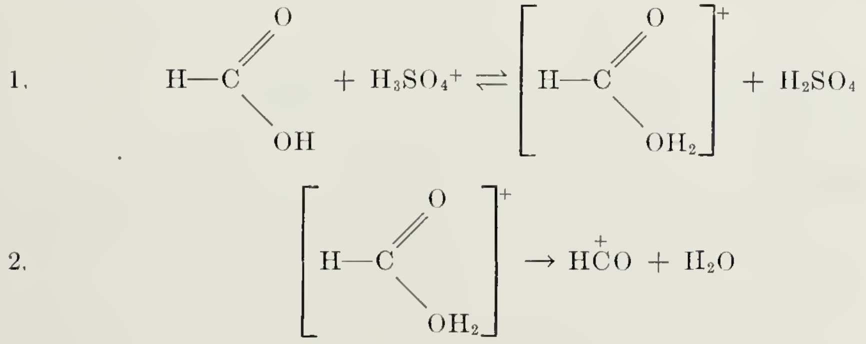
Table 6. Comparison of Calculated and Experimental Yields of Formic Acid at 160°C[a]

Pressure (atm.)	Calculated, Branch[15]	Found, Pichler[108]
500	12	11
1000	23	24
1500	32	34
2000	40	46

[a] Per cent by weight, formic acid in water.

Pichler and Buffleb[108] investigated the variables affecting the synthesis of formic acid from carbon monoxide in copper-lined autoclaves. Poor conversions to formic acid for the uncatalyzed reaction of carbon monoxide and water were obtained; the highest yield was an $0.8N$ solution of formic acid at 180°C and 1,500 atm. carbon monoxide initial pressure with 25 milliliters of water in the autoclave. With acid catalysts such as phosphoric acid and under the above otherwise identical conditions, 5 to $6N$ formic acid was obtained. The effect of pressure was also studied. The experimental results agreed rather well with the calculations from the data of Branch obtained in 1915 (Table 6). At 225°C and 1,500 atm., Pichler obtained a $3.7N$ or 17 per cent solution of formic acid. At 218°C, Branch calculated that a 20 per cent solution of formic acid would be obtained at 1,850 atm. and a 17 per cent solution would be obtained at 1,500 atmospheres.

Although only little work on the kinetics of formic acid synthesis with a view toward mechanism has been published, the reverse reaction, the decomposition of formic acid by acid catalysis, has been studied. The following mechanism has been suggested[58].



3. $H\overset{+}{C}O + H_2SO_4 \rightarrow CO + H_3SO_4^+$

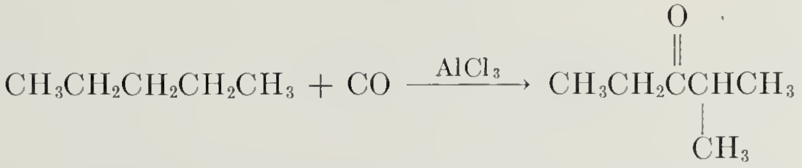
The mechanism of the synthesis of formic acid under high pressure of carbon monoxide may be considered to be the reverse of the above scheme.

Most of the formic acid used today is made by the acidification of sodium formate obtained by the treatment of carbon monoxide with sodium hydroxide.

$$CO + NaOH \xrightarrow[160\text{-}200°C]{10\text{-}15\text{ atm.}} HCOONa \xrightarrow{H^+} HCOOH$$

Reactions with Saturated Hydrocarbons

Aliphatic Hydrocarbons. The reaction of carbon monoxide with saturated aliphatic compounds has not been extensively studied. The reaction is achieved at room temperature in the presence of aluminum chloride and high partial pressures of carbon monoxide. In what is perhaps the earliest published study[65], *n*-pentane was shaken with aluminum chloride in the presence of 100 atm. of carbon monoxide at 50°C and a yield of 40 to 50 per cent of ethyl isopropyl ketone was secured:



$$CH_3CH_2CH_2CH_2CH_3 + CO \xrightarrow{AlCl_3} CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{|}}{C}HCH_3$$

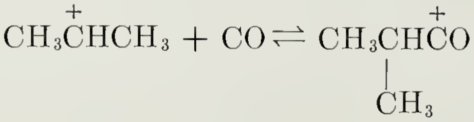
Some 2-methylvaleric acid was also isolated and identified.

More recently, in an effort to advance the knowledge of the mechanism of the reaction, propane was treated with aluminum chloride-hydrogen chloride and 125 atm. of carbon monoxide at 80°C. The products of the reaction were isobutyric acid (5 per cent); isobutyl-isobutyrate (44 per cent), and 2,5-dimethyl-4-hexen-3-one (23 per cent) with yields based on the carbon monoxide consumed. The products can be explained on the basis that isobutyraldehyde is the primary product of the reaction, and its formation by the following chain mechanism was proposed[109]:

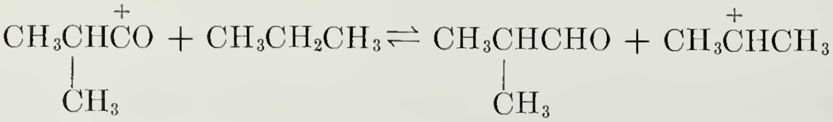
$$HCl + CO \rightleftharpoons HCOCl$$

$$HCOCl + AlCl_3 \rightleftharpoons HCOAlCl_4 \rightleftharpoons H\overset{+}{C}O(AlCl_4)^-$$

$$CH_3CH_2CH_3 + H\overset{+}{C}O(AlCl_4)^- \rightleftharpoons CH_3\overset{+}{C}HCH_3 + HCHO + AlCl_4^-$$

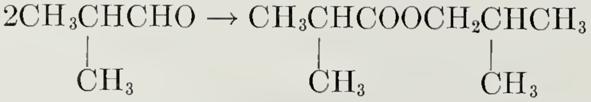


$$CH_3\overset{+}{C}HCH_3 + CO \rightleftharpoons CH_3\underset{\underset{CH_3}{|}}{C}H\overset{+}{C}O$$



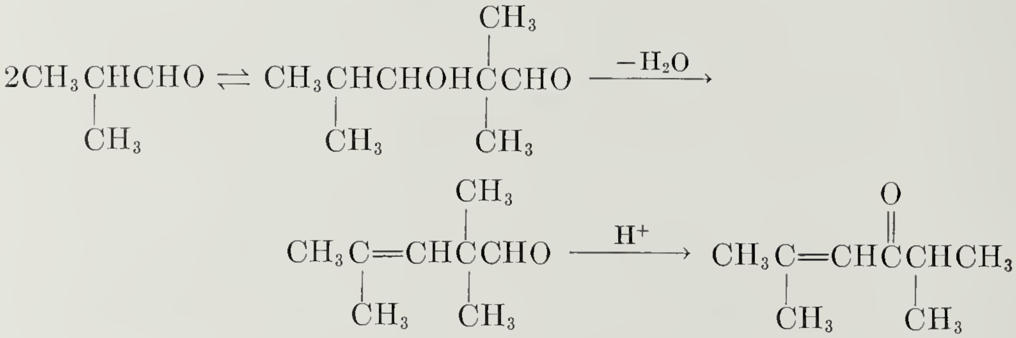
$$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{+}{C}O + CH_3CH_2CH_3 \rightleftharpoons CH_3\underset{\underset{CH_3}{|}}{C}HCHO + CH_3\overset{+}{C}HCH_3$$

The isobutyraldehyde formed in this manner was assumed to undergo various condensations to the final isolatable products. Isobutyl-isobutyrate was accounted for by assuming a Tischenko intermolecular oxidation-reduction:



$$2CH_3\underset{\underset{CH_3}{|}}{C}HCHO \rightarrow CH_3\underset{\underset{CH_3}{|}}{C}HCOOCH_2\underset{\underset{CH_3}{|}}{C}HCH_3$$

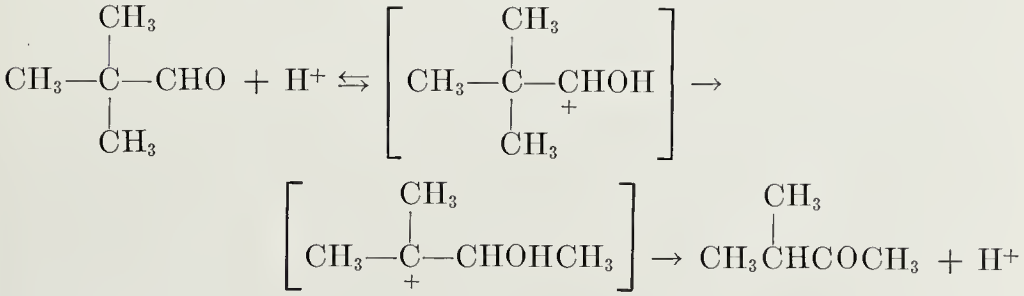
The formation of 2,5-dimethyl-4-hexen-3-one was accounted for by the assumption that an aldolization followed by dehydration and isomerization had occurred:



$$2CH_3\underset{\underset{CH_3}{|}}{C}HCHO \rightleftharpoons CH_3\underset{\underset{CH_3}{|}}{C}HCHOH\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CHO \xrightarrow{-H_2O}$$

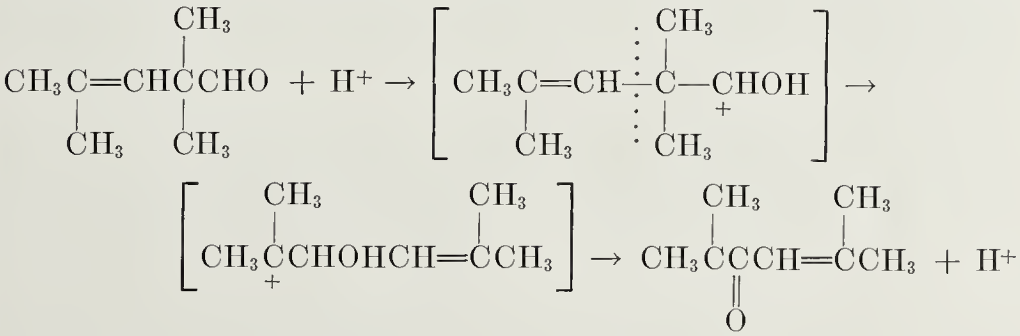
$$CH_3\underset{\underset{CH_3}{|}}{C}{=}CH\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CHO \xrightarrow{H^+} CH_3\underset{\underset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{C}HCH_3$$

The acid catalyzed rearrangement in the last step is analogous to the isomerization of other tertiary aldehydes. In the simplest example, 2,2-dimethylpropanal (pivalic aldehyde) has been isomerized to methyl isopropyl ketone by either sulfuric acid[36] or by aluminum chloride[66]. The following mechanism may be written for the transformation:



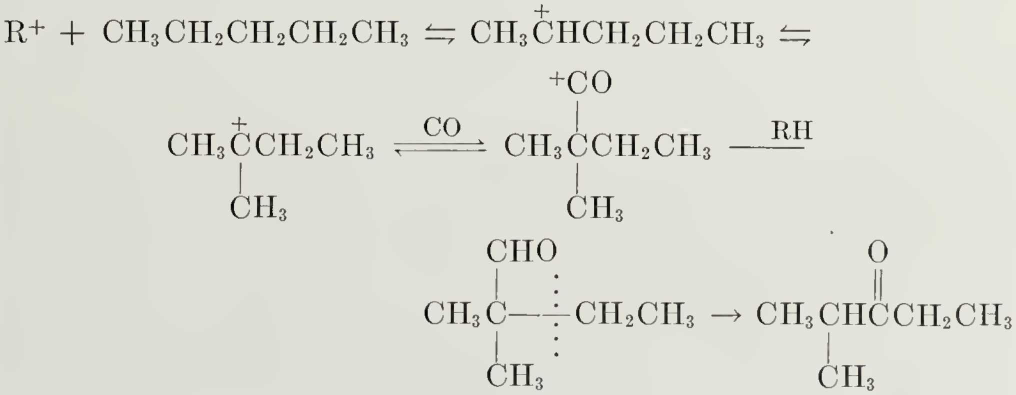
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO + H^+ \rightleftarrows \left[CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{C}HOH\right] \rightarrow \left[CH_3-\underset{+}{\overset{CH_3}{C}}-CHOHCH_3\right] \rightarrow CH_3\overset{CH_3}{C}HCOCH_3 + H^+$$

A similar rearrangement of the aldehyde postulated to occur in the propane reaction leads to the isolated ketone:



$$CH_3\underset{CH_3}{C}{=}CH\underset{CH_3}{\overset{CH_3}{C}}CHO + H^+ \rightarrow \left[CH_3\underset{CH_3}{C}{=}CH\,\vdots\,\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{C}HOH\right] \rightarrow \left[CH_3\underset{+}{\overset{CH_3}{C}}CHOHCH{=}\overset{CH_3}{C}CH_3\right] \rightarrow CH_3\overset{CH_3}{C}\underset{O}{\underset{\|}{C}}CH{=}\overset{CH_3}{C}CH_3 + H^+$$

On the basis of such a rearrangement, it is possible to explain the formation of ethyl isopropyl ketone from n-pentane given as the first example of the reaction of aliphatic hydrocarbons with carbon monoxide. It can be assumed that n-pentane, under acid conditions, rearranges to isopentane and the tertiary carbon atom in the branched-chain isomer is the site of initial attack to produce the chain-carrying carbonium ion:



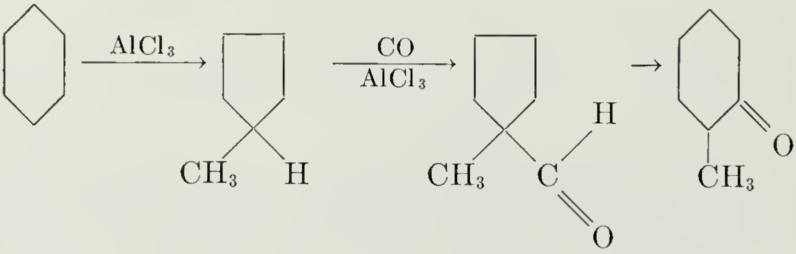
$$R^+ + CH_3CH_2CH_2CH_2CH_3 \rightleftarrows CH_3\overset{+}{C}HCH_2CH_2CH_3 \rightleftarrows$$

$$CH_3\underset{CH_3}{\overset{+}{C}}CH_2CH_3 \overset{CO}{\rightleftarrows} CH_3\underset{CH_3}{\overset{+CO}{C}}CH_2CH_3 \xrightarrow{RH}$$

$$CH_3\underset{CH_3}{\overset{CHO}{C}}-\vdots-CH_2CH_3 \rightarrow CH_3\underset{CH_3}{C}H\overset{O}{\overset{\|}{C}}CH_2CH_3$$

The fact that the identical ketone is produced[65], when isopentane is used as the starting material, is consistent with the assumption that the normal isomer rearranges prior to reaction with carbon monoxide. *n*-Butane and isobutane both give methyl isopropyl ketone[66] and here again it is reasonable to assume that the *n*-isomer rearranges to the iso-compound prior to reaction. The methyl isopropyl ketone was postulated to arise from the prior formation and rearrangement of trimethylacetaldehyde because under identical conditions, the aldehyde rearranged.

Rearrangement of saturated hydrocarbons in the presence of aluminum chloride in the carbon monoxide reactions was also shown by the behavior of cyclohexane. At first[65], the carbonyl compound isolated from the reaction was assumed to be hexahydrobenzaldehyde. However, after it was shown that cyclohexane isomerizes to methylcyclopentane in the presence of aluminum chloride[101], the reaction product from cyclohexane and carbon monoxide was reinvestigated and shown conclusively[67] to be 2-methylcyclohexanone. The formation of this ketone was postulated to occur[66] as a result of the rearrangement of the intermediate 1-methylcyclopentanecarboxaldehyde:



The postulation was verified by the synthesis of the aldehyde and its almost quantitative conversion to the ketone.

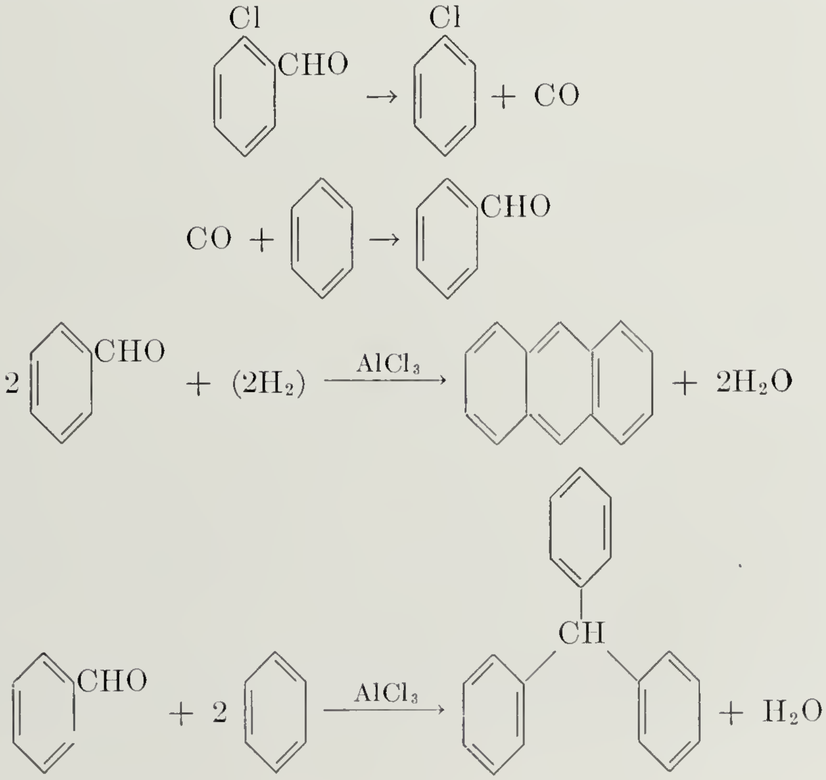
Aromatic Hydrocarbons. The Gattermann-Koch Reaction. Treatment of benzene or a substituted benzene with carbon monoxide in the presence of aluminum chloride-hydrogen chloride results in the formation of an aldehyde. With benzene, for example, benzaldehyde is formed:

The reaction was discovered by Gattermann and Koch[34, 48, 128] and further elaborated by Gattermann[49]. Gattermann and Koch prepared *p*-tolualdehyde from toluene by treating it at atmospheric pressure with a mixture of carbon monoxide and hydrogen chloride in the presence of aluminum chloride and cuprous chloride. If the cuprous chloride was omitted, the reaction proceeded to only a minor extent. Other salts such as nickel (II), cobalt(II), and iron(III) chloride may be employed and although, of the other salts, nickel is to be preferred, the yield obtained with this metal is only about half that secured with copper.

Gattermann and Koch reported that the reaction did not proceed with benzene under the conditions that were successfully employed for the participation of toluene. However, it was found subsequently that if aluminum bromide was substituted for aluminum chloride[112], or if the reaction was performed with aluminum chloride in nitrobenzene solution at 50–60°C, excellent yields of benzaldehyde could be secured.

The failure of Gattermann and Koch to secure benzaldehyde from benzene may not have been owing to the lack of its formation but perhaps to its subsequent reaction under conditions of the experiment. This is quite possible, since it has been shown[120] that benzaldehyde reacts with benzene in the presence of aluminum chloride to form anthracene and that small yields of benzaldehyde and anthracene can be secured from benzene under the conditions of the Gattermann-Koch reaction[62].

In a provocative paper, Hey[62] showed that the action of benzaldehyde on toluene gave dimethylanthracenes and no monomethylanthracene, and that *o*-chlorobenzaldehyde gave chlorobenzene and anthracene, in addition to triphenylmethane. From these experiments, Hey concluded that the aldehyde is decarbonylated during the reaction. The liberated carbon monoxide furnishes the meso (9, 10) carbon atoms in the anthracene nucleus, and the methane carbon atom in triphenylmethane. The following sequence of reactions may be visualized as occurring with *o*-chlorobenzaldehyde in benzene:



The stoichiometry of the reaction is unclear. The condensation of benzaldehyde to anthracene requires hydrogen, and the source of this hydrogen is obscure, if one accepts this reaction as being responsible for anthracene formation. The yields of anthracene in some examples were remarkably high considering the complexity of the reaction. Thus, when 23 grams of *m*-tolualdehyde was treated with aluminum chloride in 150 ml. of benzene at 60°C, 16 grams of anthracene was secured in addition to small amounts of triphenylmethane, toluene, and xylene. To demonstrate that carbon monoxide as such may be involved in the reaction, Hey bubbled the gas into hot toluene in the presence of hydrochloric acid and aluminum chloride and secured a mixture of 2,6- and 2,7-dimethylanthracenes.

The reaction was further investigated by Ungnade and co-workers[130, 131, 132] who employed a 3:1 mole excess of aluminum chloride in the reaction between *o*-chlorobenzaldehyde and benzene and obtained a remarkable 94 per cent utilization of the carbonyl carbon of the aldehyde. In these experiments, triphenylcarbinol was isolated in contrast to the triphenylmethane found by Hey. When nitrobenzaldehyde was used in the presence of benzene, diphenylnitrophenylmethanes were the sole products, and no trace of anthracene was found. When benzaldehyde was treated with aluminum chloride in the presence of a 1:1 mixture of benzene and nitrobenzene as solvent, no reaction occurred; nitrobenzene completely inhibited the reaction leading to anthracene. Ungnade and co-workers also found that when xylene, biphenyl, and diphenylmethane were used as solvents, tetramethylanthracenes, biphenylanthracenes, and dibenzylanthracenes, respectively, were produced. Benzaldehyde alone, or in a solvent such as carbon disulfide, when treated with aluminum chloride, gave large quantities of gaseous carbon monoxide.

The unravelling of the mechanism of the above condensations should be a fertile field of investigation. It appears most probable that the aldehyde first complexes with aluminum chloride and the solvent attacks this complex in a series of displacement reactions[16].

Few polynuclear compounds have been treated successfully in the Gattermann-Koch reaction. It is reported that naphthalene could not be made to react, but more recently the reaction has been repeated with a hydrogen fluoride-boron fluoride catalyst at about 0°C and 700 atm. of carbon monoxide. A 73 per cent yield of 1-naphthalenecarboxaldehyde was secured[54]. Under similar catalytic conditions, *m*- and *p*-xylene, diphenyl, mesitylene, benzene, and toluene were all converted in a good yield to the corresponding aldehydes.

In one of the few systematic studies of the Gattermann-Koch reaction, the effect of pressure, time, temperature, and ratio of reactants on the yield of benzaldehyde from benzene was determined[64]. The presence of small quantities of water was found to be essential.

Usually the Gattermann-Koch reaction is carried out with one mole of aluminum chloride per mole of aromatic hydrocarbon. If the reaction is to be operated at atmospheric pressure, the mixture is continuously saturated with dry hydrogen chloride and carriers like cuprous chloride are desirable. Presumably, the high partial pressure of carbon monoxide (30 to 70 atm.) increases the yield and decreases the time necessary to achieve satisfactory results. Reaction temperatures are generally held quite low (25 to 60°C).

A mixture of carbon monoxide and hydrogen chloride, satisfactory for use in the Gattermann-Koch reaction, can be prepared by the treatment of chlorosulfonic acid with anhydrous formic acid[10]

$$HCOOH + ClSO_3H \rightarrow CO + HCl + H_2SO_4$$

If sufficient excess chlorosulfonic acid is employed to react with water in 85 per cent formic acid, the lower concentration of acid is satisfactory.

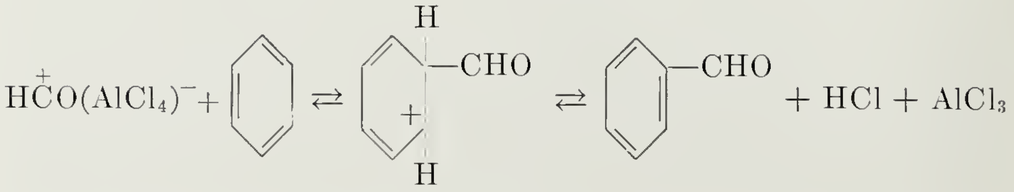
Nickel carbonyl in the presence of aluminum chloride has been used as a source of carbon monoxide in the reaction with benzene, toluene, xylene, and mesitylene in the cold[37], although the yields are not as good as those achieved by the more conventional technique. Heating the reaction lowered the yield. Iron pentacarbonyl has also been used for the same purpose[139].

Much of the work on the Gattermann-Koch reaction has been incorporated in patented material and little systematic work has been published regarding the probable mechanism of the reaction and the function of the so-called carrier catalysts like cuprous chloride. Gattermann regarded the reaction as proceeding through the intermediate formation of the hypothetical formvl chloride, $HCOCl$, which then condenses with aromatic compounds in the manner analogous to other acid chlorides in the Friedel-Crafts synthesis. The cuprous chloride probably functions as a catalyst because of its ability to bind carbon monoxide in the form of a labile molecular complex. A complex whose analysis was consistent with the formula, $HCOCl \cdot AlCl_3 \cdot CuCl$, was isolated when aluminum chloride, gaseous hydrogen chloride, and carbon monoxide were heated at 100 atmospheres in a copper-lined autoclave at 80°C[66]. Considerable absorption of both carbon monoxide and hydrogen chloride was observed, and when the cooled autoclave was opened, the yellow-brown liquid was removed and analyzed. The complex reacted vigorously with water and liberated carbon monoxide and hydrochloric acid. It reacted with toluene in the presence of anhydrous aluminum chloride to give a small but unspecified yield of *p*-tolualdehyde.

It is perhaps most simple to write a mechanism based on the formation of formyl chloride and proceeding by electrophilic attack of a formyl cation:

$$HCl + CO \leftrightharpoons HCOCl$$

$$HCOCl + AlCl_3 \leftrightharpoons H\overset{+}{C}O(AlCl_4)^-$$



The work of Eley and Campbell[41] has shown that the Gattermann-Koch synthesis with benzene is rendered thermodynamically favorable by the formation of an aluminum chloride complex of benzaldehyde as a stable end product. The data in Table 7 were secured by Dilke and Eley[39] for the reaction $C_6H_6(l) + CO(g) \rightarrow C_6H_5CHO(l)$.

TABLE 7. BENZALDEHYDE EQUILIBRIA[39]

Temperature (°K)	298	323	373
ΔF° (cal/mole)	2,060	2,830	4,350
Equilibrium constant, K × 10³	31.6	12.6	2.9

TABLE 8. CALCULATED EQUILIBRIUM CONSTANTS AND YIELDS FOR BENZALDEHYDE COMPLEXES WITH ALUMINUM CHLORIDE[39]

Temperature (°K)	298	323	373
ΔF° (cal/mole)	−380	2,360	7,630
Equilibrium constant (K)	1.9	0.026	3.6×10^{-5}
Yield (%)	93.5	16.5	0.027

According to these data, the yield of benzaldehyde at room temperature should be about 2 per cent (calculated on the benzene) and should decrease with increasing temperature. The same workers[39] found that the heat of formation for the reaction

$$\tfrac{1}{2}Al_2Cl_6(s) + C_6H_5CHO(soln.) \rightarrow C_6H_5CHO \cdot AlCl_3(s)$$

was 24.7 kcal and were able to calculate equilibrium constants for the reaction:

$$C_6H_6 + CO + \tfrac{1}{2}Al_2Cl_6 \rightarrow C_6H_5CHO \cdot AlCl_3$$

which are given in Table 8.

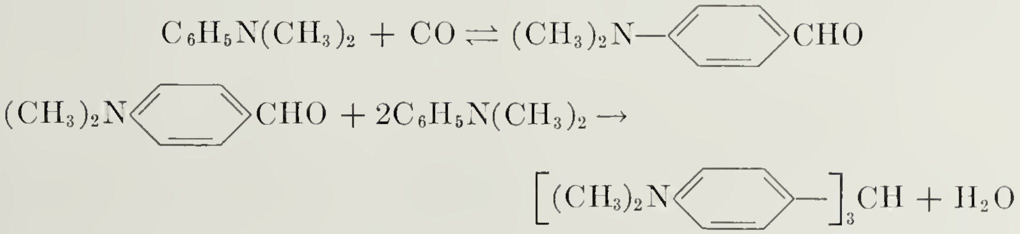
These data show that a very high yield is possible with aluminum chloride at room temperature although there is probably considerable error in the values used for the calculation of total free energy change. Experimentally, the highest yield of benzaldehyde obtainable from the reaction is about 3 per cent. Thus, although complex formation is necessary to make the reaction thermodynamically favorable, the yield depends on the reaction velocity.

The function of the carrier catalyst, which is usually cuprous chloride, has always been of considerable interest. On the basis of conductivity measurements, Dilke and Eley suggested the following equilibrium in the presence of cuprous chloride:

$$\mathrm{CO} + \mathrm{CuCl} + \mathrm{AlBr_3} \leftrightarrows \overset{+}{\mathrm{CuCO}} + \mathrm{AlBr_3Cl^-}$$

The effect of cuprous chloride cannot be to increase the thermodynamic activity of carbon monoxide. It is, however, possible that in the stationary state the reaction $\overset{+}{\mathrm{CuCO}} + \mathrm{H^+} \leftrightarrows \mathrm{Cu^+} + \overset{+}{\mathrm{HCO}}$ gives a slightly higher concentration of $\overset{+}{\mathrm{HCO}}$ than does $\mathrm{CO} + \mathrm{H^+} \rightleftharpoons \overset{+}{\mathrm{HCO}}$[39].

The Gattermann-Koch reaction can be applied to substituted aromatic compounds as well as to the parent hydrocarbons themselves. In one clever application of the reaction[88], leuco crystal violet was made in one step according to the reactions:



In one example, 150 cc of dimethylaniline and 56 grams of aluminum chloride were treated with carbon monoxide at 230 to 330 atmospheres at 25°C for about 72 hours. The yield of leuco crystal violet was 63 per cent based on consumed dimethylaniline. Chlorobenzene could be satisfactorily employed as a solvent.

Reactions with Alkyl Chlorides

In the presence of an aluminum chloride catalyst, alkyl halides react with carbon monoxide at mild temperatures. With ethyl chloride in the presence of 120 atmospheres of carbon monoxide at 40 to 50°C, a 50 per cent yield of propionic acid is obtained[65].

$$\mathrm{C_2H_5Cl} + \mathrm{CO} \xrightarrow{\mathrm{AlCl_3}} \mathrm{C_2H_5COCl} \rightarrow \mathrm{C_2H_5COOH}.$$

At very high pressures (900 atmospheres), carbon monoxide reacts with carbon tetrachloride to give trichloroacetyl chloride:

$$CCl_4 + CO \rightarrow CCl_3COCl.$$

The reaction is achieved at 200°C in the presence of an aluminum chloride catalyst (0.1 mole per mole of carbon tetrachloride) with a yield of 37 per cent. The following mechanism has been proposed[47]:

$$CCl_4 + AlCl_3 \rightarrow CCl_3^+ + AlCl_4^-$$

$$CCl_3^+ + CO \rightarrow CCl_3\overset{+}{C}O$$

$$CCl_3\overset{+}{C}O + AlCl_4^- \rightarrow CCl_3COCl + AlCl_3$$

When ferric chloride was used in place of aluminum chloride, trichloroacetyl chloride was obtained in only 7 per cent yield. Chloroform, methylene chloride, and polyhalogenated ethanes also react, but yields are much poorer. Similar reactions with methyl chloride and ethyl bromide to give acetyl chloride and acetyl bromide have been reported but, in these cases, an acid catalyst was not used[138].

Another reaction involving the preparation of an aroyl halide from carbon monoxide is the preparation of benzoyl fluoride from benzenediazonium fluoroborate by a modification of the Schieman reaction for the preparation of aromatic fluorine compounds from the stable diazonium fluoroborates[87]:

$$C_6H_5N_2BF_4 + CO \xrightarrow[1{,}000 \text{ atm.}]{C_2H_5OH} C_6H_5COF.$$

The reaction can also be successfully carried out by the use of nickel carbonyl in acid solution at room temperature.

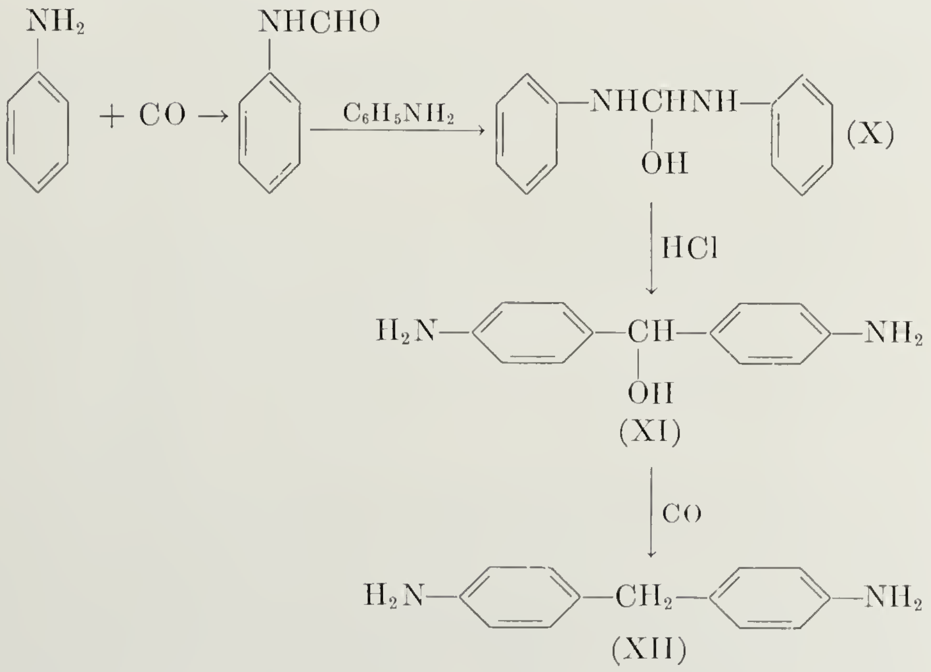
Other Acid-Catalyzed Reactions

Dimethylglycine. The reaction of a hydrochloric acid solution of formaldehyde and dimethylamine with carbon monoxide at 150 to 200°C and 800 to 1,000 atm. pressure has been reported[57] to give dimethylglycine:

$$HCHO + (CH_3)_2NH \xrightarrow{HCl} (CH_3)_2NCH_2COOH.$$

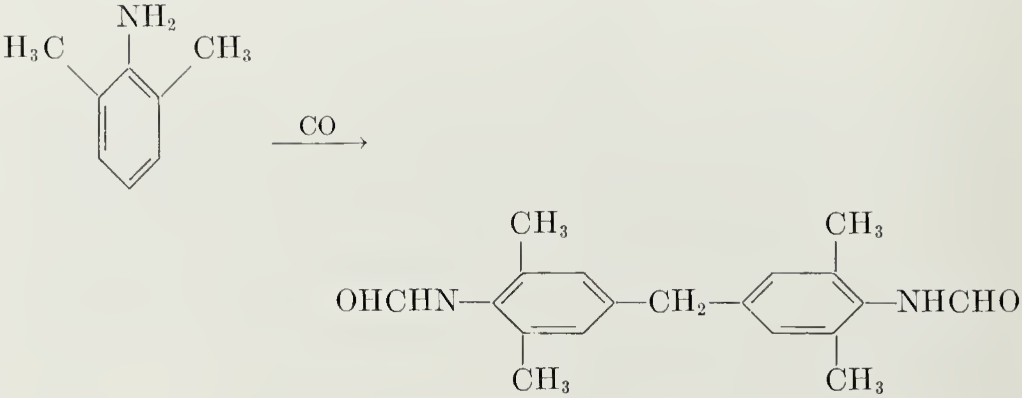
The mechanism for the reaction may be written in several ways, but it is likely that the carbonium ion $\overset{+}{C}H_2OH$ is formed since glycollic acid is a side product.

Reducing Action of Carbon Monoxide at High Pressures. A rather unusual reaction involving the acid-catalyzed addition of carbon monoxide to aromatic amines was discovered by Buckley and Ray[19]. These authors found that when aniline containing a small quantity of aniline hydrochloride was heated to 250°C with carbon monoxide at 3,000 atmospheres, the pressure fell rapidly and carbon dioxide and a brown amorphous solid were obtained. A detailed study of the reaction led to the conclusion that the initial step of the reaction was probably the interaction of aniline and carbon monoxide to give formanilide. It was postulated that this compound then reacted with more aniline to give the unstable intermediate (X) which rearranged to *p,p′*-diaminodiphenylcarbinol (XI) under the influence of the acid catalyst. The carbinol was then reduced by carbon monoxide to *p,p′*-diaminodiphenylmethane (XII)



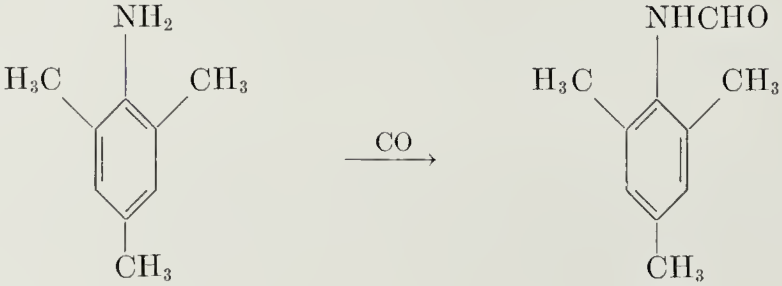
Both the diarylmethane (XII) and the carbinol (XI) contain unsubstituted positions ortho to the amino groups and could therefore react further with more carbon monoxide to give polymeric products and ultimately a completely cross-linked structure.

The behavior of substituted anilines was consistent with this interpretation. Dimethylaniline failed to react with carbon monoxide under the conditions used for aniline, and N-methylaniline gave only N-methylformanilide. Primary amines having one substituent in the *o*- or *p*-position (*o*- or *p*-toluidine) gave products closely resembling those obtained from aniline, but no evidence of cross-linking was observed. 2,6-Dimethylaniline, having only one reactive position, gave 4,4′-diformamido-3,3′,5,5′-tetramethyldiphenylmethane (XIII) as the sole product:



(XIII)

Mesidine (2,4,6-trimethylaniline), having no free *o*- or *p*-groups gave only formomesidide (XIV)



(XIV)

Buckley and Ray[20] found that many organic compounds were reduced by carbon monoxide under anhydrous conditions at high temperatures and pressures with the formation of carbon dioxide. In the absence of catalysts at 150 to 250°C and at 3,000 atmospheres, nitro, nitroso-, and azoxybenzenes were reduced to azobenzene, $C_6H_5N{=}NC_6H_5$; N-phenylhydroxylamine was reduced to aniline. In the presence of Raney cobalt, benzyl alcohol, phenylmethylcarbinol, and benzhydrol were reduced to the corresponding hydrocarbons.

The same authors[21] found that hydrazine and carbon monoxide reacted under high pressure to give a variety of products depending upon the conditions employed. At 20 to 50°C and 50 to 1,000 atmospheres of carbon monoxide, the sole products were semicarbazide and ammonia, no carbon dioxide being formed:

$$CO + 2NH_2NH_2 \rightarrow H_2NCONHNH_2 + NH_3 .$$

At 150°C and 1,000 atmospheres, 4-amino-1,2,4-triazol-3-one (XVII) was produced and at 150°C and 3,000 atmospheres, the latter was reduced to

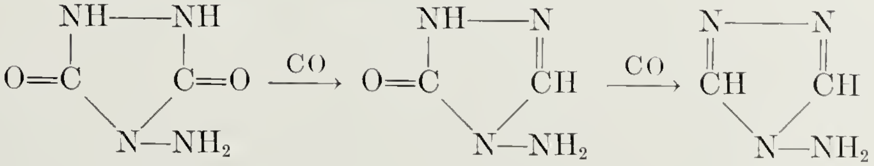
4-amino-1,2,4-triazole (XVIII). The mode of formation of these products from semicarbazide seems fairly clear. Semicarbazide on heating loses hydrazine to give hydrazodicarbonamide (XV)[35] which reacts with excess hydrazine to give 4-aminourazole (XVI)[127]. Evidently, this compound is formed in the course of the reaction of carbon monoxide with hydrazine at 150°C and its enol form must then undergo reduction by the carbon monoxide to give first (XVII) and then (XVIII).

$$2NH_2CONHNH_2$$

$$\downarrow$$

$$H_2NCONH \cdot NHCONH_2 + NH_2NH_2 \quad \rightarrow$$

(XV)



(XVI) (XVII) (XVIII)

This was confirmed by the reduction of (XVI) to (XVIII) by carbon monoxide at 150°C and 1,000 atmospheres and the reduction of (XVII) to (XVIII) at 150°C and 3,000 atmospheres.

The most remarkable feature of this series of reactions is the ease with which either the triazole or the triazolone can be produced exclusively by alteration of the reaction pressure.

REACTIONS OF CARBON MONOXIDE CATALYZED BY BASES

The Synthesis of Formates

The many acid-catalyzed reactions of carbon monoxide testify to the ease with which this molecule can act as a donor of electrons or a nucleophilic reagent once a carbonium ion is formed. The reactions in which carbon monoxide acts as an acceptor are much less extensive, and this appears to be reasonable in terms of the very large contribution that the triple bond structure makes to the ground state of the molecule. In reactions in which carbon monoxide does function as an acceptor, it is convenient to regard carbon monoxide as the double bond structure, $:C::\ddot{O}:$, with an empty orbital on the carbon atom. In this form, it can react with an electron donor:

$$B:^- + \ddot{C}::\ddot{O}: \rightarrow \left[B:\ddot{C}:\underset{\cdot\cdot}{\ddot{O}}:\right]^-$$

Berthelot's discovery[11] in 1856 of the synthesis of sodium formate according to the reaction

$$CO + NaOH \rightarrow HCOONa$$

was not successfully extended to the synthesis of other carbonyl compounds until Stahler's investigations in 1914 in which formates were successfully synthesized. Stahler[126] showed that carbon monoxide in the presence of sodium alcoholate reacted with alcohols to form the corresponding ester of formic acid. For example, he found that when the solution prepared by the addition of 23 grams of sodium to 625 grams of ethanol was left standing under 300 atmospheres of carbon monoxide at room temperature for 14 days, 423 grams of ethyl formate was secured:

$$C_2H_5OH + CO \xrightarrow{C_2H_5ONa} HCOOC_2H_5 .$$

Stahler also prepared methyl and isoamyl formate. The reaction is a general one and high yields of the ester are secured.

The kinetics of this reaction were investigated manometrically by Christiansen and Gjaldbaek[30] at pressures below 1 atmosphere in the temperature range of 35 to 54°C. The reaction was found to be first order with respect to carbon monoxide, with the rate expression: velocity $= k \cdot C_{CO} \cdot C_{OCH_3^-}$. Its rate was shown to be determined by the reaction

$$CO + CH_3O^- \rightleftharpoons [COOCH_3]^-.$$

The complex formed then reacts with methanol to give $HCOOCH_3$ and OCH_3^-, the latter thus acting as a catalyst

$$[COOCH_3]^- + CH_3OH \rightleftharpoons HCOOCH_3 + CH_3O^-.$$

Christiansen and Gjaldbaek's experiments with methanol and ethanol also showed that the reaction rate increased somewhat faster than would be expected on the basis of a linear dependence on the concentration of catalyst. The velocity constant was about three times as great for ethanol as for methanol. The energies of activation were found to be about 18.5 kcal/mole for each of the reactions. The speed of the reaction was increased when dioxane was added to the alcohol.

Gjaldbaek[51] extended the work to the two propyl and four butyl alcohols. The velocity constants at 40°C for all the alcohols studied are listed in Table 9. These velocity constants were calculated taking into account the volume of the gas and liquid phases and the distribution coefficient of carbon monoxide between the phases. Incidentally, the solubility of carbon monoxide in *tert*-butyl alcohol was found to have an exceptionally high temperature coefficient. The rate of formate formation is slowest for methanol and increases with length of chain to propyl alcohol, after which the rate probably does not vary much with chain length. The rates of isopropyl and isobutyl alcohols are about twice those with normal alcohols and are about equal to each other. The rates with secondary and tertiary alcohol are fastest although the greatest rate (with *sec*-butyl alcohol) is only 18 times that of methyl alcohol. High electron density at the oxygen atom probably favors the reaction since substituents that release electrons to oxygen favor the reaction.

During World War II, the Germans used the formate synthesis as a route to formamide and hydrogen cyanide. The batchwise production from methanol was carried out as follows in the Oppau plant of I.G. Farbenindustrie[22, 38]: To methanol contained in a stainless steel autoclave, there was added 1 per cent by weight of metallic sodium. The solution was heated to 60°C, and the autoclave was gradually charged with carbon dioxide-free carbon monoxide. Conversion to formate began at about 30 atmospheres pressure, and the temperature was allowed to rise to 90 to 110°C and maintained in this range by cooling. The pressure was gradually increased to 200 atmospheres and after absorption ceased, the autoclave was cooled and discharged. About 82 per cent of the methanol was converted to methyl formate.

TABLE 9. VELOCITY CONSTANTS OF VARIOUS ALCOHOLS IN THE FORMATE SYNTHESIS AT 40°C

	$k \times 10^5$ (sec.$^{-1}$)
Methyl	81[a]
Ethyl	288[a]
Propyl	443
Butyl	411.5
Isopropyl	836.3
Isobutyl	884.8
sec-Butyl	1,473
tert-Butyl	1,098[b]

[a] Calculated from the data of Christiansen and Gjaldbaek, reference 51.

[b] The alcoholates were prepared by dissolving sodium in the alcohols in question except in the case of *tert*-butyl alcohol where potassium was used because of the slight solubility of sodium butylate in *tert*-butyl alcohol.

For the conversion of methyl formate to formamide via the reaction: $HCOOCH_3 + NH_3 \rightarrow HCONH_2 + CH_3OH$, the methyl formate containing 5 to 10 per cent of methanol was placed in a batch autoclave and heated to 40°C. Ammonia was added at 10 to 15 atmospheres, and the exothermic reaction cooled to maintain the temperature between 60 to 70°C. The product was then fractionated.

The formamide was dehydrated by passing it over alumina at 200 to

300°C continuously, whereupon theoretical amounts of hydrogen cyanide were secured: $HCONH_2 \rightarrow HCN + H_2O$.

Serious consideration has been given to the formate synthesis as a means of producing methanol by the following steps:

$$CH_3OH + CO \xrightarrow{CH_3ONa} HCOOCH_3$$

$$HCOOCH_3 + H_2 \rightarrow 2CH_3OH.$$

An important practical application of the base-catalyzed reactions of carbon monoxide is the synthesis of sodium formate which serves as a source of formic acid. Sodium formate is prepared by the addition of carbon monoxide to hot aqueous alkali at 10 to 15 atmospheres pressure and 160 to 200°C; acidification gives formic acid:

$$CO + NaOH \rightarrow HCOONa$$

$$HCOONa + H^+ \rightarrow HCOOH + Na^+.$$

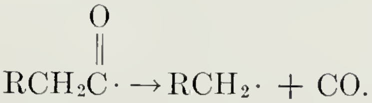
In modern processes, sodium formate is made directly from aqueous sodium hydroxide and producer gas containing about 33 per cent of carbon monoxide. Since absorption of carbon monoxide by caustic soda is slow, rather long contact times are necessary. Producer gas is compressed to 12 to 15 atmospheres and passed through a 25 to 30 per cent solution of sodium hydroxide in countercurrent flow at 160 to 200°C. The effluent liquor is evaporated to dryness. The dry sodium formate may be acidified to yield formic acid, heated to give sodium oxalate, or used as such (HCOONa).

Although the acidification of sodium formate to yield formic acid looks straightforward and simple, there are some practical difficulties. If concentrated acid is used, the formic acid will decompose to carbon monoxide and water. If dilute sulfuric acid is used, a dilute solution of formic acid is obtained; this is undesirable since formic acid and water form a constant boiling mixture at 1 atmosphere which contains only 76.5 weight per cent acid. These difficulties are avoided by use of a slurry of sodium formate in an equal weight of 91 per cent formic acid. Sulfuric acid is added cautiously, with cooling, to the equivalent amount; the formic acid is then distilled. Unless the acid is added carefully, the heat of dilution will decompose some formic acid and also cause premature volatilization of the formic acid.

Christiansen and Gjaldbaek[30] applied their kinetic techniques to the measurement of the relative rate of reaction of carbon monoxide with aqueous sodium hydroxide as compared with the rate of reaction with methanol. They found that the rate was one forty-fifth as large in water, mainly because of the lower solubility of carbon monoxide in water as compared to methanol.

Free Radical Reactions of Carbon Monoxide

There are not many examples of carbon monoxide reacting as a radical. As a matter of fact, radicals with a carbonyl group frequently decompose with loss of carbon monoxide:



$$RCH_2\overset{\overset{O}{\|}}{C}\cdot \rightarrow RCH_2\cdot + CO.$$

There are isolated examples in which carbon monoxide does react by a radical mechanism, especially when photosensitized. Thus, its reaction with ammonia:

$$NH_3 + CO \rightarrow HCONH_2$$

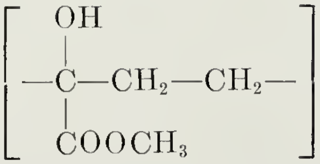
leads to formamide, and it has been reported to react with hydrogen in a mercury photosensitized reaction[4, 43].

Polymerization.

The free radical-initiated copolymerization of ethylene and carbon monoxide has recently been reported[17]. A typical polymerization[18] was conducted as follows: In an autoclave containing 3 ml of di-*tert*-butyl peroxide in 100 ml of cyclohexane, there was introduced a gas mixture consisting of 58 per cent of ethylene and 42 per cent of carbon monoxide to a pressure of 173 atm. The autoclave was heated at 135°C for 15 hours. After distillation of the cyclohexane, the polymer was left as a straw-colored wax melting at 70 to 82°C and having a composition of C_2H_4/CO of 1.5:1. Chemical and spectroscopic evidence indicated that the polymer contained the structure units $—CH_2—CH_2—$ and $—\overset{\overset{O}{\|}}{C}—$.

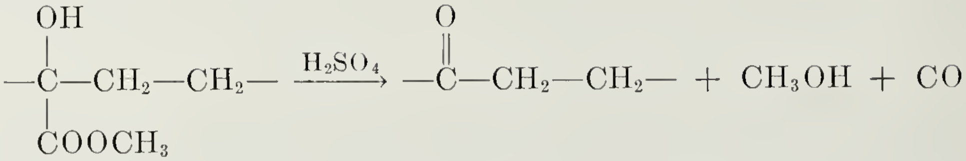
In a study of the compositional relationships in this polymerization[31], it was shown that copolymers containing more than 50 per cent of carbon monoxide were not formed under the conditions employed. This implied that two carbon monoxide molecules did not add successively in the chain propagation and hence the $—\overset{\overset{O}{\|}}{C}—$ linkages must be separated by one or more $—CH_2—CH_2—$ units. The compositions of the polyketones depended upon the temperature, pressure, and composition of the reacting mixture, and some quantitative relationships have been established[5, 31].

In an extension of the ethylene-carbon monoxide polymerization, it was found[25] that when methanol was employed as a solvent, copolymers containing chemically bound methanol were secured. Absorption spectra and chemical studies indicated that the units were probably α-hydroxy ester units,



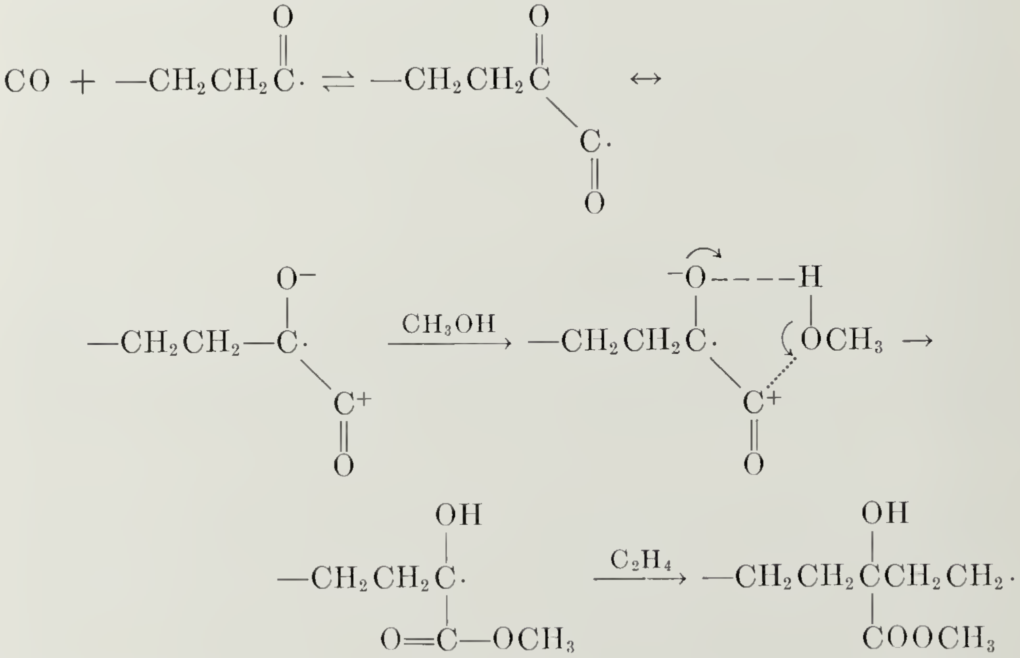
$$\left[-\underset{\text{COOCH}_3}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}-\text{CH}_2-\text{CH}_2- \right]$$

The polymerizations were conducted in the presence of a radical initiator at 135°C and at pressures of between 1,000 and 8,000 atm. One of the interesting bits of evidence in favor of the proposed structure was the decarbonylation of the polymer when treated with hot 96 per cent sulfuric acid. In analogy to known decarbonylation reactions, this was assumed to be represented by the equation:



$$-\underset{\text{COOCH}_3}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}-\text{CH}_2-\text{CH}_2- \xrightarrow{\text{H}_2\text{SO}_4} -\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{CH}_2-\text{CH}_2- + \text{CH}_3\text{OH} + \text{CO}$$

One scheme tentatively proposed for the mechanism of formation of the polymeric unit was as follows[25].

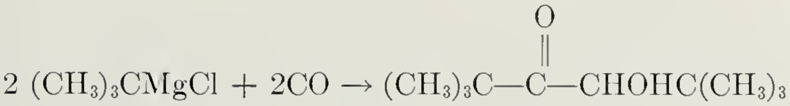


Copolymers of this type were obtained when ethylene and carbon monoxide were copolymerized in methanol, ethanol, 2-propanol, *tert*-butyl alcohol, benzyl alcohol or 2-(*p*-chlorophenoxy)-ethanol and when the ethylene was replaced by propylene, isobutylene, 1-butene, or butadiene.

Reactions of Carbon Monoxide with Some Organometallic Compounds

Grignard Reagents

Perhaps the earliest report of the reaction of a Grignard reagent with carbon monoxide was made by Vinay[135] who reported the formation of tertiary alcohols from Grignard reagents of the type R_2CHMgX and R_3CMgX. Jegorowa[69] reported that carbon monoxide reacts with isopropylmagnesium bromide to give 2,4-dimethyl-2-pentene and 2,3,4-trihydroxy-2,3,4-triisopropyl-5-oxo-6-methylheptanal. The same worker found that carbon monoxide reacts with *tert*-butylmagnesium chloride to give a hydroxyketone (2,2,5,5-tetramethyl-4-hydroxy-3-hexanone) as shown below:



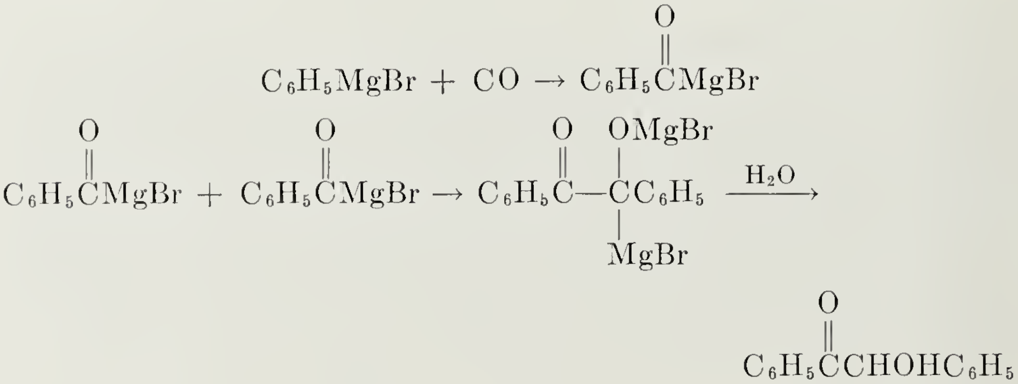
$$2\ (CH_3)_3CMgCl + 2CO \rightarrow (CH_3)_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CHOHC(CH_3)_3$$

Jegorowa obtained only ethyldimethylcarbinol ($C_2H_5(CH_3)_2COH$) from the reaction of *tert*-amylmagnesium chloride and carbon monoxide. However, no reaction occurred between carbon monoxide and methylmagnesium iodide, *tert*-heptylmagnesium iodide, phenylmagnesium iodide, or triphenylmethylmagnesium chloride.

Eidus, Elagina, and Zelinskii[40] reported that carbon monoxide under pressure reacts with butylmagnesium bromide to give 4-nonene (25.4 per cent); with butylmagnesium chloride, a 51 per cent yield of 4-nonene is obtained. Similarly, isoamylmagnesium bromide reacts with carbon monoxide under pressure to give a 51.0 per cent yield of 2,8-dimethyl-4-nonene; when the chloride is used, a 53.6 per cent yield of this olefin is obtained.

Job and Reich[70] and Job and Cassal[71] also conducted experiments with carbon monoxide and a Grignard reagent. They showed that carbon monoxide alone gave no reaction with phenylmagnesium bromide, but that with chromium(III) chloride, 1 mole of carbon monoxide was absorbed for every mole of phenylmagnesium bromide. Hydrolysis with dilute acid gave benzopinacol, acetophenone, diphenylcarbinol, diphenyl, diphenylacetophenone, and benzaldehyde. Job and Cassal attributed the chromium chloride activation of this reaction to the formation of an intermediate chromium carbonyl compound or compounds. Chromium carbonyl itself appeared to be ineffective.

A rather extensive study has been made by Fischer and Stoffers[44] of the reaction of Grignard reagents with carbon monoxide at high temperatures and elevated pressures. These workers reported that phenylmagnesium bromide, *p*-tolylmagnesium bromide, and α-naphthylmagnesium bromide reacted at 110 to 160°C and at about 100 atm. to give an acyloin as the primary product. With phenylmagnesium bromide, for example, the reaction can be written:

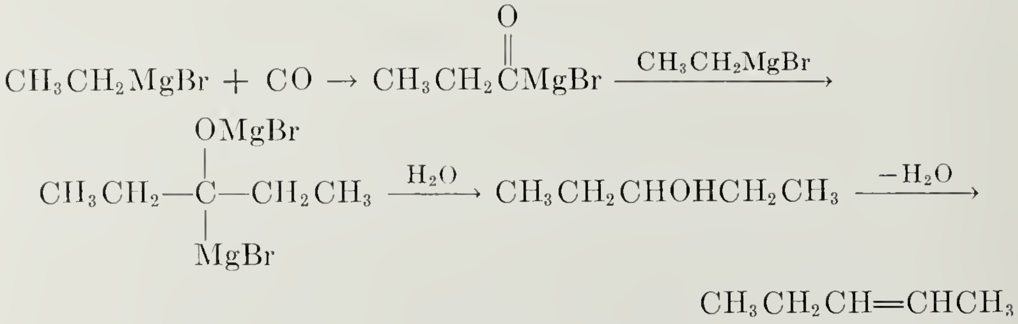


$$C_6H_5MgBr + CO \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}MgBr$$

$$C_6H_5\overset{\overset{O}{\|}}{C}MgBr + C_6H_5\overset{\overset{O}{\|}}{C}MgBr \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}\text{—}\underset{\underset{MgBr}{|}}{\overset{\overset{OMgBr}{|}}{C}}C_6H_5 \xrightarrow{H_2O}$$

$$C_6H_5\overset{\overset{O}{\|}}{C}CHOHC_6H_5$$

Fischer and Stoffers found that the reaction of aliphatic Grignard reagents lead to different types of products under their conditions; the principal product from a Grignard reagent with n carbon atoms was an olefin containing $2n + 1$ carbon atoms. The formation of 2-pentene from ethylmagnesium chloride can be explained as follows:



$$CH_3CH_2MgBr + CO \rightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}MgBr \xrightarrow{CH_3CH_2MgBr}$$

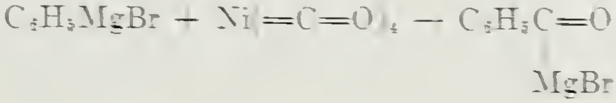
$$CH_3CH_2\text{—}\underset{\underset{MgBr}{|}}{\overset{\overset{OMgBr}{|}}{C}}\text{—}CH_2CH_3 \xrightarrow{H_2O} CH_3CH_2CHOHCH_2CH_3 \xrightarrow{-H_2O}$$

$$CH_3CH_2CH{=}CHCH_3$$

The yields of olefins were usually 60 to 70 per cent.

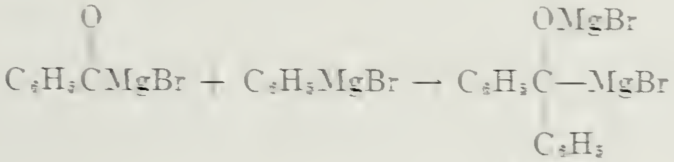
As in other reactions with carbon monoxide, workers have attempted to substitute a metal carbonyl as a carbon monoxide donor in the Grignard reaction. Zelinskii[141] reported the formation of aldehydes and ketones by the reaction between nickel carbonyl and propylmagnesium bromide and Jones[78] treated phenylmagnesium bromide with nickel carbonyl in an attempt to gain information on the structure of the carbonyl.

One of the most interesting studies of the reaction between nickel carbonyl and a Grignard reagent was reported by Gilliland and Blanchard[50]. These workers studied the reaction of methylmagnesium iodide and phenylmagnesium bromide with nickel carbonyl. In their first experiments, they noted a violent reaction accompanied by the precipitation of metallic nickel. In order to avoid the difficulties associated with the precipitate, they passed carbon monoxide continuously into the reaction mixture containing the Grignard reagent and a small quantity of nickel carbonyl. Under these conditions, the nickel carbonyl is presumably regenerated as it is consumed and carbon monoxide is continuously absorbed. The reaction with phenylmagnesium bromide may be explained by the assumption that both —C_6H_5 and —MgBr add to the carbon atom of the carbonyl.



$$C_6H_5MgBr + Ni(C{=}O)_4 \rightarrow C_6H_5\underset{\underset{MgBr}{|}}{C}{=}O$$

In an excess of Grignard reagent, the following sequence is postulated to occur.



$$C_6H_5\overset{\overset{O}{|}}{C}MgBr + C_6H_5MgBr \rightarrow C_6H_5\overset{\overset{OMgBr}{|}}{\underset{\underset{C_6H_5}{|}}{C}}{—}MgBr$$

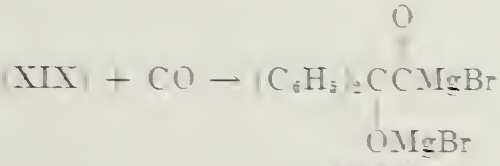
(XIX)

$$(XIX) + C_6H_5MgBr \rightarrow (C_6H_5)_3CMgBr + (MgBr)_2O$$

(XX)

Hydrolysis of (XX) leads to triphenylmethane, one of the products isolated.

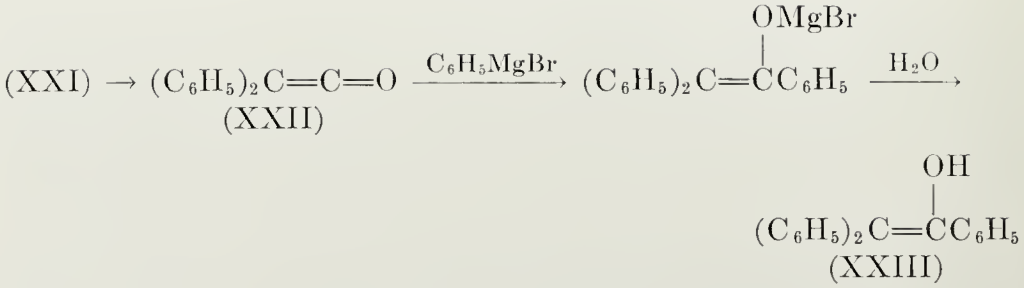
Compound (XIX) contains the —CMgBr group, and it may react with fresh carbon monoxide:



$$(XIX) + CO \rightarrow (C_6H_5)_2\underset{\underset{OMgBr}{|}}{C}\overset{\overset{O}{|}}{C}MgBr$$

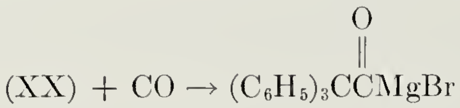
(XXI)

(XXI) can split to yield magnesium oxybromide and diphenylketene (XXII) which can react further with a Grignard reagent in a manner analogous to other known ketene reactions. The product would be triphenylvinyl alcohol (XXIII) which was actually isolated.

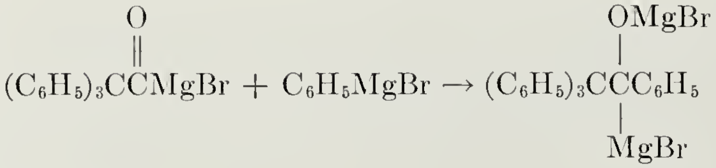


$$\text{(XXI)} \rightarrow \underset{\text{(XXII)}}{(C_6H_5)_2C{=}C{=}O} \xrightarrow{C_6H_5MgBr} (C_6H_5)_2C{=}\overset{\overset{\displaystyle OMgBr}{|}}{C}C_6H_5 \xrightarrow{H_2O} \underset{\text{(XXIII)}}{(C_6H_5)_2C{=}\overset{\overset{\displaystyle OH}{|}}{C}C_6H_5}$$

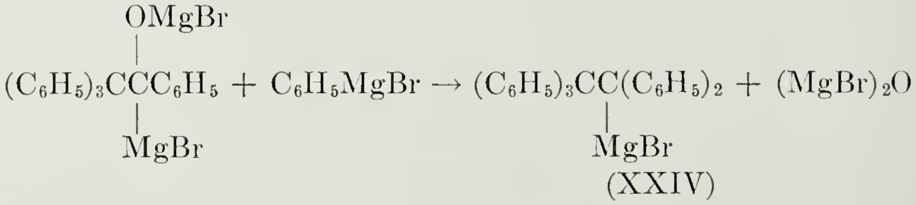
Compound (XX) likewise contains the $\begin{smallmatrix}\diagdown\\ -\\ \diagup\end{smallmatrix}$CMgBr group and can react with additional carbon monoxide to give pentaphenylethane, also isolated in this work:



$$\text{(XX)} + CO \rightarrow (C_6H_5)_3C\overset{\overset{\displaystyle O}{\|}}{C}MgBr$$



$$(C_6H_5)_3C\overset{\overset{\displaystyle O}{\|}}{C}MgBr + C_6H_5MgBr \rightarrow (C_6H_5)_3C\underset{\underset{\displaystyle MgBr}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}C_6H_5$$



$$(C_6H_5)_3C\underset{\underset{\displaystyle MgBr}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}C_6H_5 + C_6H_5MgBr \rightarrow \underset{\text{(XXIV)}}{(C_6H_5)_3C\underset{\underset{\displaystyle MgBr}{|}}{C}(C_6H_5)_2} + (MgBr)_2O$$

$$\text{(XXIV)} \xrightarrow{H_2O} (C_6H_5)_3CCH(C_6H_5)_2$$

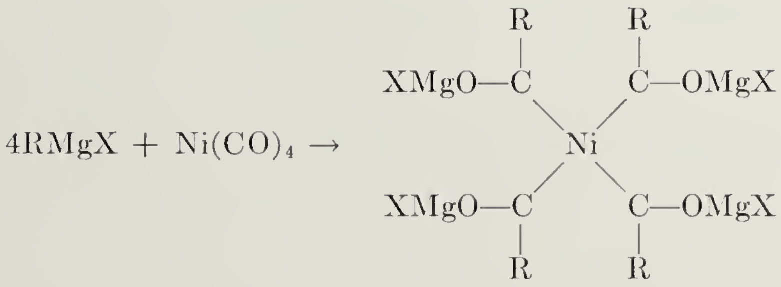
It can be seen that (XXIV) may react further to give a whole series of phenylated hydrocarbons.

When it is considered that, in the addition of Grignard reagents to carbon monoxide, the —MgBr group is bound directly to carbon and the substances so formed are new Grignard reagents that can react with carbon monoxide, and that all the intermediate complexes containing the —C=O or the —COMgBr group may react with any of the Grignard complexes present, the variety of possible products is very great indeed.

A study of the reaction has been made by Benton, Voss, and McCusker[8] who conducted the reaction in the presence of excess nickel carbonyl. Several of the types of Grignards studied were found to follow a definite single course of reaction and to produce significant yields of one type of product. The products obtained, together with the yields, are summarized as follows:

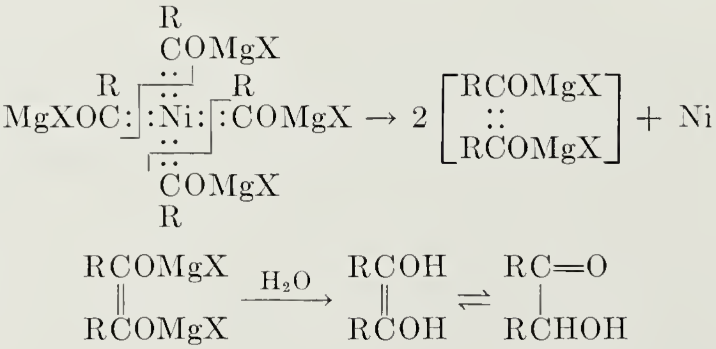
R of RMgX	*Product*	*Yield (%)*
C_6H_5—	Benzoin	70
n-C_3H_7—	*n*-Butyroin	50
n-C_4H_9—	*n*-Valeroin	50
iso-C_3H_7—	iso-Butyroin	35
tert-C_4H_9—	Unidentified	trace
n-$C_4H_9C{\equiv}C$—	Undistillable oil	

In an effort to obtain information on the mechanism of the reaction, these authors examined the voluminous black, amorphous, tarry solid which is obtained as an intermediate in this reaction. Crystallization of the solid mass was never obtained, although in some cases, small portions of the solid took on a definitely crystalline appearance. Samples of the black solid, washed thoroughly with dry ether and freed of ether in a current of dry nitrogen, were analyzed for nickel and magnesium. Analyses on several different products varied by too great an amount to enable a positive identification of the complex to be made; in all cases, however, the nickel and magnesium content approximated the values calculated for a complex in which four moles of Grignard are combined with one mole of nickel carbonyl. These results did not indicate that a pure intermediate was isolated, but they did show that the nickel and magnesium content corresponded to a complex in which organic material was present in appreciable amounts. Although the results of the analysis could be interpreted as indicating that the intermediate was a mixture of metallic nickel and an organomagnesium compound, they postulated that the intermediate has the following structure:



This intermediate contains a trivalent carbon; it is probable that if it exists there is a double bond between the carbon and nickel. The hydrolysis of the intermediate proceeds slowly with dilute hydrochloric acid and more rapidly with concentrated hydrochloric acid with the evolution of hydrogen. The amount of hydrogen evolved corresponds to the nickel content as analyzed. The reaction may then be considered to involve the breaking of the loose nickel-to-carbon bonds by the action of the hydrochloric acid and the normal hydrolysis of the remainder of the molecule to yield nickel chloride and hydroxyketone. If uncombined nickel and organomagnesium halide were present as a mixture, it would be expected that the hydrolysis of the organomagnesium halide would occur more rapidly than the solution of the free nickel in hydrochloric acid.

The breaking up of the postulated intermediate may occur in the following manner:



$$\begin{array}{c} \mathrm{R} \\ \mathrm{COMgX} \\ \mathrm{\overset{R}{MgXOC}\!:\,:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Ni}}:\,:\overset{R}{COMgX}} \\ \mathrm{COMgX} \\ \mathrm{R}\end{array} \rightarrow 2\begin{bmatrix}\mathrm{RCOMgX}\\ ::\\ \mathrm{RCOMgX}\end{bmatrix} + \mathrm{Ni}$$

$$\begin{matrix}\mathrm{RCOMgX}\\ \|\\ \mathrm{RCOMgX}\end{matrix} \xrightarrow{H_2O} \begin{matrix}\mathrm{RCOH}\\ \|\\ \mathrm{RCOH}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{RC{=}O}\\ |\\ \mathrm{RCHOH}\end{matrix}$$

an acyloin

However, as has been pointed out, the first reaction of Grignards on carbon monoxide is not across the double bond; it has been shown that both —R and —MgX of the Grignard add only to the carbon atom of carbon monoxide forming a new Grignard reagent. Benton, Voss, and McCusker claim that the Grignard adds across the double bond in carbon monoxide. This may be possible in the nickel carbonyl catalyzed reaction; it is not likely that the Grignard adds across the double bond in uncatalyzed reactions.

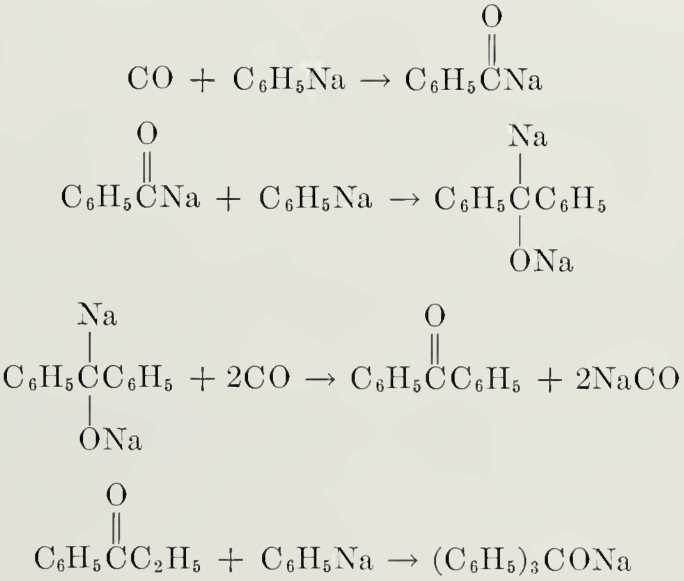
The Reaction of Carbon Monoxide with Metal Alkyls

Although the reaction between carbon monoxide and sodium alkyls proceeds readily under mild conditions, the reaction has not been well explored. Wanklyn[136] reported that the action of carbon monoxide on a compound presumed to be ethylsodium resulted in the formation of diethyl ketone. Schlubach[121] treated mercury dialkyls and diaryls with metallic sodium in the presence of carbon monoxide and the resulting mixtures containing sodium alkyls or aryls absorbed carbon monoxide. He found that the reaction of diethylmercury with sodium and carbon monoxide lead to a complex mixture from which he isolated, in addition to diethylketone, small quantities of triethylcarbinol and propionic acid. An appreciable quantity of neutral and acidic high-boiling material was also obtained.

The products of the reaction from diphenylmercury, sodium, and carbon monoxide, in benzene solution were easier to identify. The following products were obtained in the yield specified, based on the quantity of starting diphenylmercury:

Product	*Yield*
Benzophenone $(C_6H_5)_2CO$	30
Triphenylcarbinol $(C_6H_5)_3COH$	25
Benzoic acid $C_6H_5CO_2H$	16
High-boiling oils	15

Schlubach wrote the reactions leading to these products as follows:



$$CO + C_6H_5Na \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}Na$$

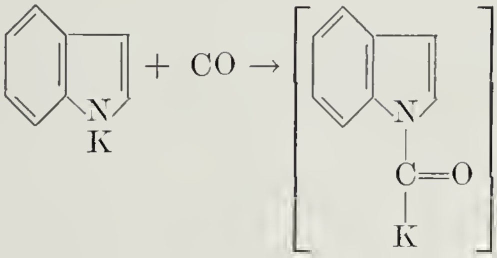
$$C_6H_5\overset{\overset{O}{\|}}{C}Na + C_6H_5Na \rightarrow C_6H_5\overset{\overset{Na}{|}}{\underset{\underset{ONa}{|}}{C}}C_6H_5$$

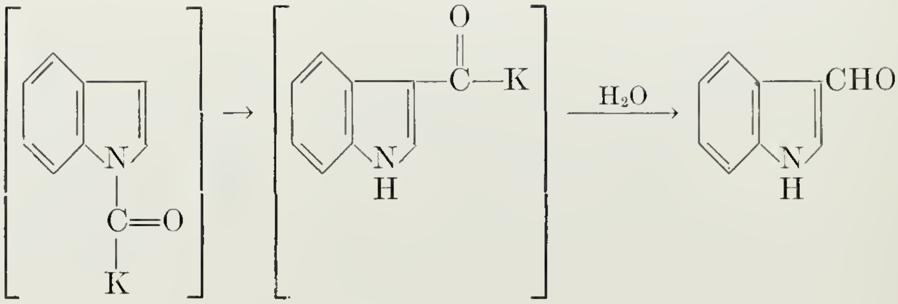
$$C_6H_5\overset{\overset{Na}{|}}{\underset{\underset{ONa}{|}}{C}}C_6H_5 + 2CO \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5 + 2NaCO$$

$$C_6H_5\overset{\overset{O}{\|}}{C}C_2H_5 + C_6H_5Na \rightarrow (C_6H_5)_3CONa$$

Although some evidence for the presence of sodium carbonyl and the disodium benzophenone was deduced, their presence was far from proven, and it is unlikely that the reactions are as straight-forward as shown.

The preparation of 3-indolecarboxylic acid by a reaction between indolemagnesium iodide and carbon dioxide[94] led Tyson and Shaw[129] to explore the possibility of treating metal salts of indole with carbon monoxide in order to secure 3-indolecarboxaldehyde. They successfully treated potassium indole with carbon monoxide at elevated pressures. This reaction, resulting in the formation of a new carbon-carbon bond, may be written as illustrated below:



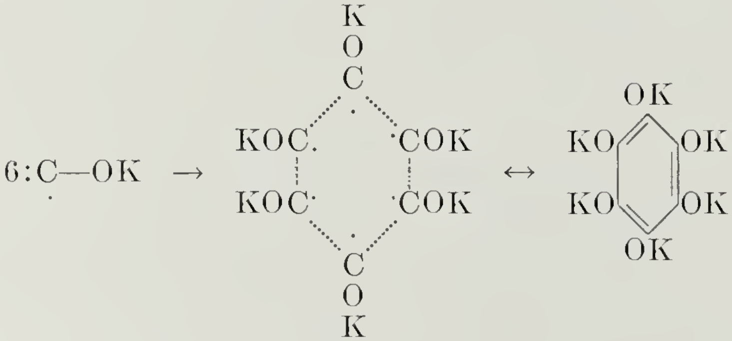


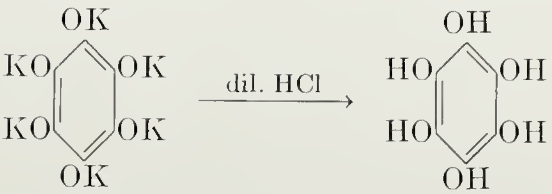
Dimethylformamide was found to be an appropriate solvent for this reaction, although pyridine or excess indole could be used, but with decreased yields. The influence of various reaction conditions could be summarized as follows: Over the pressure and temperature ranges investigated, 47 to 480 atm. and 25 to 200°C, respectively, the optimum conditions were found to be 480 atm. at 135 to 150°C for an autoclave with a total capacity of 120 ml, half-full of liquid reactants. The yield of aldehyde was 57 per cent, based upon the potassium salt of indole. Potassium indole gave a 24 per cent higher yield than sodium indole and a 48 per cent higher yield than lithium indole. The increase in atomic weight of the metal tends to make the nitrogen-metal bond more ionic, which evidently favors the reaction. The use of indole itself or indolemagnesium bromide, the latter in diethyl ether, gave negative results.

THE REACTION OF CARBON MONOXIDE WITH ALKALI METALS

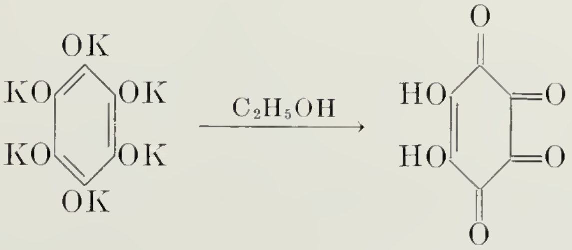
In 1834, Liebig[86] passed carbon monoxide over heated potassium and obtained potassium hexahydroxybenzene or "potassium carbonyl"; when the fresh mass was treated with dilute hydrochloric acid, hexahydroxybenzene was secured. This rather remarkable synthesis of the benzene ring may be written in the following manner:

$$:\mathrm{C}{=}\ddot{\mathrm{O}}: + \mathrm{K}^{\cdot} \rightarrow :\underset{\cdot}{\mathrm{C}}{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{K}$$



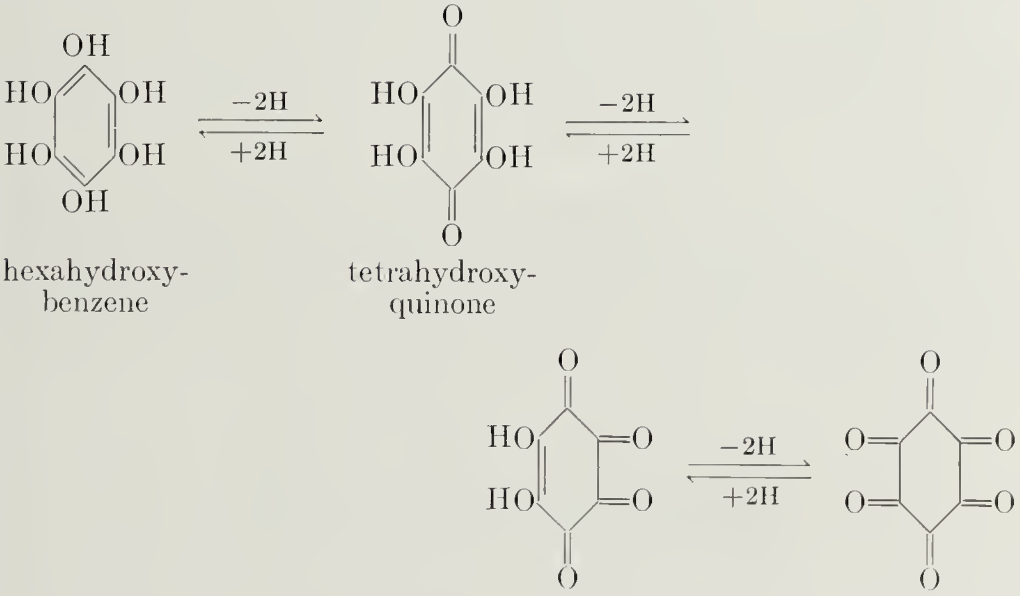


Nietski and Benckiser[103] confirmed the work of Liebig and found that rhodizonic acid could be obtained by treating potassium hexahydroxybenzene with alcohol



rhodizonic acid

Nietski and Benckiser also obtained tetrahydroxyquinone and triquinoyl from the reaction of potassium and carbon monoxide. The oxidation-reduction potentials and the ionization constants of the interconvertible series consisting of the following four compounds were studied by Preisler, Berger, and Hill[110].



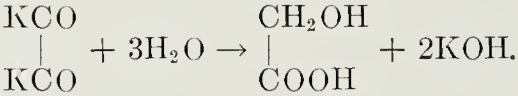
hexahydroxybenzene

tetrahydroxyquinone

rhodizonic acid

triquinoyl

Joannis[72] prepared alkali metal compounds corresponding to the formulas KCO and NaCO by the action of carbon monoxide on potassium and sodium, respectively. In a later paper, Joannis[73] reported the treatment of "potassium carbonyl" with water in the presence of liquid ammonia. After evaporation of the ammonia, exactly enough sulfuric acid was added to form potassium sulfate; to this a mixture of ethyl alcohol and ether was added and the salt filtered off. Glycollic acid was obtained from the filtrate, which is evidence that at least part of the carbonyl existed as dipotassium glyoxal, KCO—COK. The reaction with water to form glycollic acid may be written:

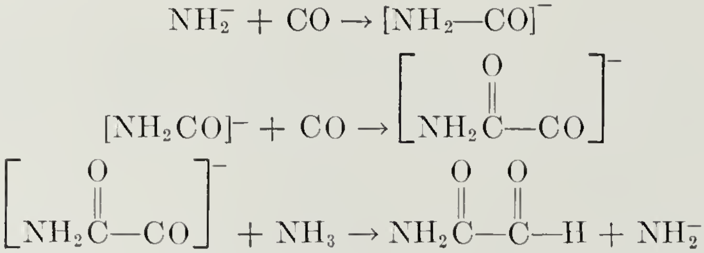


$$\begin{array}{c}\mathrm{KCO}\\ |\\ \mathrm{KCO}\end{array} + 3H_2O \rightarrow \begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{COOH}\end{array} + 2KOH.$$

Hackspill and van Altnea[55] treated cesium with carbon monoxide at 0°C and obtained minute shining spheres of chamois-yellow color which were gently decomposed by water. In dilute sulfuric acid, the addition of 2,4-dinitrophenylhydrazine gave the bis-[2,4-dinitrophenylhydrazone] of glyoxal, OHC—CHO.

Pearson[107] prepared the carbonyls of lithium, rubidium, and cesium by passing pure dry carbon monoxide through a solution of the metal in liquid ammonia formed at −60°C. Lithium carbonyl, LiCO, a white powder which darkened on standing, detonated violently on treatment with water forming lithium carbonate, carbon, and hydrogen. Rubidium carbonyl, RbCO, was a white solid which dissolved in water. Calcium carbonyl, $Ca(CO)_2$, a cream-colored powder, partially dissolved in water with the evolution of heat. When heated in vacuo, the lithium compound began to dissociate at 300°C, the rubidium carbonyl at 350°C, and the calcium carbonyl at 200°C; in each case, the corresponding carbonates and oxides and carbon were formed.

It has recently been reported[122] that the reaction of sodium and carbon monoxide in liquid ammonia yields glycollic acid amide and rhodizonic acid. Leonard and Fram[85], applying the suggestions regarding the polymerization of vinyl monomers in liquid ammonia[7, 42], proposed the following chain mechanism:

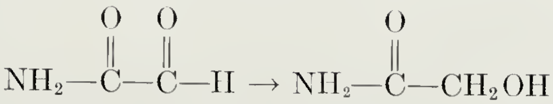


$$NH_2^- + CO \rightarrow [NH_2-CO]^-$$

$$[NH_2CO]^- + CO \rightarrow \left[NH_2\overset{\overset{O}{\|}}{C}-CO\right]^-$$

$$\left[NH_2\overset{\overset{O}{\|}}{C}-CO\right]^- + NH_3 \rightarrow NH_2\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H + NH_2^-$$

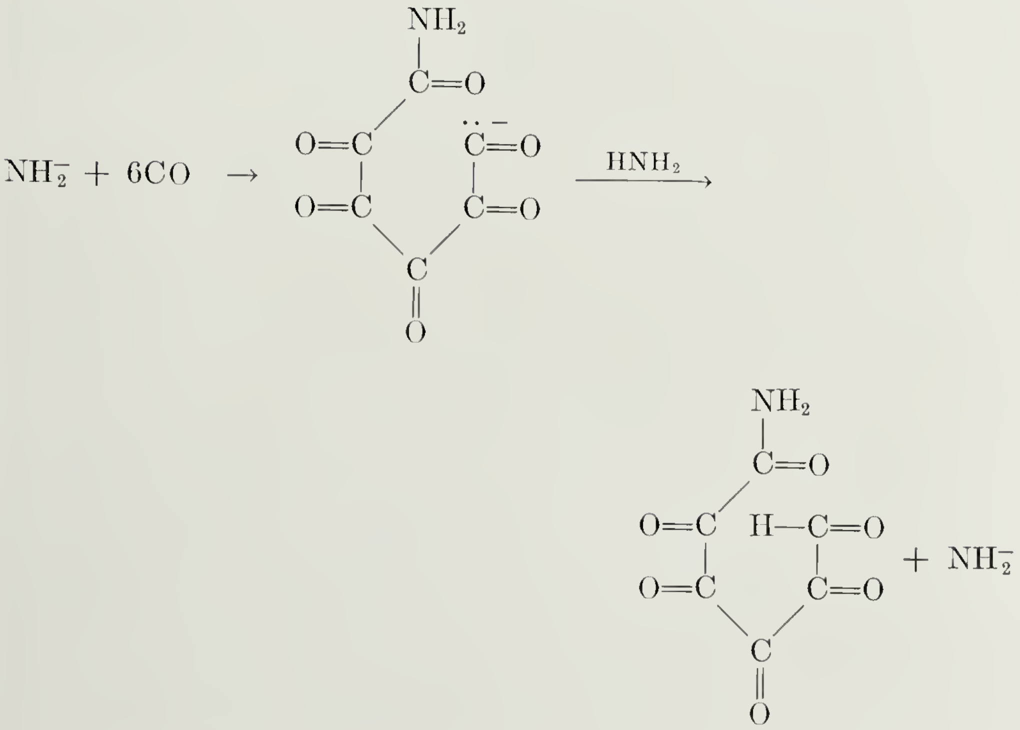
The glyoxalic acid amide is then reduced to glycollic acid amide:



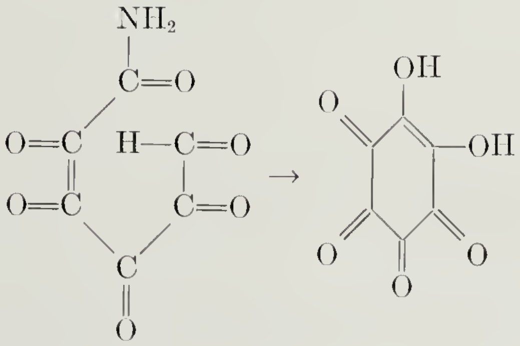
$$NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-H \rightarrow NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2OH$$

which can be isolated in 15 to 20 per cent yield.

The formation of rhodizonic acid is explainable by the same mechanism:



The acid amide is then transformed to rhodizonic acid via an acyloin or benzoin-type of condensation:



REACTIONS OF CARBON MONOXIDE CATALYZED BY NICKEL COMPOUNDS OR NICKEL CARBONYLS

Acetylenic Compounds

From a commercial point of view, the most important reaction in this category is the synthesis from acetylene of acrylic acid and its derivatives first developed by Reppe and his co-workers[32, 113]. They found that the reaction of acetylene with nickel carbonyl and aqueous hydrochloric acid at 45 to 50°C gave acrylic acid, whereas in the presence of other compounds possessing an active hydrogen, for example, alcohols, amines, etc., the corresponding derivatives of acrylic acid were obtained. The synthesis of ethyl acrylate by this route can be represented as follows:

$$4C_2H_2 + Ni(CO)_4 + 4EtOH + 2HCl \rightarrow 4CH_2{=}CHCOOEt + NiCl_2 + H_2 .$$

The nickel carbonyl furnishes carbon monoxide and because the synthesis results in the formation of an acid or its derivatives, the synthesis has been called "carboxylation." Less than the stoichiometric quantity of hydrogen is liberated and the fate of the hydrogen consumed has not been elucidated. In the acrylate synthesis to be described below, it is probably partially utilized in the reduction of acrylate to propionate.

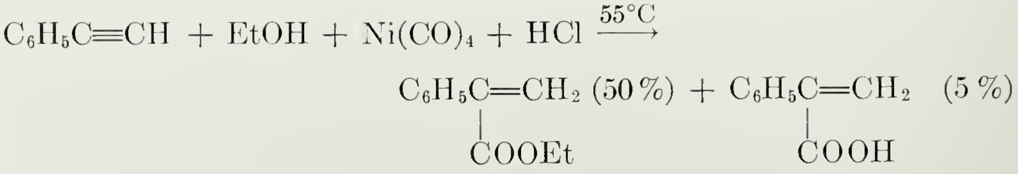
In these reactions, nickel carbonyl must be used in stoichiometric quantities since it is the sole source of carbon monoxide. This process has therefore been called the "stoichiometric" carboxylation. As a practical synthesis of ethyl acrylate, this method has several disadvantages and Reppe and his collaborators devised a catalytic procedure. A solution of a nickel halide catalyst, for example, nickel(II) bromide, in a mixture of water and ethanol was treated at 150 to 180°C with carbon monoxide and acetylene (1:1) at about 30 atmospheres pressure. This method has been called "catalytic" carboxylation. It is possible that the nickel halide is converted *in situ* to nickel carbonyl and that this method is essentially the same as the stoichiometric procedure. The activity of the nickel halides increases sharply from chloride to bromide to iodide (the fluoride is inactive). Nickel iodide, however, causes polymerization of acrylates and hence nickel bromide is the preferred salt.

Recently, the Rohm and Haas Company has put an acrylate plant on stream which is a combination of the two processes[117]. High yields of acrylates are secured, and the process may be run as rapidly as the heat of reaction can be removed[100]. The reaction time is so short that the size of the reactor is small in comparison with the capacity of the unit. This process retains the advantage of a catalytic process in that much smaller amounts of nickel must be recovered and recycled than in the stoichiometric process.

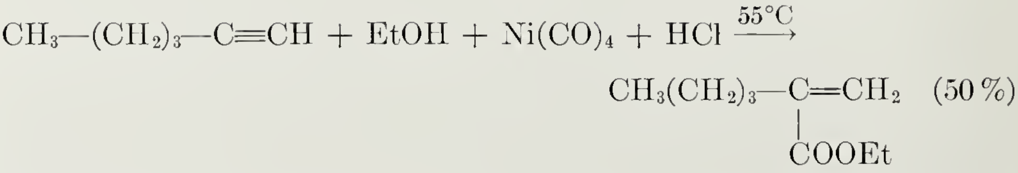
A stoichiometric mixture of acetylene and carbon monoxide gas remains unchanged, for an apparently indefinite time, when passed through alcohol containing nickel carbonyl, or nickel carbonyl and hydrogen chloride at atmospheric pressure and temperatures of 0 to 75°C. If the stoichiometric reaction of acetylene, alcohol, nickel carbonyl, and acid is first started, carbon monoxide gas may then be introduced into the reaction to produce acrylate by combining with acetylene and alcohol under mild conditions. In other words, the catalytic reaction between acetylene, carbon monoxide, and the alcohol can be superimposed upon the stoichiometric reaction involving nickel carbonyl and hydrogen chloride. This latter reaction apparently produces the catalyst necessary for the process to function. The carbonyl group in the acrylate product is derived both from the carbon monoxide gas and from the nickel carbonyl. The ratio of carbon monoxide gas to the carbon monoxide content of the nickel carbonyl varies from 60/40 to 80/20. In other words, 60 to 80 per cent of the total carbonyl available for reaction comes from carbon monoxide gas, and 40 to 20 per cent from nickel carbonyl. Other preferred operating conditions include a temperature of 30 to 50°C, a hydrochloric acid to nickel carbonyl equivalent ratio of 1/1.01 to 1/1.2, acetylene to total carbon monoxide ratio of 1.01/1 to 1.1/1, and an alcohol to total carbon monoxide ratio of 1.1/1 to 3/1, alcohol usually being a convenient solvent to improve the fluidity of the reaction mixture. This process is run at atmospheric pressure, and is suitable for continuous operation. Conversions are high, there being practically no recycle other than excess alcohol, and yields are in the range of 80 to 90 per cent, based on acetylene and total carbon monoxide. In contrast to the stoichiometric process which may give as much as 15 per cent of saturated ester, the crude acrylate contains only a small amount of ethyl propionate (less than 1.5 per cent).

By replacement of the alcohol with water, high yields of acrylic acid can be produced from acetylene and carbon monoxide[125]. In this case, an organic acid should be used in place of hydrochloric acid; it is most convenient to use acrylic acid. This added acid comes out of the process in the form of nickel acrylate and in the steps of converting the nickel back to nickel carbonyl, the acrylic acid is recovered and a part is recycled to the process. In order to achieve the maximum ratio of carbon monoxide gas to nickel carbonyl, a solvent is used in the acrylic process, preferably a ketone that is at least partially water-miscible. The reaction is almost as rapid with tertiary alcohols as with primary and secondary alcohols, and gives high yields of tertiary butyl acrylate which cannot be produced economically by any other known process.

The stoichiometric process with monosubstituted acetylenic substrates has been rather extensively studied by Jones and co-workers. Phenylacetylene and 1-hexyne gave the products shown[74]

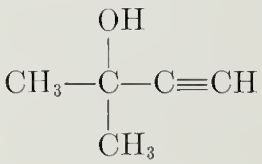


$$C_6H_5C{\equiv}CH + EtOH + Ni(CO)_4 + HCl \xrightarrow{55^\circ C} \underset{\substack{|\\ COOEt}}{C_6H_5C{=}CH_2}\ (50\%) + \underset{\substack{|\\ COOH}}{C_6H_5C{=}CH_2}\ \ (5\%)$$



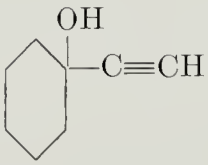
$$CH_3{—}(CH_2)_3{—}C{\equiv}CH + EtOH + Ni(CO)_4 + HCl \xrightarrow{55^\circ C} CH_3(CH_2)_3{—}\underset{\substack{|\\ COOEt}}{C}{=}CH_2\ \ (50\%)$$

In the attempt to apply the procedure to α,β-acetylenic alcohols, some difficulties were experienced. Thus, with the secondary alcohol, propylethynylcarbinol, $CH_3CH_2CH_2CHOHC{\equiv}CH$, no reaction was noted at conditions under which 1-hexyne and phenylacetylene reacted smoothly. However, when the acetate of this alcohol was treated with nickel carbonyl in ethanol containing acetic acid, the reaction proceeded smoothly and reproducibly at 70°C, but the product was the free acid, $CH_3CH_2CH_2CHOAc\underset{\substack{|\\ COOH}}{C}{=}CH_2$, secured in 40 per cent yield. When the reaction was repeated except that 0.5–2 mole equivalents of water was added, the acid was isolated in even better yield (48 per cent). From these and other experiments, these investigators concluded that the free acids and not the esters are formed initially in every case, and the presence of water, either added or formed *in situ* by side reactions, was necessary. They apparently regarded the esters formed in their initial experiments with 1-hexyne and phenylacetylene to be secondary products produced by the esterification of the free acid during the reaction. When these substrates were treated in the aqueous ethanol-acetic acid solvent the free acids were produced smoothly in about the same yield. The tertiary α,β-acetylenic carbinols such as dimethylethynylcarbinol and 1-ethynylcyclohexanol,

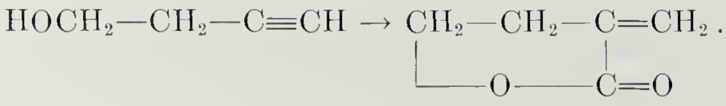


$$CH_3{—}\overset{\substack{OH\\ |}}{\underset{\substack{|\\ CH_3}}{C}}{—}C{\equiv}CH$$

and



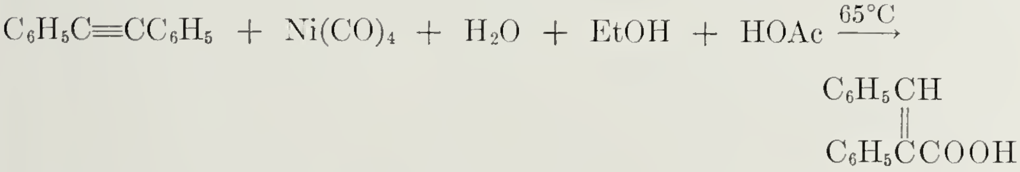
did not react appreciably under any conditions, nor did their respective acetates. β,γ-Acetylenic carbinols gave γ-lactones, for example:



$$HOCH_2{—}CH_2{—}C{\equiv}CH \rightarrow \begin{array}{l} CH_2{—}CH_2{—}C{=}CH_2\,. \\ \lfloor\!{—}O{—}{—}C{=}O \end{array}$$

Shortly after the first paper by Jones and co-workers, Bergmann and Zimkin published a short paper[9] which contradicted the former authors in two important respects. Bergmann and Zimkin found that dimethylethynylcarbinol reacted smoothly at room temperature with nickel carbonyl in anhydrous butanol to which hydrogen chloride was added, although Jones *et al.* had reported that in aqueous ethanol-acetic acid no reaction occurred. Furthermore, Bergmann and Zimkin showed conclusively that their product contained $(CH_3)_2C(OH)CH{=}CH{-}CO_2Bu$, and thus addition of carbon had taken place in a direction opposite to that which Jones and co-workers had shown for other monosubstituted acetylenes.

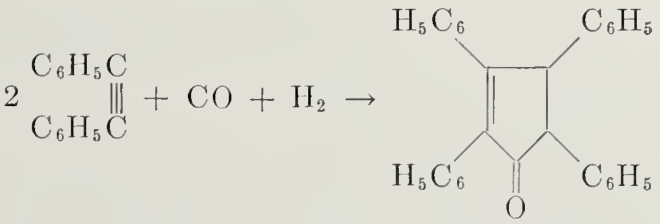
Jones, Shen, and Whiting[75] extended their studies to disubstituted acetylenes. They found that diphenylacetylene reacted readily:



$$C_6H_5C{\equiv}CC_6H_5 + Ni(CO)_4 + H_2O + EtOH + HOAc \xrightarrow{65°C} \begin{array}{c} C_6H_5CH \\ \| \\ C_6H_5CCOOH \end{array}$$

Decarboxylation of the α-phenylcinnamic acid gave cis-stilbene showing that cis addition of —H and —COOH to the triple bond had taken place. The cis addition was confirmed by other work.

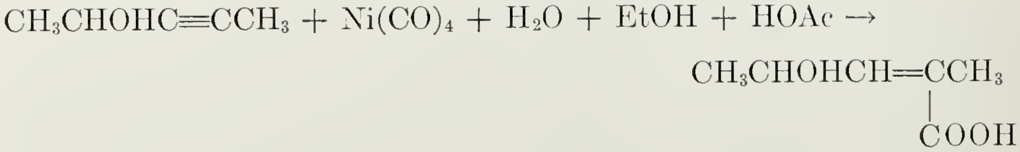
When diphenylacetylene was treated with nickel carbonyl and hydrogen chloride at 40°C in a benzene-ethanol solvent, Mueller and McArtor[97] obtained a 34 per cent yield of ethyl α-phenylcinnamate. When dioxane and ethanol were used as solvents, this ester was also produced, but the principal reaction product was a white granular solid which was neutral and unsaponifiable. This compound proved to be 2,3,4,5-tetraphenylcyclopenta-2-en-1-one (XXV). The stoichiometry of formation of this dihydrotetracyclone may be represented as:



(XXV)

Tetracyclone has been reduced to (XXV) under a variety of conditions[123] and it seems probable that the reaction of diphenylacetylene in dioxane produced tetracyclone which was subsequently reduced.

In their second paper, Jones and co-workers[75] found that the secondary α,β-acetylenic carbinol, in contrast to the tertiary, did react:



$$\mathrm{CH_3CHOHC{\equiv}CCH_3 + Ni(CO)_4 + H_2O + EtOH + HOAc \rightarrow CH_3CHOHCH{=}\underset{\displaystyle COOH}{\underset{|}{C}}CH_3}$$

The proof of structure was conclusive. The possibility of other products being present to a minor extent was noted. In a third paper[76], the same authors attempted to extend the carboxylation reaction to acetylenic halides such as 1-iodoacetylenes. However, these compounds were reduced by the nickel carbonyl to the corresponding acetylenes, and the reaction which would normally proceed with such acetylenes was inhibited. They also studied the reactions of some vinylacetylenes and confirmed the earlier observations of Bergmann and Zimkin[9] that such compounds produce dimeric products; however, they assigned (on spectroscopic grounds) a somewhat different structure than Bergmann and Zimkin had tentatively assigned.

In a fourth article, Jones, Shen, and Whiting[77] studied the effects of variations in the reaction conditions on the yield of acids from various acetylenes treated with nickel carbonyl in aqueous-ethanolic acetic acid. Some of their results are summarized below:

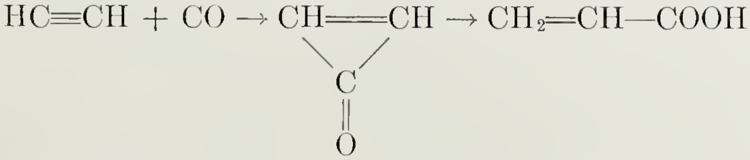
Induction Period and Reaction Temperature. The duration of the induction period which is characteristic of the carboxylation reaction varies with the acetylenic compound, the solvent and acid employed, and the temperature; it is apparently fairly constant provided these factors are not varied. While the induction period for most acetylenic compounds in aqueous-ethanolic acetic acid is about one minute at 70 to 75°C, β,γ-acetylenic alcohols require 6 to 10 minutes even at 80°C; acetylene itself in acetone and concentrated hydrogen chloride reacts readily at 40°C.

Solvent. The nature of the solvent appears to be relatively unimportant. Successful reactions have been observed with phenylacetylene and acetic acid in methanol, ethanol, isopropanol, *tert*-butanol, *n*-butanol, acetone, dioxane, ethyl acetate, pyridine, and anisole.

Water. Whereas use of aqueous solvents commonly gives yields of 40 to 50 per cent, use of anhydrous solvents gives only 20 to 30 per cent yields. The conclusion is that water can participate as the "HX" (active H component), but that alcohols cannot. In the absence of added water, side-reactions using 70 to 80 per cent of the acetylenic material apparently lead to the formation of enough water to make possible the formation of some α-methylenic acid.

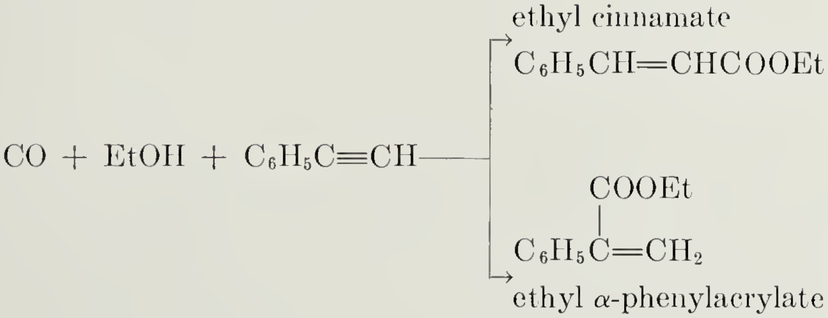
Acid "HX" Component. The facts observed with typical acetylenic substrates are: With alcoholic solvents, the free α-methylenic acid is practically the sole product when acetic acid is used but esters are obtained in increasing amounts as the strength of the acid (HX) is increased.

One important aspect of the carboxylation reaction which needs further clarification is the direction or addition of —H and —COOH. Reppe early postulated a cyclopropenone intermediate which was then split with water:

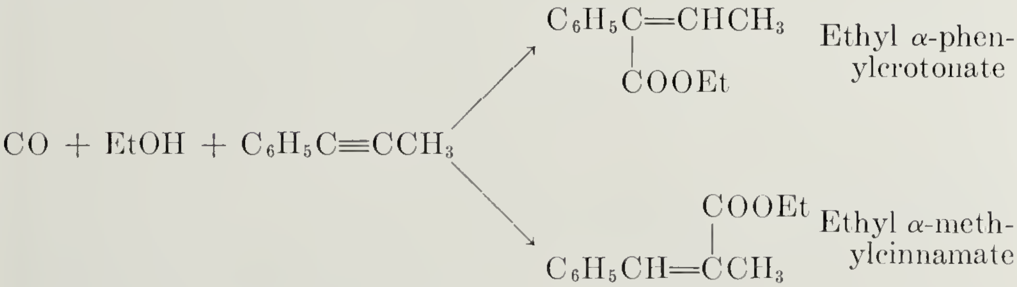


$$HC{\equiv}CH + CO \rightarrow \underset{\underset{\displaystyle O}{\|}}{CH{=}C{=}CH} \rightarrow CH_2{=}CH{-}COOH$$

The direction of splitting is immaterial in this example since the molecule is symmetrical. The reaction with phenylacetylene could lead to two products:



However, only ethyl α-phenylacrylate is obtained. On the other hand, the unsymmetrical methylphenylacetylene has been reported to give two products:



The systematic studies begun by Jones and co-workers will bring some generalizations to this rather complex reaction. As a matter of fact, the exact stoichiometry of the reaction is still not known.

Olefinic Compounds

The reaction of olefins with carbon monoxide in the presence of steam or alcohols to produce acids and esters has already been discussed. In these homogeneous reactions, the catalyst was an acid, and the products were the branched acids expected from a reaction involving a carbonium ion intermediate.

After Reppe had discovered the carboxylation reaction using acetylenic compounds, he attempted to transfer this knowledge and experience to the reactions of olefinic compounds.

With Stoichiometric Quantities of Metal Carbonyls. In contrast to the acrylic compounds, the formation of carboxylic acids from olefins, water, and carbon monoxide proceeded at higher temperatures, and consequently even the stoichiometric process required closed converters. In the presence of sufficient acetic acid to combine with the nickel, olefins heated with nickel and carbon monoxide for several hours at 160 to 170°C, gave high yields of carboxylic acids with preponderance of the α-methyl substituted carboxylic acid. Glacial acetic acid, octadecene, and nickel carbonyl at 170°C gave a mixed anhydride of 2-methylstearic acid and acetic acid.

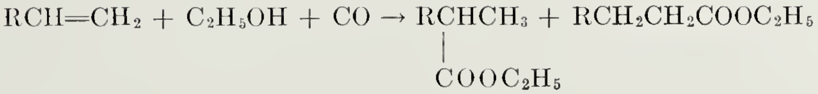
Under similar conditions, the use of alcohols led to the corresponding esters, whereas with mercaptans, temperatures of 260°C were necessary before reaction occurred.

With Catalytic Quantities of Nickel Compounds. The attempt to synthesize carboxylic acids and their derivatives from olefins by catalytic reaction with carbon monoxide was first directed toward the reactions of olefins, carbon monoxide, and water. It was found that the presence of equivalent quantities of mineral acid for combination with the nickel was not essential if high pressures of carbon monoxide were employed. Initially, the halides of carbonyl-forming metals, especially nickel and cobalt halides, were used as catalysts. The activity of the catalysts increased from chloride to iodide; the reaction temperatures ranged from 180 to 220°C, the carbon monoxide pressures from 100 to 200 atmospheres. Olefins from C_4 to C_{18} were treated, as well as technical olefins prepared by cracking paraffin or by synthesis from carbon monoxide and hydrogen. It was claimed that olefins in the C_4 to C_{18} range could readily be converted to the corresponding acids with a yield of over 90 per cent[114].

A point of interest was the regular presence of carbonyls in the reaction products when the above catalysts were used. Consequently, nickel carbonyl itself was introduced in catalytic quantities in the presence of small amounts of nickel iodide and good yields were obtained. Although there are conflicting reports in the literature, there is no doubt that both straight chain and α-methyl substituted acids are obtained from straight chain terminal olefins. With nickel carbonyl and iodine at 185°C and 250 to 300 atmospheres of carbon monoxide, a 60–40 distribution of the two isomers is produced; the branched isomer is usually obtained in greater yield. It has been reported that the reaction of isobutylene with carbon monoxide and water in the presence of nickel carbonyl and iodine produces pivalic and 3-methylbutyric acids in a 60:40 ratio. With propylene, a mixture of 48.5 per cent of butyric and 51.5 per cent of isobutyric acids was obtained[114].

The synthesis of esters of aliphatic acids in the presence of halides always was accompanied by a series of undesirable side reactions; some of the possible reactions are listed.

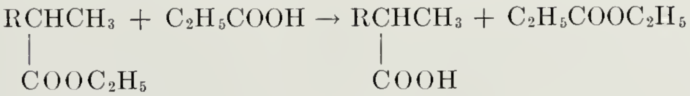
Chief Reaction

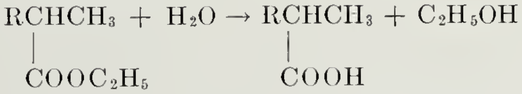
I.

$$RCH{=}CH_2 + C_2H_5OH + CO \rightarrow \underset{\substack{|\\ COOC_2H_5}}{RCHCH_3} + RCH_2CH_2COOC_2H_5$$

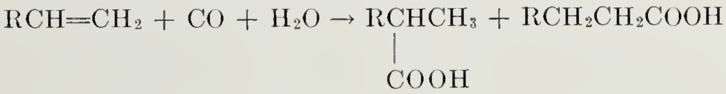
Side Reactions

II. $C_2H_5OH + CO \rightarrow C_2H_5COOH$

III. $C_2H_5OH + C_2H_5COOH \rightarrow C_2H_5COOC_2H_5 + H_2O$

IV.

$$\underset{\substack{|\\ COOC_2H_5}}{RCHCH_3} + C_2H_5COOH \rightarrow \underset{\substack{|\\ COOH}}{RCHCH_3} + C_2H_5COOC_2H_5$$

V.

$$\underset{\substack{|\\ COOC_2H_5}}{RCHCH_3} + H_2O \rightarrow \underset{\substack{|\\ COOH}}{RCHCH_3} + C_2H_5OH$$

VI.

$$RCH{=}CH_2 + CO + H_2O \rightarrow \underset{\substack{|\\ COOH}}{RCHCH_3} + RCH_2CH_2COOH$$

VII. $2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$

VIII. $C_2H_5OC_2H_5 + CO \rightarrow C_2H_5COOC_2H_5$

IX. $C_2H_5OH \rightarrow CH_2 = CH_2 + H_2O$

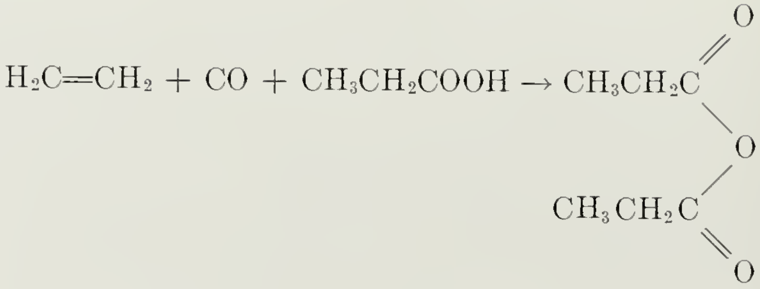
X. $H_2C{=}CH_2 + CO + H_2O \rightarrow C_2H_5COOH$

XI. $C_2H_5OH \rightarrow CH_3CHO + H_2$

The extent to which these side reactions occur depends on the conditions of the reaction[114]. A short reaction time favors the main reaction. Longer reaction times and higher temperatures promote reactions (II), (III), and (IV). The formation of free aliphatic acids (VI and X) from the olefin and the water formed in (III), (VII), and (IX) is unimportant, as is the splitting of the ester (V). Ether formation (VII) occurs mainly when methanol is used as the alcohol.

In the synthesis of propionic acid from ethylene, carbon monoxide, and water, the observation was made that considerably more ethylene and carbon monoxide were consumed than corresponded to the quantity of water used. It was found that 50 per cent or more of propionic anhydride was formed according to the following equations:

$$\text{(a)}\ H_2C{=}CH_2 + CO + H_2O \rightarrow CH_3CH_2COOH$$

(b)


$$\text{(b)}\ H_2C{=}CH_2 + CO + CH_3CH_2COOH \rightarrow CH_3CH_2C(=O){-}O{-}C(=O)CH_2CH_3$$

The last equation is the reverse of a reaction discovered by Mailhe[93] in 1909, who heated anhydrides of carboxylic acids with finely divided nickel at 220 to 240°C, thus obtaining olefins, carbon monoxide, and carboxylic acids.

The carboxylic acid anhydrides can be prepared even more simply by the treatment of a carboxylic acid directly with carbon monoxide and the olefin. At 230°C, a 1:1 mixture of carbon monoxide and ethylene at 200 atmospheres pressure reacted with propionic acid containing 8 per cent of nickel propionate to give about 80 per cent of propionic anhydride.

Newitt and Momen[102] designed experiments to obtain quantitative information about the conditions favorable to the syntheses of the pure acid, esters, and amides from olefins, carbon monoxide, and water, alcohols, or amines, respectively. Their results indicate that there is a general reaction of the type

$$C_nH_{2n} + CO + HX \rightarrow C_nH_{2n+1}COX$$

where HX is a neutral or basic molecule. Because these authors used higher temperatures and a reduced nickel catalyst without added halide, their results cannot be compared with those of Reppe.

Newitt and Momen reported that an optimum yield of 46.6 per cent of propionic acid could be obtained by treatment of a stoichiometric mixture of ethylene, carbon monoxide, and water in a static system at a pressure of 248 atmospheres and a temperature of 300°C in a reaction period of 2 hours. In contrast to the observation made by Hardy[59] who used strong acid catalysts, Newitt and Momen found that their products from ethylene, carbon monoxide, and water contained no alcohol and only a small quantity of polymerized product. They found that the reduced nickel catalyst was active in promoting both the synthesis and the thermal decomposition of propionic acid and also the decomposition of carbon monoxide. Increase of pressure favored the synthesis and also the undesirable side reaction $2CO \rightarrow CO_2 + C$ and tended to prevent decomposition of the acid. Increase of temperature lowered the yield of acid and favored the decomposition of carbon monoxide.

Further experiments were carried out to ascertain whether, by the use of an excess of olefin, esters could be produced according to the reaction:

$$2C_2H_4 + CO + H_2O \rightarrow CH_3CH_2COOC_2H_5\,.$$

With a reduced nickel catalyst, only traces of ester were found in the products. When, however, a mixed catalyst consisting of reduced nickel and phosphoric acid, containing 2 per cent of copper phosphate was used, yields of ester representing about 5 per cent of the ethylene in the initial gases were obtained. At 300°C and 221 atmospheres, a yield of 25 per cent of free acid and 5.4 per cent of ester was obtained; at 255°C and 173 atmospheres the same yield of ester but only 3.2 per cent of acid was obtained.

A stoichiometric mixture of propylene, carbon monoxide, and steam in the presence of a reduced nickel catalyst at 300°C and 220 atmospheres gave a 2.8 per cent yield of isobutyric acid. Under the same conditions, doubling the amount of olefin in the initial mixture raised the yield to 5.2 per cent. It is interesting to note that butyric acid (and isopropyl alcohol) were not found in the products.

Using the same catalyst, Newitt and Momen obtained a 46.2 per cent yield (based on aniline) of propionanilide by treating a 2:4:1 mixture of ethylene, carbon monoxide, and aniline at 325°C and 300 atmospheres. At 300°C and 250 atmospheres, a 3:3:1 mixture of ethylene, carbon monoxide, and benzyl alcohol gave a 9.2 per cent yield of benzyl propionate (based on alcohol). A 2:2:1 mixture of ethylene, carbon monoxide, and phenol at 230 atmospheres and 275°C, in the presence of the same catalyst, gave 8.9 per cent of phenyl propionate.

The carboxylation of olefins in the presence of a nickel catalyst has also been reported by Hagemeyer[56] who used a "3-component" catalyst system. In a typical experiment, he placed in an autoclave 300 grams of water containing 4 per cent of a catalyst consisting of a 1:1:1 mixture of nickel chloride hexahydrate, sodium iodide, and nickel acetate. The autoclave was closed and a 1:1 mixture of ethylene and carbon monoxide was added to a pressure of 200–400 atmospheres. The mixture was heated at 280 to 300°C. The over-all conversion of ethylene was 82 per cent, and a 93 per cent yield of propionic acid and a 7 per cent yield of propyl alcohol based on the ethylene consumed was secured in addition to 7.6 grams of nickel carbonyl. The application of this catalyst system to alcohols will be discussed in greater detail in the next section.

Alcohols

The synthesis of acetic acid from methanol and carbon monoxide in the presence of nickel, cobalt, and iron has recently been investigated by

Bhattacharyya and Sourirajan at the Indian Institute of Science. These studies[12, 124] indicated that the halides of nickel, cobalt, and iron were superior to the metals themselves, and also that, among the halides, the iodides were superior to the bromides and chlorides as catalysts for the syntheses. Further, silica gel was found to be superior to either kieselguhr, pumice, or kaolin as the catalyst support. Nickel iodide deposited on silica gel exhibited the maximum catalytic activity. Acetic acid, methyl acetate, carbon monoxide, carbon dioxide, hydrogen, and methane, together with the unreacted alcohol and carbon monoxide appeared to be the only products of the reaction. No ether or oil products were detected.

The yield of acetic acid was optimum when the concentration of nickel iodide on silica gel was 84.2 per cent (calculated on the basis of SiO_2 content), the pressure was 260 atmospheres, and the temperature was 180 to 230°C; the yield of acetic acid did not vary significantly in this temperature range. Incorporation of thoria, magnesia, iodine, or copper iodide in the catalyst did not improve the yield of acetic acid. The per cent conversion of methanol to acetic acid increased with increasing dilution of methanol with water up to a maximum; further increase in dilution had little effect on the yield of acetic acid. With a catalyst containing 84.2 per cent of nickel iodide on silica gel and 95 per cent methanol under a pressure of 260 atmospheres at 180°C, a total conversion of 59.2 per cent of methanol in a period of 2 hours was obtained. The products consisted of free acid (45.9 per cent), methyl acetate (3.7 per cent), and gaseous by-products (9.6 per cent). With a similar cobalt iodide[13] catalyst under the same conditions, a 39.7 conversion of methanol in a period of 2 hours was obtained; the products, in this case, consisted of acetic acid (17.8 per cent), ester (3.6 per cent), and gaseous by-products (18.3 per cent). With ferrous iodide[14] at 175°C, a conversion of 31.7 per cent of methanol was obtained under the same conditions; of this, 11 per cent was free acid, 4.2 per cent was ester, and 16.5 per cent was gaseous decomposition products of methanol.

Studies on the synthesis of propionic acid[124] by the reaction of ethyl alcohol and carbon monoxide gave results very similar to those obtained for the reaction of methyl alcohol and carbon monoxide. Propionic acid, ethyl propionate, carbon dioxide, a mixture of gaseous saturated hydrocarbons and hydrogen, unreacted carbon monoxide and ethyl alcohol were found to be the only products of the reaction. The formation of acid was, however, less, whereas the yield of ester and gaseous decomposition products were more than those observed in the case of the synthesis of acetic acid. Again, it was found that the iodides were superior to the metals or their bromides or chlorides, and that nickel iodide was superior to cobalt iodide or ferrous iodide as the catalyst for the synthesis. The optimum conditions for the best yields of propionic acid were found to consist of (1) a catalyst containing the metal iodide deposited on a quantity of silica gel equivalent to the weight of the metal in the iodide, (2) a temperature of 230°C, (3) a pressure of about 320 atmospheres, and (4) an ethyl alcohol concentration of 95 per cent (5 per cent water). Under the above conditions, with nickel iodide-silica gel as the catalyst, a total conversion of 69.8 per cent of ethyl alcohol was obtained in a period of 2 hours of which free propionic acid corresponded to 37.5 per cent, ethyl propionate 11.4 per cent, and gaseous decomposition products 20.9 per cent.

In all the above experiments, the behavior of the catalyst was rather interesting. When the products of the reaction were released from the bomb at the temperature of the reaction, the reduced metal catalysts and the chloride catalysts retained their maximum activity indefinitely (their activity for the synthesis was very low). However the bromide and the iodide catalysts exhibited their maximum activity only in the first experiment and their activity decreased considerably in the second and subsequent experiments. The "spent" bromide and iodide catalysts could be reactivated completely by the addition of a few drops of cold water on the surface of the spent catalysts. Further, in the case of the above catalysts, the problem of catalyst deactivation did not arise at all if the reaction products were released from the bomb at a sufficiently low temperature (60 to 80°C), under which conditions they appeared to retain their maximum activity indefinitely.

From these observations, the Indian workers concluded that the presence of traces of water in the catalyst was essential for its maximum activity and that the activity itself must be attributed to some new compound formed during the synthesis. The real catalyst for the synthesis appears to be neither the salt nor the carbonyl alone, but a complex which is stable at high temperatures only under high pressures.

An examination of the original and spent nickel iodide catalyst resulted in two important observations: (1) The spent catalyst was far less hygroscopic than the original catalyst and (2) the spent catalyst contained a small quantity of a water-insoluble compound which was not in the original catalyst. A small quantity of this compound (0.2–0.3 grams) was formed in each experiment. A few experiments were conducted with free nickel iodide catalyst and about 0.5 gram of the new compound was collected by dissolving the catalyst mass in water and separating the water-insoluble portion. The presence of nickel and iodine was established in this water-insoluble substance. Although its complete composition was not established, it was possible that the compound might be a nickel-carbon monoxide-iodine complex. The yield of acetic acid was not affected when part of the nickel iodide catalyst was replaced by this new compound.

Bhattacharyya and Sourirajan were not the first to postulate that a compound of carbon monoxide with a halide of either nickel, cobalt, or iron was the catalyst for these high-pressure reactions. In the catalytic synthesis of acrylates, the true catalyst when nickel salts were used was believed to be a hypothetical addition compound of the nickel salt and carbon monoxide, and not the nickel carbonyl as might be supposed on the basis of the stoichiometric procedure previously described. This belief is supported by the work of Hieber[63] who found that cobalt iodide adds one mole of carbon monoxide at 150°C and 200 atmospheres forming the unstable compound, $CoI_2 \cdot CO$. Under the experimental conditions, it may be assumed that the formation of nickel halide-carbon monoxide compounds of the type $NiX_2(CO)_2$ takes place.

Reppe found that certain organic complexes of nickel chloride and nickel bromide were more active than the nickel halides alone; a complex formed by the reaction of triphenylphosphine with nickel halides or nickel carbonyl was particularly promising. The following well-defined compounds[32] are formed when triphenylphosphine and nickel carbonyl react:

$$(C_6H_5)_3P + Ni(CO)_4 \xrightarrow{20°C} [(C_6H_5)_3P]Ni(CO)_3 + CO \quad \text{m.p. 123°C.}$$

$$2(C_6H_5)_3P + Ni(CO)_4 \xrightarrow{50°C} [(C_6H_5)_3P]_2Ni(CO)_2 + 2CO \quad \text{m.p. 192°–194°C. (decomp.)}$$

Very little nickel carbonyl is isolated from the reaction products if triphenylphosphine is added to the starting material.

The work of Adkins and Rosenthal[2] on the synthesis of acids from alcohols, carbon monoxide, and water in the presence of a nickel catalyst is of interest. According to the reports of Reppe, when alcohols were heated at 250 to 300°C under 200 to 300 atmospheres in the presence of carbon monoxide, nickel, and iodine (or copper iodide), good yields of acids were obtained.

$$ROH + CO \xrightarrow[I_2(CuI)]{Ni} RCOOH.$$

All attempts by Adkins and Rosenthal to duplicate Reppe's work failed until it was found that in order to obtain acid, both nickel chloride and hydrogen chloride were needed as catalysts. The optimum conditions can best be described by a typical experiment: 2-Octanol (41 grams), water (15 grams), nickel carbonyl (17 grams), nickel chloride hexahydrate (5 grams), and concentrated hydrochloric acid (3 ml) were placed in a glass liner of a 190-ml silver-lined steel bomb and carbon monoxide admitted to a pressure of 900 psi. The bomb was heated at 300°C for 15 hours; the yield was 76 per cent of 2-methyloctanoic acid.

If any one of these reagents or catalysts was omitted, the reaction was unsuccessful. The water and nickel carbonyl were used in excess whereas nickel chloride and hydrochloric acid were used in catalytic quantities; an increase in the amount of each of the last two named catalysts did not increase the yield of acid obtained. A temperature of 275°C was found to be necessary for the carboxylation of secondary and tertiary alcohols, and 300°C for primary alcohols. Below 275°C, only unreacted alcohol or olefins formed by dehydration were recovered.

Adkins and Rosenthal found that in every reaction in which the alcohol used was pure and not prone to rearrangement, the product was homogeneous and was the branched acid; in no case was a straight-chain acid produced as Reppe claimed. A possible course of the reaction is the dehydration of the alcohol to an olefin, which then undergoes carboxylation to the branched acid. Reasonable evidence for this path is the fact that both 1-octanol and 2-octanol, which yield the same olefin on dehydration gave the same acid, 2-methyloctanoic, in this reaction.

$$C_6H_{13}CH_2CH_2OH \quad \text{or} \quad C_6H_{13}CHOHCH_3 \xrightarrow{-H_2O}$$

$$C_6H_{13}CH{=}CH_2 \xrightarrow[H_2O]{CO} C_6H_{13}CH(CH_3)COOH.$$

As can be seen in Table 10, aliphatic primary and secondary alcohols of the same carbon chain length gave the same product, a 2-methylalkanoic acid, but the yields from the secondary alcohols were higher. Thus, 1-butanol and 2-butanol yielded 2-methylbutyric acid in 47 and 70 per cent yield, respectively; 1-heptanol and 2-heptanol gave 2-methylheptanoic acid in 33 and 70 per cent yield; and 1-octanol and 2-octanol yielded 2-methyloctanoic acid in 30 and 76 per cent yield. The reaction of the secondary alcohols at lower temperatures with the production of higher yields of acids appears to be related to the relatively greater ease of their dehydration.

When the alcohol contained an aromatic ring, the only product isolated was the alkylbenzene formed by the hydrogenolysis of the terminal hydroxy group. Thus, 2-phenyl-1-ethanol, 3-phenyl-1-propanol, and 4-phenyl-1-butanol yielded ethyl-, n-propyl-, and n-butylbenzene, respectively. When methyl-β-naphthylcarbinol was carbonylated, a resin was obtained, presumably arising from the polymerization of β-vinylnaphthalene, the dehydration product of the alcohol. Glycols yielded monocarboxylic acids, through the carbonylation of one hydroxyl and the hydrogenolysis of the other. Thus, 1,5-pentanediol and 1,6-hexanediol gave 2-methylpentanoic and 2-methylhexanoic acids, respectively. The hydrogen required for these hydrogenolyses probably results from the water gas equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2 .$$

Hagemeyer[56] treated olefins and alcohols with carbon monoxide in the presence of a "3-component" catalyst consisting of: (1) A carbonyl-forming metal salt, (2) an acceptor metal, and (3) a promoter. The halides of nickel, cobalt, and iron fulfill the requirements of the first component. Suitable acceptor metals include Ni, Co, Fe, Ag, Cu, Cd, Zn, or the lower aliphatic carboxylic salts of these metals. Carbonyl formation and the rate of the reaction seem to be accelerated by the presence of an acceptor metal which combines with the negative ion or radical of the carbonyl-forming metal salt. For example, with nickel chloride and powdered copper, the reaction may be represented as follows:

Table 10. Carboxylation of Alcohols with Nickel Carbonyl at 300°C[a]

Alcohol	CO Pressure (psi)	Time (hr)	Acid Formed	Yield (%)
Butanol	850	21	2-Methylbutanoic	47
Pentanol	650	16	2-Methylpentanoic	16
Hexanol	900	13	2-Methylhexanoic	55
Heptanol	800	18	2-Methylheptanoic	33
Octanol	700	18	2-Methyloctanoic	30
2-Ethyl-1-butanol	650	24	2-Ethyl-2-methylbutanoic	40
3-Cyclohexyl-1-propanol	600	23	3-Cyclohexyl-2-methylpropanoic	49
Neopentyl	650	21	C_6 acids	21
2-Butanol	600	20	2-Methylbutanoic	70
2-Heptanol	700	22	2-Methylheptanoic	70
2-Octanol	825	19	2-Methyloctanoic	76
Cyclopentanol[b]	700	22	Cyclopentanecarboxylic	84
4-Methyl-1-hexanol[b]	900	22	4-Methylcyclohexanecarboxylic	53
β-Decanol[b]	700	17	Decahydronaphthoic acids	77
tert-Amyl[b]	900	23	2,2-Dimethylbutanoic	35

[a] In all runs, 5 grams of nickel chloride hexahydrate, 15 grams of water, 17 grams of nickel carbonyl, 3 ml. of concentrated hydrochloric acid, and approximately 0.2 mole of alcohol were used.

[b] Run at 275°C.

$$NiCl_2 + 2Cu + 6CO \rightarrow Ni(CO)_4 + 2CuCl \cdot CO.$$

The bivalent nickel cation is reduced to zero-valent nickel with the copper furnishing the electrons needed for this reduction. The reactor wall may function as the acceptor metal, especially if it is lined with silver, copper, or nickel. Promoters include, according to Hagemeyer, the alkali metal salts of the halogens, sulfur, selenium, halogens, zinc chloride, alkyl halides, *o*-phosphoric acid, trialkylphosphates, and boric acid. The reactions were performed at 280 to 300°C under a pressure of 200 to 240 atmospheres. Some of the results are shown in Table 11.

Ethers

One of the most interesting reactions reported by Reppe in his study of the carboxylation reaction was the conversion of tetrahydrofuran to adipic acid by treatment with nickel catalysts, in the presence of water[115].

TABLE 11. CARBOXYLATION OF ALCOHOLS (HAGEMEYER)[a]

Substrate		Catalyst system			Products (grams)
Alcohol	Grams	Metal Salt (grams)	Acceptor (grams)	Promoter (grams)	
CH_3OH	320	10 $NiCl_2 \cdot 6H_2O$	5 Ni	4 NaI	212 CH_3COOH, 8 $Ni(CO)_4$, 127 CH_3COOCH_3
C_2H_5OH	230 + 45 H_2O	10 $NiCl_2 \cdot 6H_2O$	5 Ni	4 NaI	263 C_2H_5COOH, 7 $Ni(CO)_4$, 60 $C_2H_5COOC_2H_5$
C_2H_5OH	230 + 45 H_2O	8 NiS	4 Zn	4 NaI	274 C_2H_5COOH
$(CH_3)_2CHOH$	300 + 90 H_2O	7 CoS	5 Ni	4 NaI	300 $(CH_3)_2CHCOOH$, 42 $(CH_3)_2CHCOOCH(CH_3)_2$
n-C_4H_9OH	370 + 45 H_2O	20 NiI	10 Ni	12 NaI	48 $CH_3CH_2CH_2CH_2COOH$

[a] From Reference 56.

$$+ 2CO + H_2O \rightarrow HOOCCH_2CH_2CH_2CH_2COOH$$

This reaction was carried out with nickel iodide at 240 to 270°C and at a pressure of 200 atmospheres of carbon monoxide with a reported yield of 75 to 80 per cent[116]. Very little adipic acid was formed in the absence of halogen; iodine was much more effective than either bromine or chlorine. In all of the experiments, nickel carbonyl was present in the reaction products and the highest yields of acid were secured when both nickel carbonyl and nickel iodide were used. The effectiveness of this combination of carbonyl and iodide lends some support to the postulate that nickel carbonyl halides ($Ni(CO)_2I_2$) are the effective catalysts. An iodine concentration of 1 to 2 per cent was required.

Many products besides adipic acid are formed in this reaction of tetrahydrofuran with carbon monoxide and water, and it appears that the yields claimed[116] are probably too high. There are numerous competing reactions; some of the side products isolated are α- and γ-methylbutyrolactone, δ-valerolactone, n- and isovaleric acids, methylglutaric acid, ethylsuccinic acid and cyclopentanone.

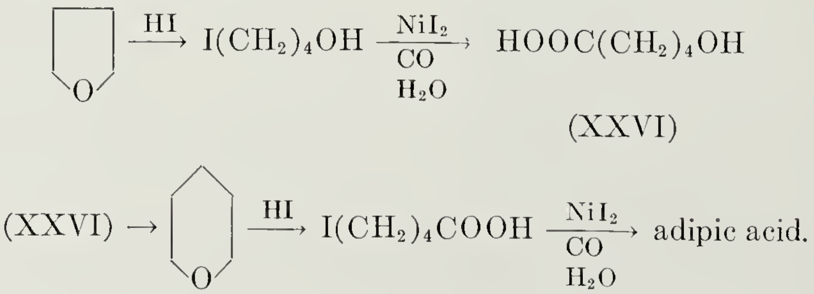
Reppe[115] has postulated that hydrogen iodide is formed from nickel iodide in this reaction according to the following equation:

$$NiI_2 + 5CO + H_2O \rightarrow Ni(CO)_4 + 2HI + CO_2 .$$

The hydrogen iodide may react with nickel carbonyl to regenerate nickel iodide

$$2HI + Ni(CO)_4 \rightarrow NiI_2 + 4CO + H_2$$

or may function as a reagent in the cleavage of cyclic ethers to form iodoalkanols. These then react with carbon monoxide and water to form hydroxycarboxylic acids; in this reaction, nickel carbonyl iodide is probably the carbon monoxide carrier. The following scheme may be written for the formation of adipic acid from tetrahydrofuran.



The greater reactivity of iodine-containing catalysts parallels the activity of the corresponding alkyl halides. Compounds containing hydroxyl groups that can be replaced by halogen atoms only with great difficulty or not at all under the conditions of the carboxylation, fail to undergo the reaction to any extent (phenol does not react). On the other hand, bromobenzene yields benzoic acid smoothly. Benzyl bromide, whose halogen atom is easily removed, can be converted practically quantitatively with stoichiometric amounts of triphenylphosphine-nickel carbonyl. Similarly, benzyl alcohol yields phenylacetic acid with nickel triphenylphosphinealkylbromide* as catalyst, whereas no acid is obtained if the halogen is omitted. The same yields of adipic acid are obtained from either 1,4-butanediol or tetra-

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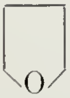
* See Reference 32, pp. 259–265 for a discussion of these compounds as catalysts in reactions involving carbon monoxide.

hydrofuran, the diol being in equilibrium with the ether under reaction conditions:

 $+ H_2O \rightleftharpoons HOCH_2CH_2CH_2CH_2OH.$

Cobalt catalysts are effective for the synthesis of adipic acid from tetrahydrofuran even in the absence of halogen.

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CHAPTER 2

THE OXO REACTION

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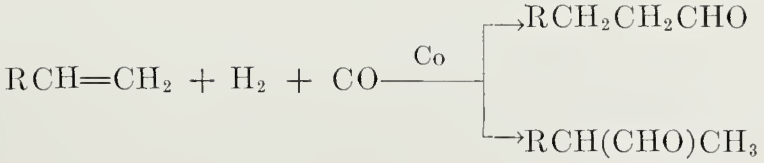
INTRODUCTION

The earliest recorded experiments in which oxygenated compounds were produced from hydrogen-carbon monoxide mixtures were those performed by Mittasch and Schneider and incorporated into patents issued to the Badische Anilin and Soda Fabrik in 1913[4]. These workers found that hydrogen and carbon monoxide reacted at 100 to 200 atmospheres pressure at 300 to 400°C in the presence of alkali-activated cobalt and osmium oxides to form a liquid product containing alcohols, aldehydes, ketones, acids, and saturated and unsaturated hydrocarbons. Further development of this line of investigation, in particular, the use of difficultly reducible oxides such as zinc oxide as catalysts, led eventually to the establishment of the commercial methanol synthesis. Investigations along a different line in which the iron group metals were used as catalysts had equally important consequences. In 1923 Franz Fischer and Hans Tropsch[22], working at the Kaiser-Wilhelm Institut, discovered that hydrogen and carbon monoxide when passed over alkalized iron turnings at 100 to 150 atmospheres and 400 to 450°C formed an oily liquid which they called "synthol" (synthetic oil). Under these conditions the oil was chiefly oxygenated, but in experiments (1925) in which the pressure was lowered to about 7 atmospheres, the "synthol" consisted chiefly of olefinic and paraffinic hydrocarbons suitable for motor fuel. This process for the production of synthetic fuels (or chemicals)from carbon monoxide-hydrogen mixtures has since become known as the Fischer-Tropsch reaction.

The industrial importance of the Fischer-Tropsch synthesis excited much research work in most of the industrialized countries of the world. In 1926 Elvins and Nash[20] in England called attention to the fact that the product from the low-pressure hydrocarbon synthesis of Fischer-Tropsch always contained small quantities of oxygenated compounds. In 1929 Smith, Hawk, and Golden[74], at the U. S. Bureau of Mines, added ethylene to the carbon monoxide-hydrogen mixture before passing it over a cobalt catalyst and found that the yield of oxygenated compounds was increased. Meanwhile, research work on the synthesis was being actively pursued in Germany, especially at Ruhrchemie A. G. in Oberhausen-Holten where one of Franz Fischer's former students from the Kaiser Wilhelm Institut, Otto Roelen, was directing a group of research workers. In 1937 they performed experiments on the recycling of the tail gas and on the addition of various substances to the tail gas prior to the recycling. It was found that when olefins were added, part of the olefins were hydrogenated, part were incorporated into higher molecular weight hydrocarbons, and part were converted to oxygen-containing compounds. The experiment of Smith, Hawk, and Golden was repeated and the aldehydic portion of the product was separated by means of 2,4-dinitrophenylhydrazine. Only the phenylhydrazone of propionaldehyde was found. Roelen felt that the small quantity of propionaldehyde had been formed from the added ethylene and reasoned that such a reaction involving the condensation of three moles of gas would be highly pressure-dependent. Furthermore, earlier work had shown that to increase the yield of oxygenated materials with a cobalt catalyst, temperatures lower than those required for the Fischer-Tropsch reaction were desirable. In July and August of 1938 experiments were performed using water gas ($1H_2:1CO$), ethylene and a cobalt catalyst at 100 atmospheres and 50 to 150°C. The product was found to consist principally of propionaldehyde together with some diethyl ketone. Thus Roelen's study of the Fischer-Tropsch reaction, in which hydrocarbons were the main product and oxygenated compounds a minor constituent, led to the discovery of a new reaction in which oxygenated compounds only and no hydrocarbons were produced. Roelen considered the reaction to be a general one for all olefins[69]. In the patent applications and correspondence it became convenient to call the reaction an "oxo" synthesis. It was soon discovered, however, that only with ethylene was an appreciable quantity of ketone formed; the aldehyde (or its condensation products) was usually the chief product. The reaction is therefore more correctly called an aldehyde synthesis rather than an oxo synthesis, but the linguistic appeal of the simple short word has already won it a permanent place in the literature of chemical technology. The over-all reaction is most easily visualized as involving the addition of a hydrogen atom and a formyl group (H—CHO) across the double bond of an olefin, and for this reason the name "hydroformylation" has been proposed[1]. The general reaction can be represented as follows:



$$\mathrm{RCH{=}CH_2 + H_2 + CO} \xrightarrow{\mathrm{Co}} \left[\begin{array}{l} \rightarrow \mathrm{RCH_2CH_2CHO} \\ \\ \rightarrow \mathrm{RCH(CHO)CH_3} \end{array}\right.$$

In the discussion which follows, the names oxo and hydroformylation will be used interchangeably to denote the above reaction. It will be shown that hydrogenation reactions can occur in lieu of, in competition with, or subsequent to the oxo reaction. Hence, it is convenient to refer to "oxo" or "hydroformylation conditions" to denote the conditions of temperature, pressure, and catalyst required for the oxo and related reactions. These conditions are approximately 75 to 200°C, 100 to 300 atmospheres of synthesis gas* and a cobalt catalyst (reduced metallic cobalt, a cobalt salt or a carbonyl of cobalt). Dicobalt octacarbonyl, cobalt hydrocarbonyl, and tricobalt dodecacarbonyl may all be present under these conditions.

THE PRINCIPAL REACTION

Commercial Charge Stocks and Products

The starting materials for the oxo synthesis, as operated in the United States, are propylene, copolymers of propylene and butylene, and butylenes. The largest manufacturing capacity is devoted to the production of "isooctyl" alcohols from mixed heptylenes, which in turn are produced from the copolymerization of propylene with butylenes. The "isooctyl alcohol" produced is a mixture of at least ten different C-8 primary alcohols, among which are 3,5-dimethylhexanol, 3,4-dimethylhexanol, 4,5-dimethylhexanol, 3-, 4-, and 5-methylheptanol; the dimethylhexanols are the principal components. Isooctyl alcohol is produced principally for its conversion to isooctyl phthalate, a valuable plasticizer in polyvinyl chloride formulations. This is an example of the familiar pattern of American chemical manufacture: chemicals to make more chemicals. Propylene is the feed material in one large oxo plant which produces butyraldehyde and isobutyraldehyde. This is one of the few operations in which the aldehyde is isolated and purified; usually the aldehyde mixture is reduced immediately to the corresponding mixture of alcohols. Isolation of the aldehydes is particularly feasible when they are low-boiling. In another large oxo plant,

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* Synthesis gas is the general name given to all mixtures of carbon monoxide and hydrogen. When a particular synthesis gas is discussed, the ratio of H_2:CO is usually given in parentheses.

butylenes are the feed material and amyl alcohols are the product. These amyl alcohols are all primary alcohols and thus differ from the C-5 alcohols isolated from fermentation processes. Other oxo syntheses are based on the use of propylene trimer and propylene tetramer to produce decyl and tridecyl primary alcohols. Suggested uses for these materials and their conversion to other useful chemicals are contained in advertising material available from the five large commercial manufacturers (Standard of New Jersey, Standard of Indiana, Tennessee Eastman, Carbide and Carbon Chemicals, and Gulf Oil Corp.) engaged in oxo preparation.

In Germany, the main interest in the oxo process during World War II was the production of alcohol sulfates as washing and wetting agents. The charge stock was an olefinic mixture in the C_{11-17} range secured by thermal cracking of the soft wax produced in the Fischer-Tropsch process. Actually, the process was never operated to any extent in Germany during World War II.

In England, diisobutylene is used as a feed stock and the C-9 alcohols produced are used in plasticizer manufacture. In Italy, the early interest in the oxo reaction was directed toward the manufacture of propionaldehyde from ethylene.

In a typical operation, a mixture of heptylenes boiling at 76 to 99°C is mixed with recycle product and sufficient cobalt naphthenate (or other form of soluble cobalt) is added to give a concentration of 0.2 per cent cobalt based on the total feed. The solution is pumped through a preheater and into a reactor where the liquid passes upward cocurrently with synthesis gas. The reactor may be an empty tube or it may be filled with an inert material such as Raschig rings. The temperature of the reactor is held at about 175°C and the pressure of synthesis gas ($1H_2$:1CO) is kept at about 200 atmospheres. The reaction is very exothermic; the conversion of ethylene to propionaldehyde is accompanied by the liberation of 34.8 kcal/mole. The recycle product helps in removing the heat of reaction.

Scope and Limitations of the Reaction

Thermodynamics. The feasibility of the oxo reaction can be determined by evaluating the magnitude of the free energy change, $\Delta F°$, which is the thermodynamic driving force for the reaction. Rather extensive data are available for the oxo reaction involving ethylene:

$$CH_2{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO$$

The heats of formation, ΔH, for ethylene, carbon monoxide and propionaldehyde have been calculated to be +12,496, −26,416, and −48,707 cal/mole at 25°C, respectively, from which it is apparent that the ΔH of the reaction is −34,787 cal/mole. Substitution of this value in the free energy equation, $\Delta F^\circ = \Delta H - T\Delta S^\circ$, where T is absolute temperature and ΔS° is change in entropy, gave the value, $\Delta F = -34{,}787 + 58.1\ T$,[98] from which the equilibrium constant K was calculated from the usual relationship, $\Delta F^\circ = -RT \ln K_p$. The values obtained in this manner by Wenner[98] and somewhat different values secured by Natta, Pino and Mantica[47] are shown in Table 1. These data show that the formation of propionaldehyde from ethylene and synthesis gas is very favorable at 1 atmosphere and moderate temperature. The reaction obviously is not subject to equilibrium restrictions. Although the oxo synthesis does not proceed at atmospheric pressure with a dicobalt octacarbonyl catalyst, measurable rates have been observed at as low as 10 atmospheres pressure and, indeed, the reaction has been shown to occur readily at room conditions when cobalt hydrocarbonyl is mixed with an olefin. It is of interest to note that the hydroformylation of an olefin usually occurs practically to the complete exclusion of its hydrogenation, even though the free energy change, ΔF°, for the reaction:

TABLE 1. FREE ENERGY AND EQUILIBRIA VALUES FOR THE HYDROFORMYLATION OF ETHYLENE

Temperature (°C)	ΔF° (cal/mole)		K_p	
	Ref 98	Ref 47	Ref. 98	Ref. 47
25	−17,473	−14,460	6.5×10^{12}	4.05×10^{10}
100	−13,116	−8,930	4.8×10^{7}	1.71×10^{5}
150	−10,211	−5,220	1.9×10^{5}	4.99×10^{2}
200	−7,306	−1,390	2.4×10^{3}	4.39

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$$

at 25°C is −22,608 cal/mole[48] compared to −14,460 for the oxosynthesis. Hydrogenation becomes competitive only when the olefinic linkage is conjugated.

Catalysts. The first catalyst to be used in the oxo synthesis was the conventional Fischer-Tropsch cobalt catalyst containing cobalt:thoria magnesia:kieselguhr in the proportions 100:5:8:200. This was the standard Fischer-Tropsch catalyst used by Ruhrchemie in their synthetic fuel plants and was thus readily available in large quantity. When in the reduced state, this catalyst is very active in the oxosynthesis, but the last three components, although they impart important properties to the catalyst for use in the Fischer-Tropsch synthesis, are superfluous for the oxo reaction. The Fischer-Tropsch synthesis is a heterogeneously catalyzed reaction and the condition of the surface of the catalyst, its method of preparation, and the manner in which it is activated, are of utmost importance. On the other hand, there is little doubt at the present time that the oxo synthesis is a homogeneous reaction in which the soluble cobalt carbonyls are the catalysts. When metallic cobalt is used in the oxo synthesis, its efficiency will depend, therefore, on the ease with which it is transformed to the carbonyl.

Although dicobalt octacarbonyl may be formed from an activated cobalt metal by using carbon monoxide, the conversion of cobalt salts to the carbonyl usually requires hydrogen. As a matter of fact, when an oxo reaction is carried out in the presence of cobalt salts, somewhat higher temperatures are required for a successful reaction than are necessary when the cobalt is added as the carbonyl. Thus, for example, the hydroformylation of 1-octene at 200 to 300 atmospheres of synthesis gas ($1H_2:1CO$) with cobalt acetate requires a temperature of 150 to 160°C. However, if the same concentration of cobalt is introduced as dicobalt octacarbonyl, the reaction goes very rapidly at 115 to 125°C. Obviously the formation of the carbonyl from the salt requires the higher temperature.

It may be of interest to consider what appears to be the rather simple conversion of cobaltous acetate to dicobalt octacarbonyl. The valence of cobalt in the carbonyls is zero; in cobaltous (II) acetate it is, of course, two. The reduction of cobalt (II) to cobalt (0) requires two electrons; in this system these are furnished by hydrogen.

$$H_2 \rightarrow 2H^+ + 2e; \; Co^{++}\,(OAc)_2^- + 2e \rightarrow Co^\circ + 2(OAc)^-$$

In the presence of synthesis gas, it is likely that the reduction of cobalt (II) to zerovalent cobalt occurs simultaneously with the formation of the carbonyl, the carbon monoxide pulling the conversion along:

$$H_2 \rightarrow 2H^+ + 2e$$

$$2H^+ + 2e + Co(OAc)_2 \rightarrow Co + 2HOAc$$

$$2Co + 8CO \rightarrow Co_2(CO)_8$$

In support of such a concerted mechanism, it may be noted that the reduction of cobalt salts to metallic cobalt in the presence of hydrogen alone requires high temperatures and long times. Furthermore, the conversion to the carbonyl of metallic cobalt even in as active a state as Raney cobalt appears to require a longer time than does the similar conversion of cobaltous acetate or carbonate under comparable conditions.

It should be apparent from the above discussion, that practically any form of cobalt may be used as a catalyst for the oxo synthesis since under the usual conditions conversion to the dicobalt octacarbonyl occurs. This is also true of organic cobalt salts such as cobalt octanoate or naphthenate;

the crude form in which these salts are sold (as accelerators for drying oils) is suitable for use in the oxo reaction.

Although the contention that iron is an oxo catalyst frequently appears in print and many oxo patents claim iron as a catalyst, there is no clear-cut evidence to support such a contention. On the contrary, the best available evidence indicates that under the conditions in which cobalt functions as a catalyst, iron is inactive. In some of the early discussions on the nature of the catalysis, it was pointed out that cobalt and iron were oxo catalysts because these metals form hydrocarbonyls, whereas nickel did not form a hydrocarbonyl and hence was not a catalyst. However, a hydrocarbonyl of nickel, $[NiH(CO)_3]_2$, has recently been prepared[6]. At the present time it appears that the catalysis of the oxo reaction is limited to cobalt.

Effect of Olefin Structure. Every simple olefin submitted to the oxo synthesis has been shown to undergo the reaction. There is, however, an appreciable difference in the rate at which olefins of various structures react and it may be profitable at this time to present the facts about the effect of structure on rate and leave a possible interpretation of these facts to a later discussion.

The rates of hydroformylation at 110°C of twenty-six olefin hydrocarbons were studied by Wender and co-workers at the U. S. Bureau of Mines[84]; the data are summarized in Table 2. A fifty-fold variation was found between the fastest and slowest rates. The olefins listed in Table 2 are conveniently divided into five structural classes for purposes of comparison.

(1) Straight Chain Terminal Olefins. This type of olefin reacts most rapidly. There is a small drop in rate with increase in chain length, but the effect becomes smaller with increase in carbon number. The decrement may be due to the increased difficulty of orientation of the double bond in the higher molecular weight olefins with respect to the dicobalt octacarbonyl.

(2) Straight-Chain Internal Olefins. Two conclusions may be drawn from the data on this type of olefin given in Table 2: (1) The rate of hydroformylation of straight-chain internal olefins is about one-third that of the corresponding terminal olefin, and (2) the position of the double bond, as long as it is internal, has little or no effect on the rate, i.e., 2-heptene and 3-heptene react with essentially the same speed. There is some support here for the conclusion that steric effects are important in the reaction; the accessible terminal double bond reacts at a greater rate in all cases. The isomerization of double bonds catalyzed by dicobalt octacarbonyl under hydroformylation conditions will be discussed later.

(3) Branched Terminal Olefins. Within the range of olefins studied, branching always results in a decrease in rate. The largest decrease in rate is obtained for olefins with a methyl group at one of the carbon atoms of the double bond (compare 1-hexene and 2-methyl-1-pentene). Further branching along the chain results in a further decrease in rate; even a single methyl

branch on the β carbon atom (4-methyl-1-pentene) results in a small but probably significant decrease. Camphene is an example of an extreme case; the rate of reaction of this compound, which has an exocyclic bond attached to a bulky and highly branched carbon chain, is less than one-thirtieth that of 1-hexene.

(4) Branched Internal Olefins. Internal olefins which are branched react most slowly. Although 1-hexene and 2,3-dimethyl-2-butene are isomeric,

Table 2. Rates of Hydroformylation of Olefins at 110°C[a] [84]

	Specific Reaction Rate 10^3 k. min.$^{-1}$[b]
A. Straight-chain terminal olefins:	
1. 1-Pentene	68.3
2. 1-Hexene	66.2
3. 1-Heptene	66.8
4. 1-Octene	65.6
5. 1-Decene	64.4
6. 1-Tetradecene	63.0
B. Straight-chain internal olefins:	
7. 2-Pentene	21.3
8. 2-Hexene	18.1
9. 2-Heptene	19.3
10. 3-Heptene	20.0
11. 2-Octene	18.8
C. Branched terminal olefins:	
12. 4-Methyl-1-pentene	64.3
13. 2-Methyl-1-pentene	7.82
14. 2,4,4-Trimethyl-1-pentene	4.79
15. 2,3,3-Trimethyl-1-butene	4.26
16. Camphene	2.2
D. Branched internal olefins:	
17. 4-Methyl-2-pentene	16.2
18. 2-Methyl-2-pentene	4.87
19. 2,4,4-Trimethyl-2-pentene	2.29
20. 2,3-Dimethyl-2-butene	1.35
21. 2,6-Dimethyl-3-heptene	6.23
E. Cyclic olefins:	
22. Cyclopentene	22.4
23. Cyclohexene	5.82
24. Cycloheptene	25.7
25. Cycloöctene	10.8
26. 4-Methyl-1-cyclohexene	4.87

[a] Conditions: 0.50 mole of olefin, 65 ml of methylcyclohexane as solvent, 2.8 grams (8.2×10^{-3} moles) of dicobalt octacarbonyl and an initial pressure at room temperature of 233 atmospheres of 1:1 synthesis gas.

[b] Every olefin was run at least twice except camphene and cycloöctene. A statistical analysis of 55 runs yielded a standard deviation from the mean for the repeated runs of only ±1.5 per cent.

for instance, the former reacts about fifty times as fast as the latter. It is clear that a methyl branch at the carbon atom α to the double bond results in a definite decrease in rate (compare 2-hexene and 4-methyl-2-pentene). It is of interest to note that 2,6-dimethyl-3-heptene reacts more rapidly than 2-methyl-2-pentene or 2,3-dimethyl-2-butene. The explanation for this surprising fact will be offered later in this chapter.

(5) Cyclic Olefins. Since all cyclic olefins are internal olefins, they may perhaps be compared with the straight-chain internal olefins. As is shown in Table 2, however, both cyclopentene and cycloheptene react more rapidly than the corresponding straight-chain internal olefins. In addition, there is a minimum in the rate of reaction at the 6-membered ring.

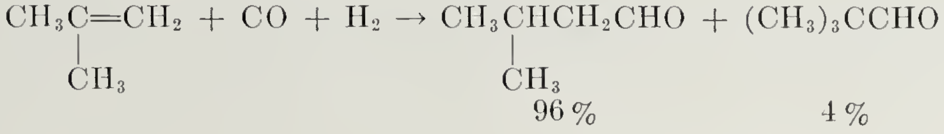
The above facts indicate that although all simple olefins participate in the hydroformylation reaction, the rates of reaction are structure dependent. Later discussions will deal with the significance of these facts and will also treat the effect of conjugation of the simple olefinic linkage with another unsaturated center.

Most of the straight-chain olefins studied in the oxo reaction have been those in which the double bond is in the terminal position. The product from such olefins is usually a mixture of aldehydes consisting of about 60 per cent of the straight-chain and 40 per cent of the branched chain isomers. When straight-chain olefins which contain the double bond in other than the terminal position are subjected to the oxo reaction, the products which result are almost identical with those obtained from the isomeric olefin in which the double bond is in the terminal position. For example, the distribution of alcohols secured from 1-pentene and 2-pentene at 120 to 160°C is about the same[41]: 50 to 55 per cent of hexanol, 35 to 40 per cent of 2-methyl-1-pentanol and 10 per cent of 2-ethyl-1-butanol.

However at 110°, it has been found[24] that 1-pentene gives about 80 per cent hexanol and 15 per cent 2-methyl-1-pentanol and that with 2-pentene, the proportions are about 70 and 28 per cent, respectively.

A general rule which evolves from this discussion is that, starting with a straight-chain olefin, and in the temperature range 120 to 160°C, about 60 per cent of normal and about 40 per cent of α-branched aldehyde or alcohol are obtained, no matter where the double bond is located.

Olefins possessing the structure $R\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$ add the formyl group predominantly to the terminal carbon atom. With isobutylene, for example, the chief product is isovaleraldehyde although about 4 per cent of trimethylacetaldehyde is also obtained[85]:



$$\underset{\displaystyle CH_3}{\underset{|}{CH_3C}}{=}CH_2 + CO + H_2 \rightarrow \underset{\displaystyle 96\,\%}{\underset{\displaystyle CH_3}{\underset{|}{CH_3CH}}CH_2CHO} + \underset{\displaystyle 4\,\%}{(CH_3)_3CCHO}$$

When a branched olefin containing the double bond in other than the terminal position is submitted to the oxo reaction, the products which result are almost identical with those secured from the isomeric olefin in which the double bond is in the terminal position[41]. Thus, essentially the same products result from 2-methyl-2-butene as from either 3-methyl-1-butene or 2-methyl-1-butene: 55 per cent of 4-methyl-1-pentanol, 45 per cent of 3-methyl-1-pentanol and 5 per cent of 2,3-dimethyl-1-butanol.

OTHER REACTIONS OCCURRING UNDER OXO CONDITIONS

Those Affecting Yields from the Principal Reaction

As might be expected from a reaction in which aldehydes are produced, extensive side-reactions may occur, thus adversely affecting the yield of desired product. Process-wise, the most extensively studied oxo reaction is the two-stage conversion of mixed C-7 olefins to isooctyl alcohol. In this process, a small amount of low-boiling material is obtained, but the bottoms (material remaining after the alcohols are distilled) constitute 20 to 30 per cent of the product. The wide variety of products, other than alcohols, which can be present is listed below[46, 67]:

C-7 olefins and paraffins
C-8 olefins
C-8 paraffins
C-8 aldehydes
C-24 acetals
C-15 ketones
C-16 hemiacetals
acids, esters, aldols and ketols

Some of these side reactions will be discussed below.

Hydrogenation of Olefins. The hydrogenation of an olefin is thermodynamically favored over its hydroformylation. As has been pointed out, the standard state free energy changes at 25°C for the two reactions with ethylene:

$$\text{(a)}\quad CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$$

$$\text{(b)}\quad CH_2{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO$$

are −22,608 cal/mole for the hydrogenation and −14,460 cal/mole for the hydroformylation[48]. Despite the thermodynamic preference for the hydrogenation, treatment of simple olefins, especially at low temperatures (110 to 140°C) results in practically no saturated hydrocarbon being formed.

The production of saturated hydrocarbons, however, has been noted occasionally in oxo reactions. Thus, for example, treatment of a C-7 feed at temperatures above 125°C with various ratios of synthesis gas ($0.5H_2:1CO$ to $2H_2:1CO$) at 200 atmospheres pressure results in some C-7 saturated hydrocarbons[67]. When C-8 and higher olefins were treated in acetic acid solution at 250 to 270°C in the presence of 700 atmospheres of 1:1 synthesis gas, as much as 30 per cent of the olefin was converted to hydrocarbon[70].

This discussion has been confined to simple olefins. When the double bond is conjugated to another unsaturated center (double bond, carbonyl group, phenyl group, etc.) then the hydrogenation of the double bond not only becomes of importance but in certain instances becomes the chief reaction. Such examples will be discussed under the section dealing with modifications of the principal reaction.

Polymerization of Olefins. Although the presence of the strong acid, cobalt hydrocarbonyl, $HCo(CO)_4$, has been frequently postulated during the oxo reaction, no good evidence for the polymerization of olefins during the oxo reaction has been reported. It might be expected that an olefin such as isobutylene, which is prone to polymerize in the presence of strong acids, would yield some C-9 aldehyde owing to dimerization followed by hydroformylation. The occurrence of C-9 alcohols from isobutylene has not, however, been reported.

Hydrogenation of Aldehydes. It has been amply demonstrated that hydrogenations can and do occur under the usual oxo conditions. The aldehydes produced by the oxo reactions can be hydrogenated under the oxo conditions, especially when contact times are relatively long and temperatures are at the high end of the oxo temperature range (170 to 200°C). Thus, for example, butyraldehyde has been hydrogenated in good yield to butanol[86] at 180°C and 200 atmospheres of synthesis gas (2:1). When the oxo reaction is operated to secure alcohols as a final product, the partial hydrogenation of the aldehyde to alcohol in the hydroformylation step is of little consequence. However, when the process is operated to secure aldehydes as principal products, then temperatures should be as low as compatible with efficient reaction rates and contact times.

Although aldehydes can be converted to alcohols under somewhat more drastic conditions, this procedure is usually not preferred since the higher temperatures and longer contact times plus the presence of the acidic catalyst result in loss of aldehydes through side reactions.

Acetal Formation. Since aldehydes and alcohols co-exist in the oxo reaction it is not surprising that acetal formation occurs:

$$RCHO + 2RCH_2OH \rightarrow RCH(OCH_2R)_2 + H_2O$$

Acetals can be isolated after the hydrogenation stage of the two-step oxo process. The bottoms from the alcohol distillation may contain up to 50 per cent of acetals which can be hydrolyzed either with steam or with 5 per cent sulfuric acid to increase the yield of the desired alcohol[11]. As a matter of fact, acetal formation has been specifically encouraged in an attempt to minimize yield-reducing side reactions of aldehydes. Thus, for example, the hydroformylation of olefins has been conducted in the presence of ethyl orthoformate[63] and the ethyl acetal of the aldehyde secured in excellent yield.

$$RCH = CH_2 + CO + H_2 + HC(OEt)_3 \rightarrow RCH_2CH_2CH(OEt)_2 + HCOOEt$$

This reaction has been performed with α,β-unsaturated esters also, and ester acetals secured in high yield. With ethyl crotonate, it was originally reported that a β-formyl ester acetal was formed exclusively, but subsequent work[29, 64] showed that this assignment of strueture was incorrect and the γ-formyl acetal ester, ethyl 5,5-diethoxyvalerate was formed, presumably by prior isomerization:

$$CH_3CH{=}CHCO_2Et \rightleftharpoons CH_2{=}CHCH_2COEt \xrightarrow[HC(OEt)_3]{H_2 + CO} (EtO)_2CHCH_2CH_2CH_2CO_2Et$$

Aldol Formation. One of the most important yield-reducing reactions in the hydroformylation synthesis is the aldolization of the aldehydes. Under certain conditions, an appreciable portion of the product can be accounted for by aldolization of the aldehydes initially produced. Thus, treatment of 28 grams of ethylene with aqueous cobaltous chloride at 160 to 185°C for two hours under a pressure of 590 to 840 atmospheres gave about 17 grams of the unsaturated aldehyde, 2-methyl-2-penten-1-al according to the following sequence[17]:

$$CH_2{=}CH_2 \rightarrow CH_3CH_2CHO \xrightarrow{CH_3CH_2CHO} CH_3CH_2CHOHCH(CH_3)CHO \rightarrow CH_3CH_2CH{=}C(CH_3)CHO$$

At longer reaction times and higher temperatures the unsaturated aldehydes would probably be hydrogenated to the saturated aldehyde or the saturated alcohol. Thus propylene has been shown to give the highly desirable 2-ethylhexanol directly:

$$CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO + (CH_3)_2CHCHO$$

$$2CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_2CHOHCH(C_2H_5)CHO \rightarrow CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OH$$

Although no detailed investigation of all the side products resulting from the oxo reaction has been published, it is likely that a small quantity of esters is present. These esters probably result from the Tischenko reaction of aldehydes. It has been shown, for example[62], that treatment of propane with carbon monoxide in the presence of the acid catalyst, aluminum chloride, gives among other products, appreciable quantities of isobutyl isobutyrate. The sequence of reactions is probably:

$$\mathrm{CO + CH_3CH_2CH_3 \rightarrow (CH_3)_2CHCHO \xrightarrow{(CH_3)_2CHCHO}}$$

$$\mathrm{(CH_3)_2CHCO_2CH_2CH(CH_3)_2}$$

In a reaction more closely related to the oxo synthesis, it has been demonstrated[49] that one of the reaction products from treatment of cyclohexene in butanol with carbon monoxide in the presence of cobalt carbonyl catalyst was butyl butyrate. Presumably, the cyclohexene oxidized the alcohol to the aldehyde which then underwent the Tischenko reaction:

$$\mathrm{C_6H_{10} + CH_3CH_2CH_2CH_2OH \xrightarrow[CO]{Co_2(CO)_8}}$$

$$\mathrm{C_6H_{12} + CH_3CH_2CH_2CHO}$$

$$\mathrm{2CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_2CO_2CH_2CH_2CH_2CH_3}$$

Ketone Formation. Originally the oxo synthesis was thought to consist of a ketone as well as an aldehyde synthesis, hence the name "oxo". However, the first work that was performed was done with ethylene, which alone of all olefins, produces appreciable quantities of ketone. Treatment of ethylene under oxo conditions gives almost as much diethyl ketone as it does propionaldehyde. Practically nothing has been done from a theoretical point of view to attempt to explain this rather unusual behavior of the lowest member of the olefin series. The fact that the concentration of the olefin in the liquid phase under oxo conditions is always small may be of significance. Ketone formation may occur to a very small extent in some hydroformylation reactions but no systematic study has been made of the occurrence of this minor product.

Modifications of the Principal Reaction

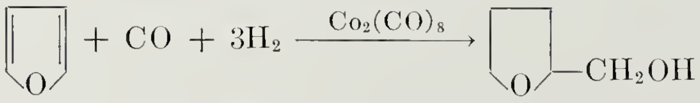
In this category, reactions which proceed under the usual oxo conditions but which do not involve the standard hydroformylation (addition of H—CHO) to any large extent, will be discussed.

Hydrogenation. This subject will be treated briefly since it has been discussed and reviewed in detail elsewhere[56].

α,β-Unsaturated Aldehydes and Ketones. Compounds possessing an olefinic bond conjugated to a carbonyl group of an aldehyde or ketone are reduced to the saturated aldehyde or ketone under the usual oxo conditions providing the temperature is kept at about 125°C. Thus crotonaldehyde gives butyraldehyde and methyl vinyl ketone gives methyl ethyl ketone[1]. Just why the conjugation leads to hydrogenation of the olefinic linkage rather than hydroformylation has not been satisfactorily explained. It is especially noteworthy that esters of crotonic acid (conjugation with carboethoxy) are largely hydroformylated (although an appreciable amount of hydrogenation to butyrate esters occurs)[31], whereas conjugation of the double bond with an aldehyde group (crotonaldehyde) results in hydrogenation. It is well known that an ester group conjugates with a double bond linkage to a lesser extent than an aldehyde function; the resonance energy of crotonaldehyde is about 2.4 kcal greater than the resonance energy of ethyl crotonate.

Conjugated Diolefins and Styrenes. The introduction of two formyl or related groups by hydroformylation of a conjugated diolefin would be a highly desirable reaction. Thus treatment of butadiene could lead to a C-6 dialdehyde and thence to a C-6 dibasic acid. However, the major product on treatment of a conjugated diolefin is a saturated aldehyde containing only one carbon atom more than the starting material. With such substrates, one double bond is hydrogenated and the other undergoes the hydroformylation reaction.

Furan behaves as though it were a conjugated diene[86]:



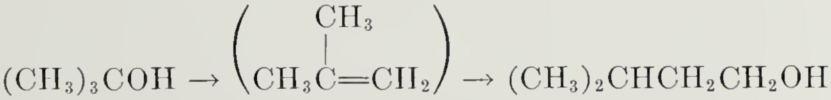
Although aliphatic α,β-unsaturated esters such as ethyl acrylate react by hydroformylation, aromatic unsaturated esters such as ethyl cinnamate are hydrogenated. In general, if the double bond is conjugated with an aromatic ring, hydrogenation is the principal reaction. Styrene gives appreciable ethylbenzene and α-methylstyrene gives isopropylbenzene almost exclusively[97].

Saturated Aldehydes and Ketones. Simple aliphatic aldehydes and ketones can be reduced to their corresponding alcohols under oxo conditions providing the temperature is in the range of 160 to 190°C. The reduction stops at the alcohol stage. If the carbonyl group is located next to an aromatic nucleus, reduction to the hydrocarbon occurs to an extent dependent upon the structure of the substrate[87]. Thus acetophenone gives a 75 per cent yield of ethylbenzene, benzophenone gives a 95 per cent yield of diphenylmethane, and fluorenone gives fluorene in 95 per cent yield.

Aromatic Carbinols. When derivatives of methanol in which one or more hydrogens are replaced by aromatic groups are treated under oxo conditions, extensive hydrogenolysis of the alcoholic function occurs and hydrocarbons are a principal product. The yield of hydrocarbon increases with the increasing replacement of hydrogens by aromatic groups[87]. Thus benzyl alcohol gives 70 per cent toluene, but benzhydrol and triphenylcarbinol give 95 per cent diphenylmethane and triphenylmethane, respectively. 1-Naphthalenemethanol on treatment under oxo conditions gives a 72 per cent yield of 1-methylnaphthalene. The aromatic aldehydes and ketones in which the carbonyl group is conjugated to an aromatic nucleus almost certainly are reduced to hydrocarbons via the carbinols.

Dehydrogenation Reactions. It has been possible by treating olefins with secondary alcohols in the presence of carbon monoxide and cobalt carbonyl to utilize the hydrogen from the alcohol to effect hydroformylation of the olefin. Thus, for example, cyclohexene and isopropyl alcohol in the presence of about 250 atmospheres of carbon monoxide gave acetone and cyclohexylcarbinol[50]. A hydrogen acceptor other than the catalyst apparently is essential since attempts to dehydrogenate secondary alcohols by treatment of them with carbon monoxide and cobalt carbonyl was unsuccessful. In order to avoid equilibrium restrictions, the gas was bled and repressured with pure carbon monoxide in order to purge hydrogen, but the dehydrogenations did not occur. Although the analytical problem in such reactions is a difficult one if ketone formation is used as a criterion (since ketal formation is possible), the indications were against the possibility of achieving dehydrogenations. Thus tetralin could not be successfully dehydrogenated to naphthalene[40].

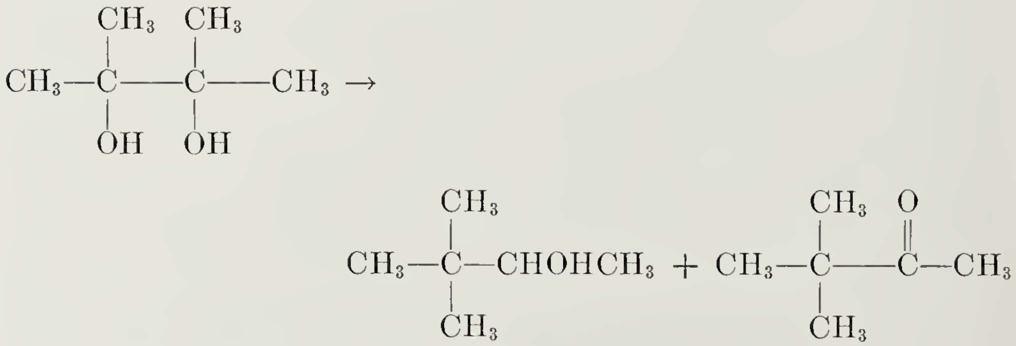
Homologation of Alcohols. Treatment of methanol with synthesis gas and dicobalt octacarbonyl at about 190°C results in a 40 per cent conversion to ethanol[88]. Similar treatment of secondary and tertiary alcohols results in the formation of the primary alcohols which would be expected from the olefinic dehydration products of the substrate alcohols[89]. Thus *tert*-butyl alcohol is rapidly converted to isoamyl alcohol, via isobutylene:



$$(CH_3)_3COH \rightarrow \left(CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2\right) \rightarrow (CH_3)_2CHCH_2CH_2OH$$

Of course, methanol cannot give an intermediate olefin. Other primary alcohols, for some reason not fully understood, cannot be as successfully employed as substrates for conversion to homologous alcohols. The homologation of methanol is practically arrested at the ethanol stage, although ethanol itself has been converted in small yields to propanol and butanol[100] albeit at higher pressures and longer contact times. With benzyl alcohol, a 30 per cent yield of the homologous 2-phenylethanol is secured under oxo conditions[87]. The homologation reaction appears to be restricted in the primary alcohol series to methanol and carbinols with one aromatic group. One important competing reaction is hydrogenolysis; in the case of methanol, methane is formed and with benzyl alcohol, toluene is produced. The split between homologation and hydrogenolysis in a series of meta- and para-substituted benzyl alcohols has been studied[90]; the results appear to indicate some type of acid catalysis.

Rearrangements. There has been only one reported instance of a skeletal rearrangement during the oxo synthesis. Thus, treatment of pinacol gave among other products, some pinacolyl alcohol, and some pinacolone[91]. Although these are rearranged materials, they contain the same number of carbon atoms as the starting material. Accordingly, there is yet no example in which a hydroformylation product has been secured which arises from a skeletal arrangement of the olefin.



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHOHCH_3 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Double Bond Isomerization. Asinger and Berg[3] found that dodecene was isomerized to a mixture which consisted of all the possible double bond isomers in almost equal ratios when the olefin was treated with either a Fischer-Tropsch cobalt catalyst or cobalt metal at temperatures between 150°C and 250°C and at 100 atmospheres pressure of carbon monoxide. When 1-hexene was heated at 110°C for one hour in the presence of dicobalt octacarbonyl and 133 atmospheres of carbon monoxide, 9 per cent of the 1-hexene was converted to internal hexenes[84]. When the temperature was raised to 150°C under the same conditions, 29 per cent of the terminal olefin was isomerized to internal olefins. The yield of 2-hexene and 3-hexene increased to 61 per cent when 1-hexene was heated at 150°C for 5 hours. Only traces of 1-hexene were formed when 2-hexene was treated in a similar manner. It thus appears that dicobalt octacarbonyl in the presence of carbon monoxide, readily catalyzes the isomerization of terminal olefins and that the extent of isomerization increases with temperature and time.

Double bond isomerization has been reported to occur under some conditions of the oxo synthesis. In one interesting experiment in which 1-hexene was treated with pure cobalt hydrocarbonyl in the absence of synthesis gas, the recovered hexene had all been isomerized to 2-, and 3-hexene[92]. However, during the oxo reaction as normally conducted, it has been found that little or no isomerization occurs[24, 84]. This fact will be elaborated in a later discussion. As has been pointed out, carbon addition occurs in a manner that such isomerization is implicit since essentially the same products are obtained from isomeric internal and terminal olefins.

Reactions of Olefins with Amines. One of the most desirable but difficultly realizable reactions is the addition of ammonia or amines to simple (unconjugated) olefins. One of the few examples of such a reaction appears in a patent[44] and involves conditions somewhat similar to those under which the oxo reaction is successfully conducted. Thus when ethylene was treated with ammonia in the presence of cobalt and 500 atmospheres of synthesis gas ($4H_2{:}1CO$) at about 200°C, a mixture of *n*-propylamines was secured in which the di-*n*-propylamine predominated. Propylene and dimethylamine under somewhat similar conditions gave, among other products, some dimethyl-*n*-propylamine:

$$(CH_3)_2NH + CH_3CH{=}CH_2 \rightarrow (CH_3)_2NCH_2CH_2CH_3$$

In addition some N,N-dimethylbutyramide, $CH_3CH_2CH_2CON(CH_3)_2$, was also secured.

Reactions of Acetals. When a methanol solution of formaldehyde dimethylacetal was treated with synthesis gas ($1H_2{:}1CO$) at 600 atmospheres pressure and 165°C in the presence of cobalt, a good conversion to 1,1,2-trimethoxyethane[28] occurred:

$$CH_2(OCH_3)_2 + CO + H_2 + CH_3OH \xrightarrow{Co} CH_3OCH_2CH(OCH_3)_2 + H_2O$$

The trimethoxyethane, could in turn, be converted to a tetraalkoxypropane:

$$CH_3OCH_2CH(OCH_3)_2 \xrightarrow[H_2]{CO} CH_3OCH_2CH(OCH_3)CH(OCH_3)_2$$

This sequence of reactions was of interest in connection with a possible route to glycerol.

Since the carbonyls of cobalt are involved in the transfer of hydrogen and carbon monoxide to the olefin in the oxo reaction, a discussion of the structure, properties, and reactions of these compounds is in order at this point. The general field of the metal carbonyls will be covered with detailed consideration of the cobalt carbonyls.

PROPERTIES, STRUCTURE, AND REACTIONS OF THE COBALT CARBONYLS

For the purpose of this discussion metal carbonyls shall be defined as compounds composed of a metal and carbon monoxide. One can distinguish two types of carbonyls, i.e., the monomeric carbonyls and the polymeric carbonyls (Table 3). Some metal carbonyls exist only as monomers, e.g., $Ni(CO)_4$, some only as polymers, e.g., $Co_2(CO)_8$, and some both as monomers and polymers, e.g., $Fe(CO)_5$ and $Fe_3(CO)_{12}$. Some metal carbonyls are known to undergo substitution reactions in which carbonyl groups are replaced by various other groups (Table 4).

The systematization of this bewildering array of compounds is greatly facilitated by the concept of the Effective Atomic Number (E.A.N.). The E.A.N. is the name given to the total number of electrons which enter into the configuration of the central atom of the complex compound. If it is assumed that each $[:C{=}\ddot{O}:]$ group donates one pair of electrons to the central atom then the E.A.N. of Ni in $Ni(CO)_4$, for instance, is 36, i.e., 28 (atomic number of Ni) plus 2 × 4 (electrons donated by the four CO groups). Thus the E.A.N. of Ni in $Ni(CO)_4$ is equal to the atomic number of krypton which is the inert gas of the completed period in which Ni is situated. As may be seen from Table 3, the principle governing the composition of all known monomeric carbonyls is this attainment of the E.A.N. equal to the atomic number of the inert gas. The same principle is also operative in the substituted carbonyls (Table 4) where it may be assumed that each $[:C{=}N{-}R]$, $[:PCl_3]$, and $[:P(C_6H_5)_3]$ group donates two electrons and each $[\vdots N{=}O]$ and $[\vdots C{-}OH]$ group three electrons.

Table 3. Monomeric and Polymeric Carbonyls

Cr(24)	Mn(25)	Fe(26)	Co(27)	Ni(28)
$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$	$Ni(CO)_4$
Mo(42)	Tc(43)	Ru(44)	Rh(45)	Pd(46)
$Mo(CO)_6$		$Ru(CO)_5$ $Ru_2(CO)_9$ $Ru_3(CO)_{12}$	$Rh_2(CO)_8$ $Rh_4(CO)_{12}$	
W(74)	Re(75)	Os(76)	Ir(77)	Pt(78)
$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_2(CO)_9$	$Ir_2(CO)_8$ $Ir_4(CO)_{12}$	

That the composition of the polymeric carbonyls also conforms to the principle of E.A.N. may be deduced as follows[72]. Inspection of Table 3 shows that where the "monomer" has an E.A.N. of 35, e.g., $Co(CO)_4$ in $Co_2(CO)_8$ or $Fe(CO)_{4.5}$ in $Fe_2(CO)_9$, the polymeric carbonyl contains two metal atoms; where the E.A.N. of the "monomer" is 34, e.g., $Fe(CO)_4$ in $Fe_3(CO)_{12}$

the polymeric carbonyl contains three metal atoms and where it is 33, e.g., $Co_4(CO)_{12}$ the polymeric carbonyl contains four metal atoms. This relation between the E.A.N. of the next inert gas (G), the atomic number of the metal (M), the number of metal atoms (x), and the number of carbonyl groups (y) is expressed by the following formula from which any metal carbonyl of the general form $(M)_x(CO)_y$ can be derived:

$$G - \frac{xM + 2y}{x} = x - 1$$

TABLE 4. SOME SUBSTITUTED CARBONYLS

Fe	Co	Ni
$Fe(CO)_4(CN{\cdot}R)$		$Ni(CN{\cdot}R)_4$
$Fe(CO)_3(CN{\cdot}R)_2$		$Ni(CO)(CN{\cdot}R)_3$
$Fe(CO)_3(SbCl_3)_2$		$Ni(PCl_3)_4$
$Fe(CO)_4[P(C_6H_5)_3]$		$Ni(CO)_3[P(C_6H_5)_3]$
$Fe(CO)_3[P(C_6H_5)_3]_2$		$Ni(CO)_2[P(C_6H_5)_3]_2$
$Fe(CO)_2(NO)_2$	$Co(CO)_3(NO)$	
$Fe(CO)_2(COH)_2$	$Co(CO)_3(COH)$	$Ni_2(CO)_4(COH)_2$

TABLE 5. VOLATILITY OF METAL CARBONYLS

	M.W.	B.P.
$Ni(CO)_4$	171	46°C
$HCo(CO)_4$	172	Vapor pressure, 5 mm at −30°C
$Fe(CO)_5$	196	102°C
$Co_2(CO)_8$	342	Sublimes at room temperature in a current of CO
$Fe_3(CO)_{12}$	504	Sublimes at 50–70°C at 10^{-5} mm

The concept of E.A.N. does not only correlate the composition of the metal carbonyls on a purely formal basis but also implies a relationship between the carbonyls and the inert gases. This relationship, according to Blanchard[8], manifests itself in the volatility of the carbonyls as demonstrated in Table 5.

In recent years considerable progress has been made in the elucidation of the structure of the metal carbonyls. This progress is due to the application of modern concepts of the chemical bond in conjunction with results obtained by electron diffraction data and Raman and infrared spectroscopy.

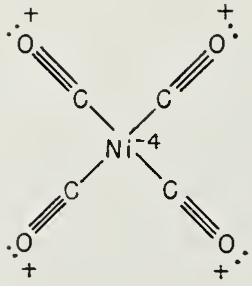
It will be instructive to discuss first the structure of nickel carbonyl[59], a typical metal carbonyl. One may visualize the formation of the nickel-carbon bonds as the sharing of the lone pair of electrons of the carbon

$(:\overset{-}{C}\equiv\overset{+}{O}:)$ with the nickel atom. The sharing of this pair of electrons would place a fourfold negative charge on the nickel atom—one for each nickel-carbon bond—as indicated in structure (I) or (II). Both structures, (I) and (II), are unsatisfactory because they place a negative charge on the nickel which is electropositive rather than electronegative. In addition, (II) shows a carbon with an unused valence orbital. These objections to structures (I) and (II) are overcome in structure (III) where electrical neutrality of the nickel atom is achieved by release of the required number of electrons (8) from the 3*d* shell of nickel so that the Ni-C bonds acquire double bond character.

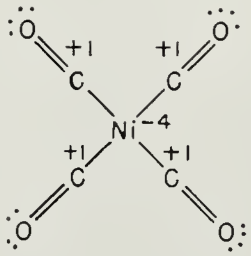
Table 6. Bond Lengths and Force Constants of Various Carbonyl Groups

Carbonyl group	$:\overset{-}{C}\equiv\overset{+}{O}:$	$Ni=C=\ddot{O}:$	$H_2C=C=\ddot{O}:$	$H_2C=\ddot{O}:$
Force constant	18.6	15.9	14.5	12.1
Bond length	1.13	1.15	1.17	1.21

The suggestion that the Ni-C bond is not a pure single bond as indicated in (I) but contains a certain amount of double bond character is supported by electron diffraction data. The calculated interatomic distance for a



I



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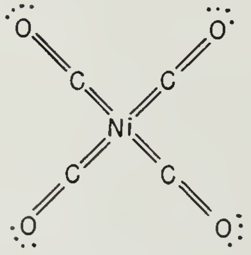
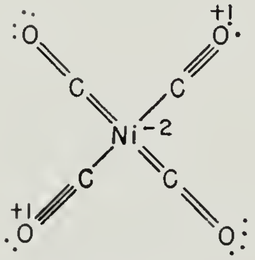


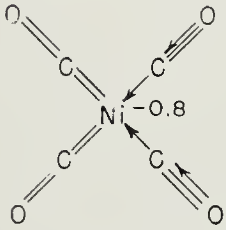
III



IV

nickel-carbon single bond is 2.00 Å while that for a nickel-carbon double bond is 1.79 Å. The experimentally obtained value is 1.82 Å, indicating a considerable amount of double bond character. In a similar way it may be shown (Table 6) that the C≡O bond in (I) is not a pure triple bond but contains a certain amount of double bond character since the C—O distance in nickel carbonyl is somewhat larger than in triply bonded carbon monoxide.

However, Table 6 also shows that with respect to force constant and bond length the carbonyl group in nickel carbonyl is more closely related to carbon monoxide than to the carbonyl group in formaldehyde. In order to account for this partial triple bond character of the carbonyl group a struc-



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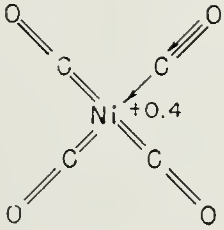
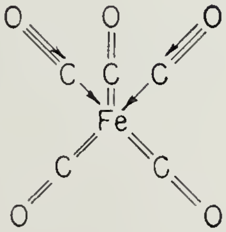
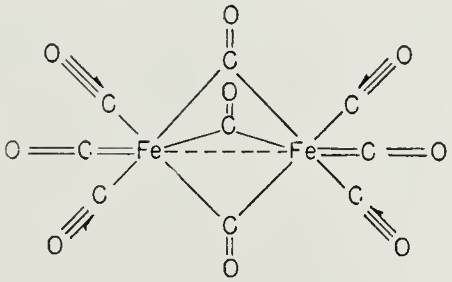


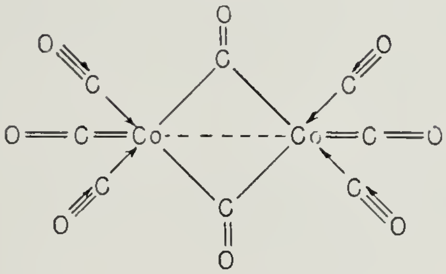
VI



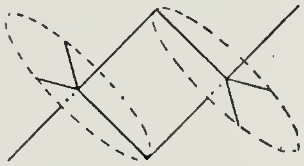
VII



VIII

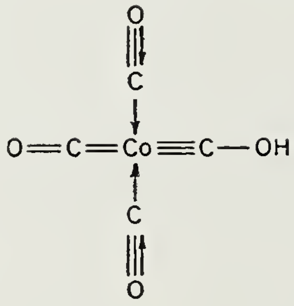


IX

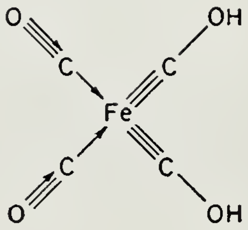


X

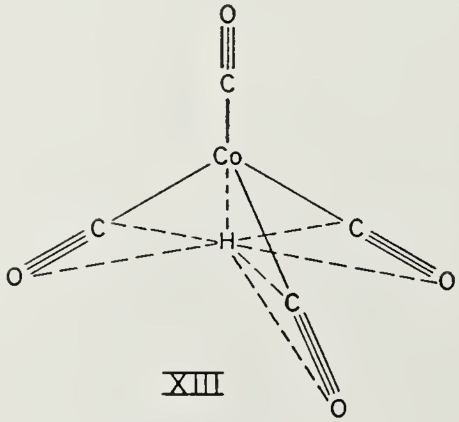
ture such as (IV) was proposed[15], where the average bond order of the Ni-C bond was 1.5 and that of the C—O bond 2.5. In structure (IV) a charge of −2 is shown on the nickel atom. However, due to the difference between the electronegativities of Ni and C, the formal charge on the nickel atom is actually only −0.4 as the following more detailed consideration[10] will show. The electronegativities of nickel[73] and carbon are 1.6 and 2.5, respectively. From the correlation between electronegativities and per cent ionic character of a bond[60] it follows that the Ni-C bond is about 20 per cent ionic and that therefore the dative single bond



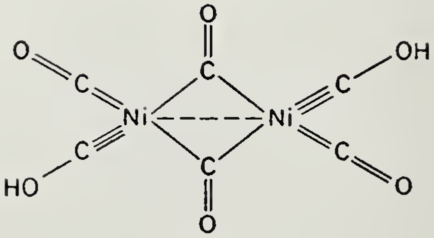
XI



XII



XIII



XIV

$$\mathrm{Ni} + :\overset{-1}{\mathrm{C}}\equiv\overset{+1}{\mathrm{O}}: \qquad \overset{-0.8}{\mathrm{Ni}}\text{——}\overset{-0.2}{\mathrm{C}}\equiv\overset{+1}{\mathrm{O}}:$$

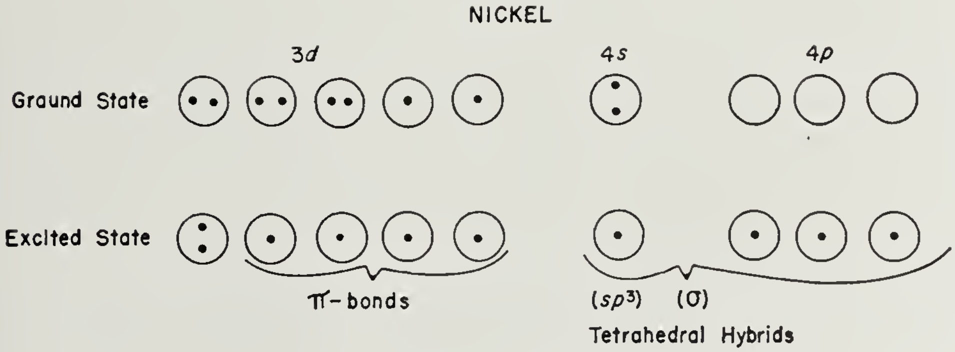
imparts a charge of −0.8, while the Ni-C double bond

$$\mathrm{Ni}: + :\mathrm{C}=\overset{\cdot\cdot}{\mathrm{O}}: \qquad \overset{+0.4}{\mathrm{Ni}}=\overset{-0.4}{\mathrm{C}}=\mathrm{O}:$$

imparts a charge of +0.4 to the Ni atom. Thus, two single plus two double bonds will impart a total charge of −0.8, (V), while one single and three double bonds (VI) will impart a charge of +0.4 to the Ni atom. It is readily seen that resonance between structures (V) and (VI) will leave the Ni atom with a charge of zero as postulated by the Principle of Electrical Neutrality[61], which states that the charge of the central atom in a complex is essentially zero. Obviously $Ni(CO)_4$ (or any of the other carbonyls) cannot be adequately described by a single formula. Besides structure (III), structures such as (V) and (VI) are possible and one must assume that $Ni(CO)_4$ can resonate among a great number of structures with various localization of bonds and charges. However, if one wishes to present $Ni(CO)_4$ by a single formula structure (III) is the one in best agreement with the properties of the metal carbonyl[14].

It was pointed out[55] that the C═O bond in Ni═C═O (nickel carbonyl) should be considered equivalent to that in CH_2═C═O (ketene). The C═O bond in ketene, though written as a double bond, has a force constant (Table 6) which is considerably higher than that of the C═O bond in formaldehyde. This difference in bond strength between the ketene and the aldehyde carbonyl is explained as follows. The σ-bond in formaldehyde carbonyl (>C═O) is an sp^2 hybrid bond while the σ-bond in ketene carbonyl (═C═O) is an sp hybrid bond. Now it is known that increase in the proportion of s to p character in the carbon bond is accompanied by an increase in bond strength[55]. Thus one is able to explain the higher force constant in the ketene carbonyl as compared to that in the aldehyde carbonyl without having to postulate a triple bond. Since in nickel carbonyl the Ni—C—O atoms lie on a straight line it is reasonable to assume that the σ-bonds of the carbon atom are sp hybrids and that the carbonyl bond is similar to that in ketene.

The structural analysis of nickel carbonyl based on electron[59] and x-ray[43] diffraction data shows that $Ni(CO)_4$ has a tetrahedral configuration. The formation of the Ni-C bonds as well as the steric configuration of $Ni(CO)_4$ may be explained by consideration of the atomic orbitals of nickel.



Because of the small energy difference in the $3d$, $4s$, and $4p$ levels in nickel promotion of electrons to the $4p$ level is possible. In the excited state sp^3 hybridization takes place giving rise to four tetrahedrally directed σ-bonds. Four additional π bonds may be formed from the remaining four unpaired $3d$ electrons. Thus a total of four σ and four π bonds, i.e., four double bonds may be formed with the four lone pairs of electrons of the four CO groups.

The principles discussed in connection with the structure of $Ni(CO)_4$ are also applicable to the structures of the iron and cobalt carbonyls as well as to the hydrocarbonyls.

$Fe(CO)_5$ has the configuration[21] of a trigonal bipyramid, the carbonyl groups being located at the apices of the pyramid, (VII).

The structure of iron enneacarbonyl, $Fe_2(CO)_9$, as determined by x-ray diffraction[66] is shown in (VIII). Each iron atom is located at the center of an octahedron, the 6 Fe-C bonds pointing to the six corners of the octahedron. The distance between the two iron atoms is 2.46 Å which is roughly twice the covalent radius of iron, a fact which makes direct metal-to-metal bonding possible. Structure (VIII) indicates the presence of two types of carbonyl groups, i.e., bridge and terminal carbonyl groups. These two types of carbonyl groups give rise to two distinct bands[71] in the infrared spectrum, one in the region of triply bonded carbonyl and one in the region of strained bridge $>C{=}O$, in excellent agreement with the configuration established by x-ray diffraction.

In contrast to iron and nickel carbonyl no electron diffraction data are available which would permit an insight into the spatial configuration of dicobalt octacarbonyl. The infrared spectrum[23] shows the presence of bands attributable to two types of carbonyl groups similar to those observed in $Fe_2(CO)_9$. Assumption of a trigonal bipyramidal hybridization around each cobalt atom and application of group analysis[23] leads to the configuration shown in (X).

The accepted structures for cobalt and iron hydrocarbonyl are shown in (XI) and (XII). Electron diffraction data[21] showed that cobalt hydrocarbonyl has a tetrahedral configuration and that one of the cobalt-carbon bonds is shorter than the other three. The cobalt-carbon triple bond in (XI) accounts for one of the cobalt-carbon bonds being shorter than the other three. Molecular volume determinations of the carbonyls have shown[32] that cobalt and iron hydrocarbonyl have a smaller volume than nickel carbonyl, further evidence for the shortening of the M—C—OH chain in the hydrocarbonyls. Structure (XII) was deduced[80] from electron diffraction data in a similar way.

It must be emphasized that the position of the hydrogen in (XI) and (XII) is based on indirect evidence. Infrared spectra of cobalt[23, 75] and iron[23] hydrocarbonyl failed to reveal any bands attributable to a linkage of hydrogen with either cobalt, carbon, or oxygen. Recently Edgell and Gallup[18, 19] proposed structure (XIII) for cobalt hydrocarbonyl where the hydrogen is embedded in one face of the tetrahedron formed by the four carbonyl groups. According to these authors the hydrogen is immersed in a sheath of negative charge with the π-orbitals of the three carbonyl groups contributing most and a cobalt $3d$ orbital contributing some of the bonding.

Early attempts to prepare nickel hydrocarbonyl failed[33] and only recently[6] was this compound isolated in the form of its ammoniate $[NiH(CO)_3]_2 \cdot 4NH_3$. It is tempting to speculate on the structure of $[NiH(CO)_3]_2$, the only dimeric hydrocarbonyl known. In analogy to dicobalt octacarbonyl (with which nickel hydrocarbonyl is isoelectronic) a structure such as (XIV) seems reasonable.

Physical and Chemical Properties of the Carbonyls and Hydrocarbonyls of Iron, Cobalt, and Nickel

The physical properties of the carbonyls and hydrocarbonyls of iron, cobalt, and nickel are listed in Table 7.

In view of their importance for the hydroformylation and related reactions the physical and chemical properties of dicobalt octacarbonyl, the tetramer $Co_4(CO)_{12}$, and cobalt hydrocarbonyl will be discussed in greater detail.

Dicobalt octacarbonyl is not stable at room temperature unless there is a slight pressure of carbon monoxide[65]; in an atmosphere of carbon monoxide, the octacarbonyl is stable indefinitely at room temperature[79]. In the absence of carbon monoxide, dicobalt octacarbonyl decomposes slowly according to Eq. (1) into

$$2Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + 4CO \qquad (1)$$

tetracobalt dodecacarbonyl and carbon monoxide. Dicobalt octacarbonyl is readily soluble in hydrocarbon solvents such as hexane and toluene (350 grams per liter at 31°C)[87]. With polar solvents such as alcohols, ketones, amines and amides, dicobalt octacarbonyl reacts more or less rapidly as will be shown later.

The tetramer, $Co_4(CO)_{12}$, is pyrophoric, stable indefinitely in an inert solvent, is sparingly soluble in hydrocarbon solvents (a saturated solution of n-heptane contains 7.64 grams per liter), reacts with pyridine[34] according to Eq. (2)

$$3Co_4(CO)_{12} + 24C_5H_5N \rightarrow 4[Co(C_5H_5N)_6]\,[Co(CO)_4]_2 + 4CO \qquad (2)$$

and with sodium in liquid ammonia according to Eq. (3)[7]

$$Co_4(CO)_{12} + 3Na \rightarrow Co + 3NaCo(CO)_4 \qquad (3)$$

Cobalt hydrocarbonyl forms pale yellow crystals which are stable below their melting point (−26°C). Above its melting point cobalt hydrocarbonyl decomposes rapidly into hydrogen and dicobalt octacarbonyl according to Eq. (4)

$$2HCo(CO)_4 \rightarrow H_2 + Co_2(CO)_8 \tag{4}$$

TABLE 7. PHYSICAL PROPERTIES OF CARBONYLS OF Fe, Co, AND Ni

	Formula	Specific Gravity	Melting Point	Boiling Point	Color
Fe	$Fe(CO)_5$	1.466 at 18°C	−21°C	102.8°C/749 mm	Yellow liquid
	$Fe_2(CO)_9$	2.085 at 18°C	Decomposes at 100°C		Gold colored crystals
	$Fe_3(CO)_{12}$	1.996 at 18°C	Decomposes at 140°–150°C Sublimes at 60°–70°C/10^{-5} mm.		Dark green crystals
	$H_2Fe(CO)_4$	1.596 at −70°C	−70°C[a]	Very volatile[a]	Pale yellow liquid
Co	$Co_2(CO)_8$	1.73	51°C	Decomposes above 52°C[b]	Orange crystals
	$Co_4(CO)_{12}$		Decomposes above 60°C		Black crystals
	$HCo(CO)_4$	1.573 at −26°C	−26°C[c]	Very volatile[c]	White to light yellow crystals below −26°C
Ni	$Ni(CO)_4$ $[NiH(CO)_3]_2$[d]	1.324 at 14°C	−25°C	43°C/751 mm	Colorless liquid

[a] Starts to decompose at about −20°C. Vapor pressure, 14 mm at −13°C.

[b] Vapor pressure, 0.072 mm at 15°C.

[c] Starts to decompose at about −20°C. Vapor pressure, 5 mm at −30°C.

[d] Isolated as the ammoniate $[NiH(CO)_3]_2 \cdot 4NH_3$.

At room temperature and atmospheric pressure, Eq. (4) is irreversible and follows a second order reaction[75] as expressed by Eq. (5)

$$\frac{-dHCo(CO)_4}{dt} = k[HCo(CO)_4]^2 \tag{5}$$

The specific reaction rate constant, k, was found to be of the order of 3×10^{-3} (mole/liter)$^{-1}$ second^{-1}. Substitution of this value of k

$$t_{0.5} = \frac{1}{ka}$$

$t_{0.5}$ = half-life
a = initial concentration in moles/liter
k = specific reaction rate constant (mole/liter)$^{-1}$ second^{-1}

shows that liquid cobalt hydrocarbonyl which is approximately 9 molar has a half-life of 37 seconds and thus is not stable at room temperature. At a concentration of 10^{-3} moles per liter the half-life of cobalt hydrocarbonyl is about 4 days. These data thus provide an explanation for the relative stability of cobalt hydrocarbonyl in small concentrations compared to that of pure cobalt hydrocarbonyl.

In the absence of oxygen, cobalt hydrocarbonyl is stable in aqueous solution, completely dissociated and sparingly soluble, the concentration of an aqueous solution saturated at 25°C being 5.6×10^{-2} molar. Aqueous solutions of cobalt hydrocarbonyl may be titrated using phenolphthalein as an indicator.

Table 8. Infrared Spectra of Cobalt Carbonyls

$HCo(CO)_4$ gas, in helium ν, cm^{-1}	$Co_2(CO)_8$ in n-hexane ν, cm^{-1}	$Co_4(CO)_{12}$ in n-hexane ν, cm^{-1}
2121 s		
2066 s sh	2066 s	2052 s
2043 v s	2041 v s	
2004 s	2024 s sh	
1966 m s		
1929 w		
1869 w	1859 m s	1870 m s
703 s		

w = weak, m = medium, s = strong, v = very, sh = shoulder.

The absorption bands found in the infrared spectra of cobalt hydrocarbonyl, dicobalt octacarbonyl and the tetramer $Co_4(CO)_{12}$ are listed in Table 8.

Reactions of Dicobalt Octacarbonyl and Cobalt Hydrocarbonyl

Reactions of Dicobalt Octacarbonyl. The variety of reactions which dicobalt octacarbonyl can undergo may be separated into reactions involving homomolecular disproportionation, external electron transfer, and substitution of the carbonyl group.

Homomolecular Disproportionation. Dicobalt octacarbonyl reacts with a variety of compounds according to Eq. (6)[93]

$$3Co_2(CO)_8 + xB = 2[Co(B)_x][Co(CO)_4]_2 + 8CO \qquad (6)$$

where B may be ammonia, water, methanol, ethanol, pyridine, phenanthroline or formamide. This reaction may be considered as a homomolecular disproportionation in which the uncharged dicobalt octacarbonyl disproportionates into cobalt (II) cation and cobalt carbonyl anion. As the coordination number of cobalt (II) cation is 6, x may be 6 or 3, depending upon the number of functional groups in B. Thus x is 6 for pyridine and 3 for *o*-phenanthroline. The compounds capable of causing the homomolecular disproportionation of dicobalt octacarbonyl seem to have two characteristics in common: (1) They possess a pair of unshared electrons, i.e., they are bases in the Lewis sense. (2) They are capable of coordinating with cobalt (II) ion and must therefore fulfill certain geometrical requirements. Thus, while methanol and ethanol react with dicobalt octacarbonyl according to Eq. (6), neopentyl alcohol and ethyl ether do not react at all, and *tert*-butyl alcohol and benzyl alcohol only accelerate the formation of the tetramer according to Eq. (1).

When B is a primary or secondary aliphatic amine such as butylamine or piperidine, dicobalt octacarbonyl reacts with the base to form a salt according to Eq. (7):

$$B + Co_2(CO)_8 \rightarrow [BCo(CO)_4]^+ [Co(CO)_4]^- \qquad (7)$$

When B is a weak base such as pyridine or methanol, this salt is not stable[93]. The cation is less symmetrical and less stable than the anion and decomposes according to Eq. (8)

$$3[BCo(CO)_4]^+ \rightarrow 3B + 2Co^{++} + [Co(CO)_4]^- + 8CO \qquad (8)$$

forming the more stable cobalt carbonyl anion and cobalt (II) cation which, in the presence of excess B, is stabilized as the complex $[Co(B)_6]^{++}$. The over-all reaction between a weak base B and dicobalt octacarbonyl is expressed by Eq. (6).

External Electron Transfer. The reaction between sodium and dicobalt octacarbonyl, Eq. (9)

$$2Na + Co_2(CO)_8 \rightarrow 2NaCo(CO)_4 \qquad (9)$$

is an example of a reaction involving external electron transfer. This reaction proceeds smoothly and quantitatively when a benzene solution of dicobalt octacarbonyl is shaken with sodium amalgam.

Another reaction involving electron transfer is the oxidation of dicobalt octacarbonyl by hydroxyl ion[93]. When a benzene solution of dicobalt octacarbonyl is shaken with an aqueous solution of NaOH, the hydroxyl ion acts as the electron donor according to Eq. (10).

$$2Co_2(CO)_8 + 4OH^- = 4[Co(CO)_4]^- + 2H_2O + O_2 \qquad (10)$$

The redox potential of the reaction (11)

$$2[Co(CO)_4]^- = Co_2(CO)_8 + 2e;\ E^0 = -0.40 \text{ volt} \qquad (11)$$

was determined by Hieber and Huebel[35].

Replacement of the Carbonyl Group. In iron and nickel carbonyl one or more carbonyl groups are readily replaced by isonitrile or triphenylphosphine groups (see Table 4). With dicobalt octacarbonyl a different reaction takes place; in the case of CH_3NC, for instance, the structure of dicobalt octacarbonyl is not retained and an electron transfer takes place according to[36]:

$$Co_2(CO)_8 + 5CH_3NC \rightarrow [Co(CH_3NC)_5]^+ [Co(CO)_4]^- + 4CO \qquad (12)$$

Acetylene and substituted acetylenes, on the other hand, replace the two bridge carbonyls in dicobalt octacarbonyl according to[25, 76]:

$$Co_2(CO)_8 + HC{\equiv}CH \rightarrow Co_2(CO)_6C_2H_2 + 2CO \qquad (13)$$

The $RS\cdot$ group in mercaptans has also been reported[37] to replace the carbonyl group in dicobalt octacarbonyl according to:

$$Co_2(CO)_8 + 2C_2H_5SH \rightarrow Co_2(CO)_6(C_2H_5S)_2 + H_2 + 2CO \qquad (14)$$

Reactions of Cobalt Hydrocarbonyl. Although, as pointed out above, cobalt hydrocarbonyl decomposes rapidly above −26°C, organic reactions with cobalt hydrocarbonyl may be carried out with surprising ease[92]. The substrate is placed in a cold trap, cobalt hydrocarbonyl condensed onto it and the mixture allowed to warm to room temperature. Maximum yields are obtained when the substrate is a liquid at or below 0° and present in excess of cobalt hydrocarbonyl. If the substrate is a solid it should be dissolved in a low melting inert solvent such as hexane. Oxygenated solvents should be avoided, as they may retard the reaction or react with cobalt hydrocarbonyl. Thus, while triphenylcarbinol is readily reduced to triphenylmethane in either acetone or isopropyl alcohol, benzhydrol is reduced to diphenylmethane in acetone but not in isopropyl alcohol.

The reactions between cobalt hydrocarbonyl and various substrates may be classified into reactions involving

1. Isomerization
2. Homologation
3. Hydrogenolysis
4. Hydrogenation
5. Hydroformylation

Examples of these types of reactions are summarized in Table 9.

Methods of Preparation and Analysis. *Dicobalt Octacarbonyl.* Metallic cobalt and cobalt salts of aliphatic and naphthenic acids react very slowly with pure carbon monoxide at 140 to 160°C. In the presence of hydrogen, however, the cobalt salts of these acids react rapidly. A convenient method of preparation (Eq. 15) is the following:

$$2CoCO_3 + 2H_2 + 8CO \rightarrow Co_2(CO)_8 + 2H_2O + 2CO_2 \qquad (15)$$

In a 500 ml stainless-steel autoclave are placed 150 ml of petroleum ether, boiling range 32 to 63°C, and 13.7 g of cobalt (II) carbonate. The autoclave is flushed three times with carbon monoxide and then filled with an approximately equal mixture of carbon monoxide and hydrogen to a pressure of 3500 psi. The autoclave is heated with agitation to 150 to 160°C and maintained in this temperature range for about 3 hours. The maximum pressure (4300 psi) is reached at 120°C, and at the end of the reaction the pressure is about 3900 psi at 155°C. The autoclave is cooled to room temperature, whereupon the pressure drops to about 2600 psi. The gases are then vented and the autoclave is opened, preferably in a hood, to avoid inhalation of the extremely toxic vapors of cobalt hydrocarbonyl.

TABLE 9. PRODUCTS SECURED FROM VARIOUS SUBSTRATES BY REACTION WITH COBALT HYDROCARBONYL[92]

Substrate	Products
Cyclohexene	Cyclohexanecarboxaldehyde
1-Hexene (excess)	C_7 aldehydes No 1-hexene 2-Hexene 3-Hexene
α-Methylstyrene	Isopropylbenzene C_{10} aldehyde
Benzyl alcohol	Toluene
Benzhydrol	Diphenylmethane
Triphenylcarbinol	Triphenylmethane

The clear, dark solution of dicobalt octacarbonyl is pipetted from the autoclave with a syringe and filtered through filter paper into an Erlenmeyer flask; exposure to air should be kept to a minimum. If difficulty with filtration of the last few milliliters is encountered, this small amount of liquid should be discarded. The Erlenmeyer flask containing the filtrate is placed in the freezing compartment of a refrigerator overnight, whereupon large well-formed crystals of carbonyl are deposited. The solvent is decanted, and the crystals are dried by the passage of a stream of carbon monoxide through the flask for a few minutes. The dry, orange crystals of dicobalt octacarbonyl weigh 15.3 g (78 per cent of theory) and melt at 51 to 52°C with decomposition. If the crystalline material is not to be used immediately, it should be stored in a sealed tube under carbon monoxide. Rapid cooling to very low temperatures precipitates the carbonyl as a fine orange powder. In this state it decomposes in the presence of air to tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$, which is pyrophoric. It is best to allow the dicobalt octacarbonyl to remain in the refrigerator under petroleum ether until the crystalline material is required.

It is of importance to note that the above standard procedure for the preparation of dicobalt octacarbonyl in reality leads to the synthesis of cobalt hydrocarbonyl[57]. The isolation of dicobalt octacarbonyl is adventitious and results from the release of the high pressure gases at room temperature. Under these conditions, the hydrocarbonyl is rapidly decomposed to dicobalt octacarbonyl. If the autoclave is cooled to −50° before the gases are released, more than 60 per cent of the soluble cobalt is found as the hydrocarbonyl.

Where high pressure equipment is not available dicobalt octacarbonyl may also be prepared[9] by the thermal decomposition of cobalt hydrocarbonyl (Eq. 4).

Cobalt Hydrocarbonyl. The methods for the preparation of cobalt hydrocarbonyl are based on the preparation of a salt of cobalt hydrocarbonyl, followed by acidification and condensation of the liberated cobalt hydrocarbonyl.

Where high pressure equipment is not available, cobalt hydrocarbonyl may be prepared[9] by the absorption of carbon monoxide in an alkaline cobalt (II) cyanide suspension, (Eq. 16)

$$12KOH + 2K_4Co(CN)_6 + 11CO \rightarrow 3K_2CO_3 + 12KCN + 6H_2O + 2KCo(CO)_4 \tag{16}$$

and acidification of the resulting solution (Eq. 17)

$$KCo(CO)_4 + HCl \rightarrow KCl + HCo(CO)_4 \tag{17}$$

Where high pressure equipment is available, cobalt hydrocarbonyl may be prepared either from the cobalt salt of cobalt hydrocarbonyl (procedure I) by use of dicobalt octacarbonyl as a starting material (Eqs. 18 and 19),

$$3Co_2(CO)_8 + 12Pyr \rightarrow 2[Co(Pyr)_6]\,[Co(CO)_4]_2 + 8CO \tag{18}$$

$$2[Co(Pyr)_6]\,[Co(CO)_4]_2 + 8H_2SO_4 \rightarrow 4HCo(CO)_4 + 2CoSO_4 + 6(PyrH)_2SO_4 \tag{19}$$

or from the pyridinium salt of cobalt hydrocarbonyl (procedure II) with cobalt carbonate as the starting material (Eqs. 20 and 21)

$$6CoCO_3 + 24CO + 9H_2 + 6Pyr \rightarrow 6[PyrH]\,[Co(CO)_4] + 6H_2O + 6CO_2 \tag{20}$$

$$6[PyrH]\,[Co(CO)_4] + 3H_2SO_4 \rightarrow 6HCo(CO)_4 + 3(PyrH)_2\,SO_4 \tag{21}$$

A detailed description of procedures I and II follows:

Procedure I: From the cobalt salt of cobalt hydrocarbonyl.

Dicobalt octacarbonyl (3.00 g) is placed in a 300-ml Erlenmeyer flask provided with a ground glass joint. Twenty ml of C.P. pyridine are added, and the flask is fitted with a male ground joint to which is sealed a U-tube filled with sufficient mercury to make a seal. The mercury valve permits the escape of carbon monoxide and prevents access of air to the reaction mixture. The evolution of carbon monoxide is complete in a few minutes. The pyridine solution containing the salt $[Co(Pyr)_6]\,[Co(CO)_4]_2$ may be stored, provided prolonged exposure to air is avoided. A short exposure to air, such as is required for the transfer of the solution, is not detrimental.

The apparatus for the generation of cobalt hydrocarbonyl consists of a 500 ml, 3-necked flask provided with an inlet tube (constricted at the tip which is placed close to the bottom of the flask), a dropping funnel and an outlet tube. To the outlet tube is attached an absorption tube (35 x 110 mm) filled with an intimate mixture of phosphorous pentoxide and glass beads. To the absorption tube is attached a cold trap (30 x 280 mm) immersed in liquid nitrogen. The inlet tube of the cold trap should be at least 15 mm wide to prevent clogging. The outlet tube of the cold trap is connected to a tube inserted into about 20 ml of a solution of nickel *o*-phenanthroline chloride prepared by dissolving 2.8 g of *o*-phenanthroline monohydrate and 1.2 g of nickel chloride hexahydrate in 400 ml of water. This solution prevents access of air to the cold trap and indicates whether any cobalt hydrocarbonyl is carried past the cold trap; traces of cobalt hydrocarbonyl form a voluminous precipitate according to the equation

$$2HCo(CO)_4 + [Ni(o\text{-}Phthr)_3]\,[Cl]_2 \rightarrow [Ni(o\text{-}Phthr)_3]\,[Co(CO)_4]_2 + 2HCl$$

The 3-necked flask is filled with a cold solution of 25 ml of concentrated sulfuric acid and 75 ml of water, and the flask placed in an ice bath. The flask is then fitted with the inlet tube, the dropping funnel, and the outlet tube, and the pyridine solution is poured into the dropping funnel. The dropping funnel and the inlet tube are connected by a T-tube, and the system is purged with carbon monoxide. The pyridine solution is now added dropwise to the reaction flask. The rate of addition is regulated so that most of the oily droplets (cobalt hydrocarbonyl) forming on the surface of the aqueous solution have disappeared before more pyridine solution is added. If the solution is added faster than the hydrocarbonyl is removed, losses occur due to the decomposition of the hydrocarbonyl in the flask. If the gas flow is too fast, some hydrocarbonyl is carried past the cold trap. With the quantities described above, maximum yields in minimum time are obtained with a gas flow of about 300 ml per minute and addition of the pyridine solution (20 ml) during 45 to 60 minutes, followed by 15 minutes of sweeping.

From 3.00 g of dicobalt octacarbonyl, the yield of pure cobalt hydrocarbonyl is 1.80 to 1.90 g or 90 to 95 per cent of theory.

Procedure II. From the pyridinium salt of cobalt hydrocarbonyl.

Twenty grams of cobalt carbonate and 150 ml of pyridine are placed in a 500-ml stainless-steel autoclave. The autoclave is flushed three times with about 200 psi of carbon monoxide and then pressured to 3500 psi with an approximately equimolar mixture of hydrogen and carbon monoxide. After the rocking mechanism is started, the autoclave is heated to 155 to 160°C and kept in this range for about two hours. The maximum pressure attained is about 4000 psi at 140°C; the pressure then falls to a constant value of about 3100 psi at 155°C. The vessel is allowed to cool to room temperature, and the gases are vented. The yield of the pyridinium salt of cobalt hydrocarbonyl is about 90 per cent, and the solution contains about 1.6 g of the hydrocarbonyl per 10 ml of solution.

The solution of the pyridinium salt of the hydrocarbonyl is diluted with additional pyridine so that 20 ml of the pyridine solution contains approximately 2.0 g of the hydrocarbonyl. The preparation of the pure hydrocarbonyl is carried out by addition of the pyridine solution to sulfuric acid exactly as described under A.

Analysis of Dicobalt Octacarbonyl and Cobalt Carbonyl Anion. Dicobalt octacarbonyl and cobalt carbonyl anion react with iodine according to Eqs. (22) and (23)

$$Co_2(CO)_8 + 2I_2 \rightarrow 2CoI_2 + 8CO \qquad (22)$$

$$2HCo(CO)_4 + 2I_2 \rightarrow 2CoI_2 + 8CO + 2HI \qquad (23)$$

This reaction proceeds quantitatively and forms the basis of a gasometric determination[77] of dicobalt octacarbonyl and cobalt carbonyl anion. Iodine in pyridine or aqueous potassium iodide solution is added to the carbonyl solution; the amount of gas evolved serves as a measure of the amount of carbonyl (dicobalt octacarbonyl and cobalt carbonyl anion) present.

Cobalt carbonyl anion forms an orange, voluminous precipitate with nickel *o*-phenanthroline cation, Eq. (24).

$$2[Co(CO)_4]^- + [Ni(o\text{-Phthr})_3]^{++} \longrightarrow [Ni(o\text{-Phthr})_3]\,[Co(CO)_4]_2 \quad (24)$$

This precipitate is stable, insoluble in water and in hydrocarbon solvents such as benzene and readily soluble in polar solvents such as acetone or pyridine. Nickel *o*-phenanthroline cation, however, does not react with dicobalt octacarbonyl, a fact which is utilized to analyze a mixture of dicobalt octacarbonyl and cobalt carbonyl anion. One aliquot of the solution containing both dicobalt octacarbonyl and cobalt carbonyl anion is shaken with an aqueous solution of nickel *o*-phenanthroline chloride, the precipitate dissolved in pyridine and decomposed with I_2 according to Eq. (23). In a second aliquot the total amount of carbonyl present is obtained by decomposition with I_2 according to Eqs. (22) and (23). The difference between the total amount of carbonyl and that of cobalt carbonyl anion is equivalent to the amount of dicobalt octacarbonyl present.

The method described above is rapid, and, as it is based on a gasometric procedure, is well suited for the analysis of hydroformylation mixtures which may contain cobalt salts and metallic cobalt.

A method for the analysis of cobalt carbonyl anion, $[Co(CO)_4]^-$, based on the gravimetric determination of the cobalt salt, $[Co(o\text{-Phthr})_3]$ $[Co(CO)_4]_2$, has been reported by Hieber and Fraenkel[38].

KINETICS

The first studies of the kinetics of the hydroformylation reaction were published by Natta and Beati in 1945[51]. The reaction was assumed to be heterogeneously catalyzed and kinetic studies were carried out with metallic cobalt as the catalyst. In 1952, Natta and Ercoli[52] showed that with cobalt catalysts other than dicobalt octacarbonyl the rate of the reaction increased during the reaction due to the formation of soluble cobalt carbonyls. Further kinetic studies were carried out with dicobalt octacarbonyl as the source of cobalt.

Although the hydroformylation reaction is generally carried out at pressures in excess of 100 atmospheres, it also takes place at much lower pressures. It will be convenient to present kinetic data obtained above 100 atmospheres before consideration of the data obtained at lower pressures.

Rate studies at elevated pressures were generally conducted in autoclaves. It was assumed that a linear relationship existed between the amount of gas absorbed, as measured by the drop in pressure, and the decrease of the olefin concentration as a result of the reaction. Cyclohexene was generally used in kinetic studies since it yields only one aldehyde, hexahydrobenzaldehyde. The use of ethylene led to considerable difficulties because of its low concentration in the liquid phase under reaction conditions.

Effect of Partial Pressures of Carbon Monoxide and Hydrogen

Natta and Ercoli[52] found that the rate of hydroformylation of cyclohexene was first order with respect to the olefin and approximately proportional to the amount of cobalt present. Using equimolar mixtures of carbon monoxide and hydrogen, these workers found that the rate was independent of the pressure of these gases within the 100 to 380 atmosphere range of pressures (Figure 1). However, a number of workers[26, 45, 53] later demonstrated that the rate of hydroformylation increases with increasing hydrogen pressure at constant carbon monoxide pressure and decreases with increasing carbon monoxide pressure at constant hydrogen pressure. The previous observation of the independence of rate and pressure for equimolar mixtures of carbon monoxide and hydrogen was due to the approximately equal but opposite effects of increasing the partial pressure of the two gases, i.e., the rate increasing with increase of hydrogen and decreasing with increase of carbon monoxide partial pressure.

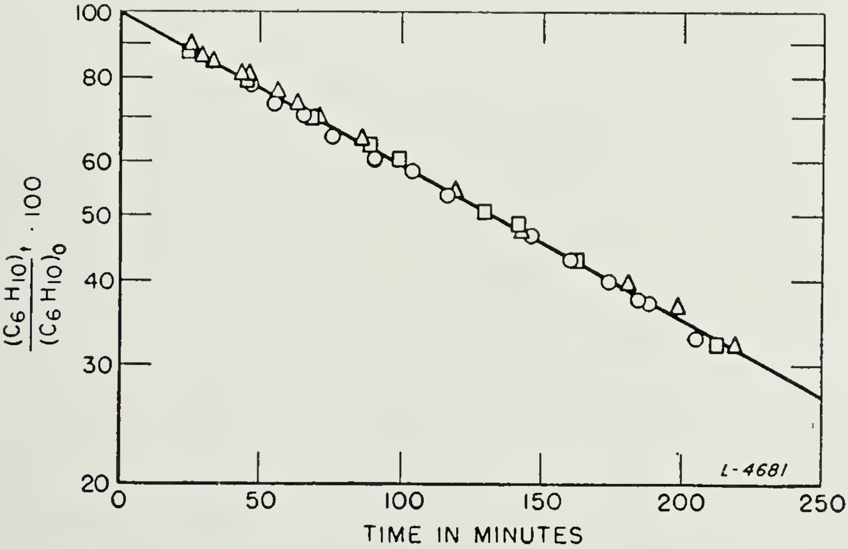


Figure 1. The rate of hydroformylation of cyclohexene at varying total pressures of equimolar amounts of CO and H; 2.7 per cent $CO_2(CO)_8$, 110°C, ○ 280–380 atm, □ 200–300 atm, △ 100–200 atm.[52]

Martin[45] measured the initial rate of hydroformylation of diisobutylene at 150°C over a range of ratios of partial pressures of hydrogen to carbon monoxide from 0.33 (50 atmospheres of hydrogen and 150 atmospheres of carbon monoxide) to 11.0 (275 atmospheres of hydrogen and 25 atmospheres of carbon monoxide) and at a number of concentrations of cobalt for each combination of gas pressures. In each case the initial rate of reaction was proportional to the quantity of cobalt (added as naphthenate) in the autoclave. The initial rate was also proportional to the olefin concentration in a series of olefin-paraffin mixtures. The results are summarized in Table 10.

The initial rates of hydroformylation in the fourth column could be represented quite well by the equation:

$$\text{initial rate} = \frac{275P_{H_2}}{0.220P_{H_2} + P_{CO}} \tag{25}$$

However, the initial rate appears to be greater, the greater the total pressure for any given ratio of partial pressures of hydrogen and carbon monoxide, and this is not represented by the equation.

The fact that the rate varies inversely with the carbon monoxide pressure led Natta, Ercoli, Castellano, and Barbieri[53], Greenfield, Metlin, and Wender[26], and Martin[45] to the postulation that the first step in the reaction involves the reaction of the olefin with dicobalt octacarbonyl to form an olefin-carbonyl complex and carbon monoxide:

TABLE 10. EFFECT OF VARIATION OF SYNTHESIS GAS COMPOSITION ON THE RATE OF HYDROFORMYLATION OF DIISOBUTYLENE AT 150° C

Initial H_2 Pressure (atm)	Initial CO Pressure (atm)	Calculated Initial Rate of Reaction (atm/hour pressure drop)	Observed Initial Rate of Reaction (atm./hour pressure drop)	Rate Calculated − Rate Observed (atm/hour pressure drop) per cent
50	50	225.4	204	+9.5
50	150	85.4	94	−10.0
150	150	225.4	248	−10.0
100	200	123.9	138	−11.4
150	100	310.2	323	−4.1
150	50	497.0	499	−0.4
150	25	711.2	759	−6.7
250	50	654.7	668	−2.0
275	25	884.5	812	+8.2

$$Co_2(CO)_8 + RHC{=}CHR \rightarrow Co_2(CO)_7 \cdot RHC{=}CHR + CO \tag{26}$$

The rate of formation and the nature of this complex will be discussed in pages 118–128, but this concept will prove useful in the interpretation of the results of other kinetic investigations.

The Effect of Temperature

The reaction rate doubles for a temperature rise of 7 to 8°C. According to the temperature region considered, the apparent energy of activation with cyclohexene appears to lie between 34 (100 to 110°C) and 29 kilocalories (110 to 120°C)[52].

The Effect of Solvent

The effect of the solvent on the rate of hydroformylation of cyclohexene at 110°C and 233 atmospheres of 1:1 synthesis gas is shown in Table 11[84]. The solvent effect is not large, although it appears to be significant; the rate is increased about one and-a-half times when methyl or ethyl alcohol is substituted for a saturated hydrocarbon. The rate in aromatic solvents is greater than in aliphatic solvents; this effect may be due to the greater polarizability of the aromatic molecule, or to the greater basicity of the aromatic hydrocarbons. It is not likely that the variations in specific reaction rates with solvent are a reflection of the difference in solubility of hydrogen and carbon monoxide in the reaction media; hydrogen, for instance, is more soluble in paraffins than in aromatics of similar molecular weight[16].

Table 11. Effect of Solvents on the Rate of Hydroformylation of Cyclohexene at 110°C

Solvent	Specific Reaction Rate, 10^3k min.$^{-1}$	Solvent	Specific Reaction Rate, 10^3k min.$^{-1}$
Methylcyclohexane	5.8	Chlorobenzene	6.5
Heptane	5.9	Benzene	6.7
Methyl ethyl ketone	5.7	Anisole	7.5
n-Butyl ether	5.9	α-Methylnaphthalene	7.9
Acetone	6.1	Ethyl alcohol	8.7
2-Ethyl-1-hexanol	6.5	Methyl alcohol	8.9

Whatever the cause, it does not appear likely that highly polar intermediates are involved in the hydroformylation reaction.

The Effect of Bases

Basic solvents have a retarding influence on reactions occurring under hydroformylation conditions[92]. Thus, the reduction of benzhydrol to diphenylmethane does not occur when pyridine is used as a solvent, and the hydroformylation of a mixture of 2,3-dimethylbutenes at 135°C and 233 atmospheres of synthesis gas can be completely inhibited by triethylamine. To obtain a more quantitative picture of the effect of bases, workers at the U. S. Bureau of Mines[26, 94] studied the hydroformylation of cyclohexene in the presence of varying amounts of amines. Their results are summarized in Table 12.

It appears that the reaction rate is increased by the addition of very small amounts of organic bases and decreased when larger amounts of these bases are present. The amount of base necessary to accelerate and to completely inhibit the reaction evidently depends on the strength of the added base. Both piperidine and triethylamine are strong bases, but triethylamine is a base with high steric requirements[12]; one may surmise that the mechanism of inhibition does not involve interaction of the base with an intermediate with exceedingly high steric requirements. It is likely that the reaction is inhibited, because the cobalt is tied up as the amine salt of cobalt hydrocarbonyl:

$$R_3N + HCo(CO)_4 \rightleftharpoons R_3NH^+ \, Co(CO)_4^-$$

TABLE 12. EFFECT OF BASES ON THE RATE OF HYDROFORMYLATION OF CYCLOHEXENE

Base	Volume of Base (ml)	$\frac{\text{Moles Base}}{\text{Moles } Co_2(CO)_8}$	10^3k min.$^{-1}$
Pyridine	0.0		5.8[a]
	.1	.15	6.6
	.3	.45	6.3
	.8	1.2	6.3
	2.0	3.1	5.3
	5.0	7.6	1.6
	10.0	15	very slow
	11.0	17	no reaction
Triethylamine	0.0		5.8[a]
	.05	.044	6.2
	.10	.087	5.8
	.50	.44	4.8
	1.0	.87	3.1
	2.0	1.7	2.1
	3.0	2.6	no reaction
Piperidine	1.0	1.2	2.6
	2.0	2.5	no reaction

Conditions: 0.50 mole of cyclohexene, 2.8 grams (8.2×10^{-3} moles) of dicobalt octacarbonyl, initial pressure of 233 atm. of 1:1 synthesis gas, 110°C, sufficient methylcyclohexane to make 65 ml of solution, including the added base.

[a] Rate in the absence of added base.

When dicobalt octacarbonyl is formed in the presence of excess pyridine, the amine salt of the hydrocarbonyl is the only product (see Eq. 20)[95].

Kinetics at Low Pressures (under 100 atmospheres)

Natta, Ercoli, and Castellano[54] have extended their studies of the kinetics of the hydroformylation reaction to pressures below 100 atmospheres. Under these conditions it is difficult to follow the reaction by observation of the pressure drop in an autoclave. These workers therefore studied the kinetics of hydroformylation at low pressures by making discontinuous isochronic (extending over a constant reaction period) measurements at various partial pressures of carbon monoxide and hydrogen under otherwise standard experimental conditions. In each run the partial pressures of carbon monoxide and hydrogen were kept constant; at the end of each run the amounts of unreacted olefin and aldehyde formed were determined. When the conversion values

$$R = \frac{\text{moles of aldehyde recovered}}{\text{moles of olefin introduced}}$$

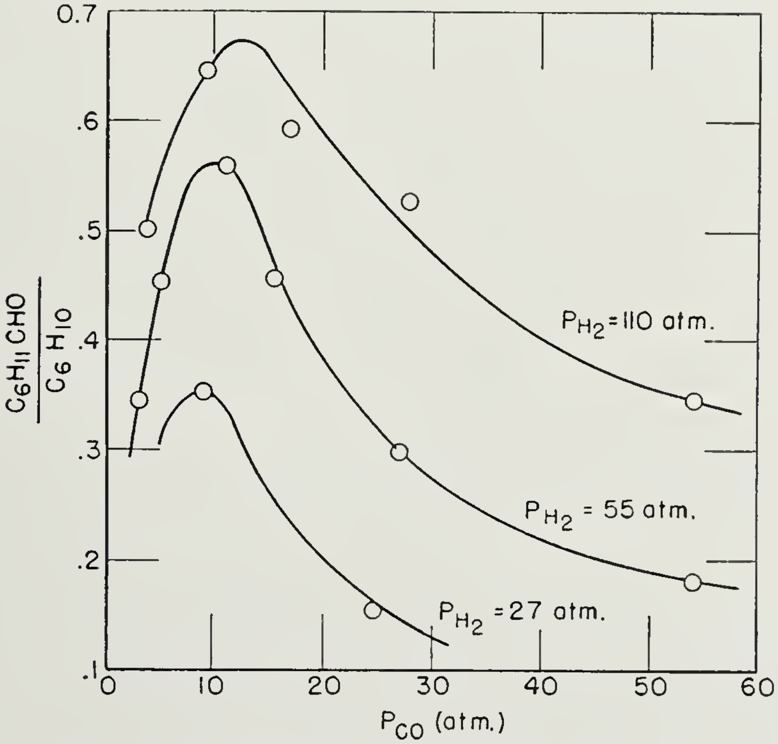


Figure 2. Rates of hydroformylation of cyclohexene as a function of CO and H_2 pressures. Isochronic experiments at constant pressure, 110°C.[54]

were plotted against time, straight lines were obtained, showing that the reaction was first order with respect to olefin even at low pressures.

The hydroformylation of cyclohexene was found to be independent of the total pressure of 1:1 synthesis gas for total pressures as low as 30 atmospheres. At total pressures of 63 to 68 atmospheres but with carbon monoxide pressures of at least 15 atmospheres, it was again found that the rate was increased by an increase in hydrogen pressure and decreased by an increase in carbon monoxide pressure.

Three series of runs were made at constant hydrogen pressures but different carbon monoxide pressures at 110°C with 100 g of a 33 to 34 per cent solution of cyclohexene in toluene and 1.4 g of dicobalt octacarbonyl. The conversion values were plotted as a function of the partial pressure of carbon monoxide (Figure 2). A similar family of curves was obtained at 120°C. These curves have a maximum for carbon monoxide partial pressures at about 8 to 9 atmospheres at 110 to 120°C. It is evident, therefore, that increasing the partial pressure of carbon monoxide beyond a certain optimum value greatly decreases the reaction rate. For equal carbon monoxide pressures, the increase in rate is approximately proportional to the increase in hydrogen pressure. The same interesting kinetic behavior with regard to the partial pressure of carbon monoxide was observed with propylene and with 2-ethyl-1-hexene.

The effect of olefin structure on rate has been presented earlier (Table 2). A further discussion of these results will be presented in pages 121–128.

Although the reaction is first order with respect to olefin concentration at low pressures, it was found that the dependence of the rate on cobalt concentration varied with the carbon monoxide pressure. Above 50 atmospheres of carbon monoxide, the rate was approximately directly proportional to the cobalt concentration (first order). For lower carbon monoxide pressures, the apparent order decreased to a value of about one-half.

MECHANISM OF THE HYDROFORMYLATION REACTION

The Function of the Carbonyls

It appears that at least three carbonyls of cobalt are involved in the addition of carbon monoxide and hydrogen to an olefin. The preparation and properties of these carbonyls, $Co_2(CO)_8$, $HCo(CO)_4$ and $[Co(CO)_3]_4$, have been described earlier in this chapter. A discussion of the probable roles of each of these compounds in the hydroformylation reaction may be in order.

Any mechanism in which carbon monoxide adds directly to the olefin is excluded by the fact that the rate of the hydroformylation reaction varies inversely with the carbon monoxide pressure. Reaction occurs in the liquid phase and carbon monoxide is transferred to the olefin from an intermediate which contains carbon monoxide bound to at least one metal atom. The probable functions of the three carbonyls mentioned above may be divided as follows:

(1) Carbon monoxide in the gas phase must be made available as a metal carbonyl in the liquid phase. This probably occurs by transformation of the tricarbonyl to the tetracarbonyl or to cobalt hydrocarbonyl.

$$[Co(CO)_3]_4 + 4CO \rightleftharpoons 2Co_2(CO)_8$$

$$[Co(CO)_3]_4 + 4CO + 2H_2 \rightleftharpoons 4HCo(CO)_4$$

(2) Hydrogen must be transferred from the gas phase to the liquid phase and the hydrogen molecule must be split. Homogeneous activation of hy-

drogen occurs by the reaction of dicobalt octacarbonyl with hydrogen in the presence of synthesis gas to form cobalt hydrocarbonyl.

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \tag{27}$$

(3) Hydrogen and carbon monoxide must be transferred from some complex or complexes to the olefin, also in the liquid phase. It is likely that all three reactants, olefin, carbon monoxide, and hydrogen, are gathered in one complex at some stage of the reaction.

Until recently, examples of the homogeneous activation of the hydrogen molecule were rare. In 1938, Calvin[13] described a system for the homogeneous catalytic hydrogenation of benzoquinone in which the catalyst was cuprous acetate. Weller and Mills[82] called attention to the striking analogy between the activation of hydrogen by cuprous acetate and that occurring under hydroformylation conditions. These workers corroborated Calvin's mechanism of the activation, which they wrote as follows:

$$(Cu^{I})_2 + H_2 \rightleftharpoons (Cu^{I})_2 \cdot H_2 \tag{28}$$

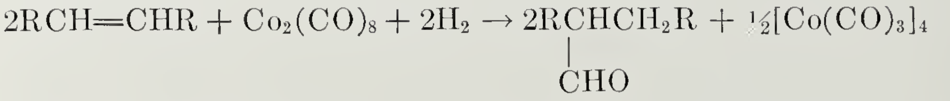
The cuprous dimer is required for the catalytic action, presumably because two strong copper-hydrogen bonds must be formed to compensate for the energy of dissociation of the hydrogen molecule. Reactions (27) and (28) have certain similarities; in both cases molecular hydrogen reacts with a dimeric metal complex to form a compound in which the hydrogen molecule has been split.

Weller[83] and Halpern[30] have written excellent discussions of the homogeneous activation of hydrogen in a number of systems.

Since cobalt hydrocarbonyl is the only one of the three carbonyls mentioned which contains hydrogen, this carbonyl may play an important role in the transfer of hydrogen to the olefin. Indeed the hydrocarbonyl may provide both hydrogen and carbon monoxide; Wender, Sternberg, and Orchin have demonstrated that the hydroformylation of olefins can proceed at atmospheric conditions with molar proportions of pure cobalt hydrocarbonyl[92]. In one experiment 4.0 grams (0.023 mole) of cobalt hydrocarbonyl was collected in a liquid-nitrogen trap containing 7.0 grams (0.085 mole) of cyclohexene. On warming, the cobalt hydrocarbonyl dissolved in the olefin without noticeable decomposition. At about 15°C the solution began to darken, a small amount of gas was given off, and the mixture became warm. Addition of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde; the yield of aldehyde was 60 per cent, based on the amount of cobalt hydrocarbonyl present. When excess 1-hexene was similarly treated with pure hydrocarbonyl, C-7 aldehydes were secured and the unconverted 1-hexene was completely isomerized to the thermodynamically more stable internal hexenes. Not only were these hydroformylations successfully conducted at atmospheric pressure with pure cobalt hydrocarbonyl but hydrogenolysis reactions, known to occur under the usual oxo conditions, were likewise successfully achieved at atmospheric pressure. Thus treatment of triphenylcarbinol, benzhydrol, and benzyl alcohol with cobalt hydrocarbonyl gave, respectively, triphenylmethane, diphenylmethane, and toluene, products identical with those secured by treatment of the respective substrates at the usual oxo conditions of high temperatures and superatmospheric pressure.

There are many reactions in which carbon monoxide is transferred to organic compounds by means of metal carbonyls. Cobalt hydrocarbonyl is unique in that it supplies both hydrogen and carbon monoxide to organic substrates.

It is also possible to carry out a hydroformylation reaction with dicobalt octacarbonyl as the sole source of carbon monoxide. A patent issued in 1951 described the reaction of olefins, dicobalt octacarbonyl, and hydrogen at 40 to 285 atmospheres pressure and temperatures between 25 and 150°C[5]; under these conditions the olefin was converted to aldehydes and primary alcohols, and the carbonyl was decomposed to metallic cobalt. In 1955, Pino, Ercoli, and Calderazzo[65] showed that aldehydes could be synthesized from olefins, hydrogen, and dicobalt octacarbonyl. When an olefin is treated with stoichiometric amounts of dicobalt octacarbonyl under a high pressure of hydrogen at room temperature, approximately 2 moles of hydrogen are absorbed per mole of dicobalt octacarbonyl. The olefin is transformed into the next higher aldehyde and appreciable amounts of well crystallized cobalt tricarbonyl are also obtained. The reaction may be represented by Eq. (29):



$$2RCH{=}CHR + Co_2(CO)_8 + 2H_2 \rightarrow 2R\underset{\displaystyle CHO}{\underset{|}{C}}HCH_2R + \tfrac{1}{2}[Co(CO)_3]_4 \qquad (29)$$

Experiments with cyclohexene and 200 atmospheres of hydrogen showed that the reaction is approximately first order with respect to the olefin in this stoichiometric synthesis of aldehydes. Small amounts of carbon monoxide added to the reaction mixture were found to have an inhibiting effect which was proportional to its partial pressure.

Since cobalt hydrocarbonyl and olefins react at room temperature to form aldehydes, it is logical to inquire as to whether the stoichiometric synthesis of aldehydes from the octacarbonyl, hydrogen, and an olefin involves the formation and further reaction of the hydrocarbonyl. It was found that cobalt hydrocarbonyl was always formed in detectable amounts in the stoichiometric synthesis from the octacarbonyl. Cobalt hydrocarbonyl is also formed when dicobalt octacarbonyl is treated with hydrogen at room temperature in the absence of olefins; the formation of hydrocarbonyl takes place with a hydrogen pressure as low as 70 atmospheres. However, the formation of cobalt hydrocarbonyl does not appear to follow the simple scheme of Eq. (27). Again, the addition of carbon monoxide in small amounts (1–4 atmospheres) to 190 atmospheres of hydrogen in the presence of 48 millimoles of $Co_2(CO)_8$ slows up the absorption of hydrogen appreciably. It has been suggested[65] that cobalt hydrocarbonyl forms at room temperature by reaction between hydrogen and a lower unstable carbonyl which would be present in equilibrium with the octacarbonyl in concentrations which would depend on the carbon monoxide pressure. There may be a readily reversible equilibrium with the lower carbonyl, $[Co_2(CO)_7]_2$:

$$2Co_2(CO)_8 \rightleftharpoons [Co_2(CO)_7]_2 + 2CO \tag{30}$$

In any case, the inhibiting action of carbon monoxide on both the synthesis of cobalt hydrocarbonyl and on the stoichiometric synthesis of aldehydes suggests that one is dealing with the same phenomenon in both instances.

The probable role of cobalt tricarbonyl has been pointed out earlier. This compound is stable in solution at least up to 80°C in an atmosphere of CO and is fairly soluble in toluene at 90°C ($\geq 5\%$). Natta, Ercoli and Castellano[54] have shown that the tricarbonyl and octacarbonyl, in the absence of hydrogen, coexist at carbon monoxide pressures corresponding to the highest reaction rates (8 to 10 atmospheres).

Although few data exist on the equilibrium between dicobalt octacarbonyl and hydrogen and cobalt hydrocarbonyl (Eq. 27), it is reasonable to assume that, for a given partial pressure of hydrogen and a given concentration of dissolved dicobalt octacarbonyl, the hydrocarbonyl concentration depends on that of the octacarbonyl. As shown by Eq. (1), this latter concentration increases with the partial pressure of carbon monoxide. It appears that the pressures corresponding to the maximum concentration of cobalt hydrocarbonyl (high CO pressures) do not coincide with those for which the rate of hydroformylation is highest (low CO pressures). However, this consideration does not eliminate a mechanism involving the formation of an intermediate from the olefin and hydrocarbonyl with the elimination of carbon monoxide.

At this point, it is well to consider whether or not cobalt hydrocarbonyl is present under oxo reaction conditions. There is abundant evidence that the hydrocarbonyl is present under these conditions of temperature and pressure *in the absence of olefins*. Hieber, Schulten, and Marin[39] prepared cobalt hydrocarbonyl from cobalt (II) sulfide and from cobalt (II) iodide by treatment with 140 to 200 atmospheres of CO and water at 160 to 180°C;

these workers stated that it was only possible to obtain pure octacarbonyl with completely anhydrous cobalt salts. The hydrocarbonyl was also prepared from metallic cobalt and from pure dicobalt octacarbonyl in the presence of CO and H_2 at 165°C. The hydrocarbonyl was identified by precipitation of the anion, $Co(CO)_4^-$, with nickel o-phenanthroline cation (Eq. 24) and by the formation of the yellow salt, $Co(CO)_4 \cdot HgCl \cdot \frac{1}{2}H_2O$ by treatment of the gas stream from the autoclave with an aqueous solution of $HgCl_2$. Keulemans[43] showed that cobalt hydrocarbonyl was formed when a mixture of CO and H_2 was passed over a bed of cobalt on pumice at 50 to 180°C and a total pressure of 100 to 200 atmospheres. Workers at the Bureau of Mines found that the pyridinium salt of cobalt hydrocarbonyl is the sole product when a cobalt salt is treated with H_2 and CO under oxo conditions in the presence of pyridine[95]. Conclusive proof for the presence of the hydrocarbonyl under oxo conditions (but in the absence of olefins) was furnished by the work of Orchin, Kirch, and Goldfarb[57] who found that the standard preparation of dicobalt octacarbonyl really furnishes large quantities of the hydrocarbonyl, and that pure preformed octacarbonyl is rapidly converted to the hydrocarbonyl (vide infra).

There is some question, however, as to whether cobalt hydrocarbonyl is present as such under oxo conditions *in the presence of an olefin*. Orchin, Kirch, and Goldfarb[57] heated a solution of dicobalt octacarbonyl to 110°C under a pressure of 110 atmospheres of carbon monoxide; hydrogen was then added rapidly to a total pressure of 220 atmospheres. The autoclave was cooled as rapidly as possible to dry-ice temperatures and the contents poured into an aqueous nickel o-phenanthroline chloride solution to test for $Co(CO)_4^-$. Analysis indicated that at least 50 per cent of the cobalt was present as the anion, presumably formed from cobalt hydrocarbonyl. When the experiment was repeated in the presence of excess 1-hexene, however, no anion was found in the reaction products. If the hydroformylation was allowed to go to completion so that the amount of 1-hexene present was very small, 62 per cent of the cobalt was found to be present as the anion. These results are interpretable on the basis that cobalt hydrocarbonyl is rapidly complexed in the presence of olefin and is therefore not present as such under the usual oxo operating conditions. The stabilizing effect of an olefin on the hydrocarbonyl had been demonstrated earlier at the U. S. Bureau of Mines[92]; whereas cobalt hydrocarbonyl decomposes rapidly at −26°C (Eq. 4) in saturated hydrocarbons, no reaction occurs in olefins until about 15°C; at this temperature the hydrocarbonyl reacts with olefins to form aldehydes.

It was pointed out earlier in this chapter that 1-hexene is rapidly isomerized to a mixture of internal hexenes by pure cobalt hydrocarbonyl at 0 to 15°C. However, double bond isomerization of terminal to internal olefins is very slow during the oxo reaction. The inference, again, is that the hydrocarbonyl is not present as such during the reaction.

Early Postulations as to Mechanism

Many of the mechanisms postulated during early work on the hydroformylation reaction involved the direct reaction between carbon monoxide and the olefin. If this were the case, hydroformylation would be favored kinetically by high pressures of carbon monoxide. These early postulations are nonetheless chemically and historically interesting and will be considered briefly at this point.

Cobalt hydrocarbonyl is a strong acid, and there is abundant evidence that it may function as an acid under hydroformylation conditions. A more or less conventional carbonium-ion mechanism has been postulated[52, 96] in which the hydrocarbonyl acts as a protonic acid and the carbonium-ion intermediate reacts with carbon monoxide:

$$\mathrm{Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4 \rightleftharpoons 2\ H^+ + 2\ Co(CO)_4^-}$$

$$\mathrm{H_2C{=}CH_2 + H^+ \rightleftharpoons CH_3CH_2^+}$$

$$\mathrm{CH_3CH_2^+ + CO \rightleftharpoons CH_3CH_2\overset{+}{C}O}$$

$$\mathrm{CH_3CH_2\overset{+}{C}O + H_2 \rightleftharpoons CH_3CH_2CHO + H^+}$$

Alternately, the acyl carbonium ion may lose a proton to form a ketene, which, in the presence of the hydrocarbonyl, is hydrogenated to an aldehyde:[58]

$$\mathrm{CH_3CH_2\overset{+}{C}O \xrightarrow{-H^+} CH_3CH{=}C{=}O \xrightarrow{H_2} CH_3CH_2CHO.}$$

In addition to the fact that these pathways are at variance with results of kinetic experiments, the distribution of products from a terminal olefin is not that expected from a carbonium-ion intermediate. Part of this difficulty may be avoided by the assumption that the initial electrophilic attack on the olefin is made competitively by $\mathrm{H^+}$ and by $\mathrm{\overset{+}{C}HO}$ formed from $\mathrm{H^+}$ and CO. The formyl carbonium-ion, $\mathrm{\overset{+}{C}HO}$, has been assumed to be an intermediate in the Gatterman-Koch reaction, which is also an acid-catalyzed reaction involving carbon monoxide. The formation of a ketene as an intermediate was offered as an explanation for the finding that an olefin substituted at the second carbon atom (isobutylene) yielded only one alcohol (isoamyl alcohol) in the oxo reaction. However, the recent finding that isobutylene reacts to give in addition to isoamyl alcohol about 5 per cent of neopentyl alcohol[85] and the fact that perfluorolefins[97] undergo the oxo reaction make this mechanism extremely improbable.

The same type of reasoning may be used to show that the addition of carbon monoxide to a radical formed by reaction of an olefin with a cobalt carbonyl radical is unlikely.

A mechanism of aldehyde formation involving the attack of hydrocarbonyl on the olefin was given in the first article on the hydroformylation reaction to appear in the American literature. Adkins and Kresk[2] proposed that the reaction under the usual hydroformylation conditions proceeded in at least four steps as follows:

$$\text{(1)}\quad 2\mathrm{Co} + 8\mathrm{CO} \overset{150^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{Co_2(CO)_8} \tag{31}$$

$$\text{(2)}\quad \mathrm{Co_2(CO)_8} + \mathrm{H_2} \overset{125^\circ\mathrm{C}}{\rightleftharpoons} 2\mathrm{HCo(CO)_4} \tag{27}$$

$$\text{(3)}\quad 4\mathrm{HCo(CO)_4} + 4\mathrm{CH_2{=}CH_2} \underset{125^\circ\mathrm{C}}{\overset{2\mathrm{H_2}}{\rightleftharpoons}} 4\mathrm{CH_3CH_2CHO} + [\mathrm{Co(CO)_3}]_4 \tag{32}$$

$$\text{(4)}\quad [\mathrm{Co(CO)_3}]_4 + 4\mathrm{CO} \overset{125^\circ\mathrm{C}}{\rightleftharpoons} 2\mathrm{Co_2(CO)_8}$$

The discovery of the hydroformylation of olefins with pure hydrocarbonyl (but at 0 to 20°C and in the absence of added hydrogen) confirms the essentials of Eq. (32). However the activation of molecular hydrogen in this step is not explained, and this series of equations implies that the rate of the reaction would be directly proportional to the pressure of carbon monoxide.

Recent Work

The fact that the rate of the hydroformylation reaction varies inversely with the carbon monoxide pressure may be explained if, in the initial stages, some reaction occurs between a carbonyl of cobalt (possibly dicobalt octacarbonyl or cobalt hydrocarbonyl) and the olefin, the latter displacing some of the CO in the carbonyl.

On the basis of kinetic data, several workers[26, 45, 53] have postulated that the first step in the synthesis involves the reaction of the olefin with dicobalt octacarbonyl to form an olefin-carbonyl complex and carbon monoxide. The following scheme has been suggested for the reaction (with cyclohexene)[53]

$$\mathrm{Co_2(CO)_8} + \mathrm{C_6H_{10}} \rightleftharpoons \mathrm{Co_2(CO)_7\cdot C_6H_{10}} + \mathrm{CO}$$

$$2\mathrm{Co(CO)_7\cdot C_6H_{10}} + 2\mathrm{H_2} \rightarrow 2\mathrm{C_6H_{11}CHO} + [\mathrm{Co(CO)_3}]_4$$

$$[\mathrm{Co(CO)_3}]_4 + 4\mathrm{CO} \rightleftharpoons 2\mathrm{Co_2(CO)_8}$$

Although this scheme predicts that the rate of hydroformylation would be inversely proportional to the CO pressure, it does not lead to a simple explanation of the variation of reaction rates with changes in the hydrogen to carbon monoxide ratio (H_2/CO).

Martin[45] showed that the following sequence of equations led to a kinetic expression that fits the data obtained with different ratios of gases at elevated pressures quite well:

$$Co_2(CO)_8 + RCH{=}CH_2 \xrightarrow{k_1} \underset{(XV)}{Co_2(CO)_7 \cdot RCH{=}CH_2} + CO \quad (33)$$

$$Co_2(CO)_7 \cdot RCH{=}CH_2 + CO \xrightarrow{k_2} Co_2(CO)_8 + RCH{=}CH_2 \quad (34)$$

$$Co_2(CO)_7 \cdot RCH{=}CH_2 + H_2 \xrightarrow{k_3} Co_2(CO)_6 + RCH_2CH_2CHO \quad (35)$$

$$Co_2(CO)_6 + 2CO \rightarrow Co_2(CO)_8$$

which gives the following equation:

$$\text{initial rate} = \frac{k_1k_3p_{H_2}}{k_2p_{CO} + k_3p_{H_2}} \rightarrow [Co_2(CO)_8][RCH{=}CH_2] \quad (36)$$

This sequence is similar to that originally suggested, except that equilibrium is not maintained between dicobalt octacarbonyl and olefin, on the one hand, and complex XV and carbon monoxide on the other. If this equilibrium is maintained, the kinetic equation above reduces to

$$\text{initial rate} = \frac{k_1k_3p_{H_2}}{k_2p_{CO}}[Co_2(CO)_8][RCH{=}CH_2].$$

Martin's results show definitely that although the initial rate of reaction increases with an increase in the ratio of hydrogen to carbon monoxide partial pressure, it does so at a diminishing rate of increase as this ratio increases.

If Martin's equation (36) is rearranged, the following expression results:

$$\text{initial rate } (r) = \frac{k_1k_3}{k_2\dfrac{p_{CO}}{p_{H_2}} + k_3} \ldots\ldots\ldots\ldots$$

whence, inverting

$$\frac{1}{r} = \frac{k_2\dfrac{p_{CO}}{p_{H_2}}}{k_1k_3} + \frac{1}{k_1}$$

This equation predicts that a straight line should be obtained when $1/r$ is

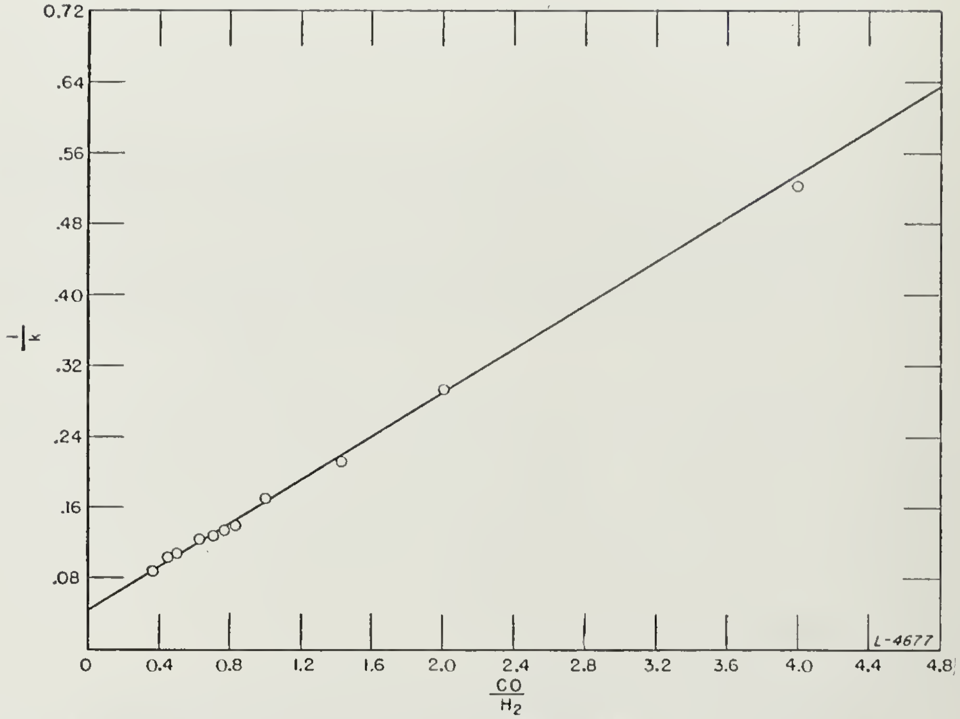


Figure 3. Reciprocal of specific reaction rate constants for cyclohexene versus CO:H_2 ratio at 110°C.

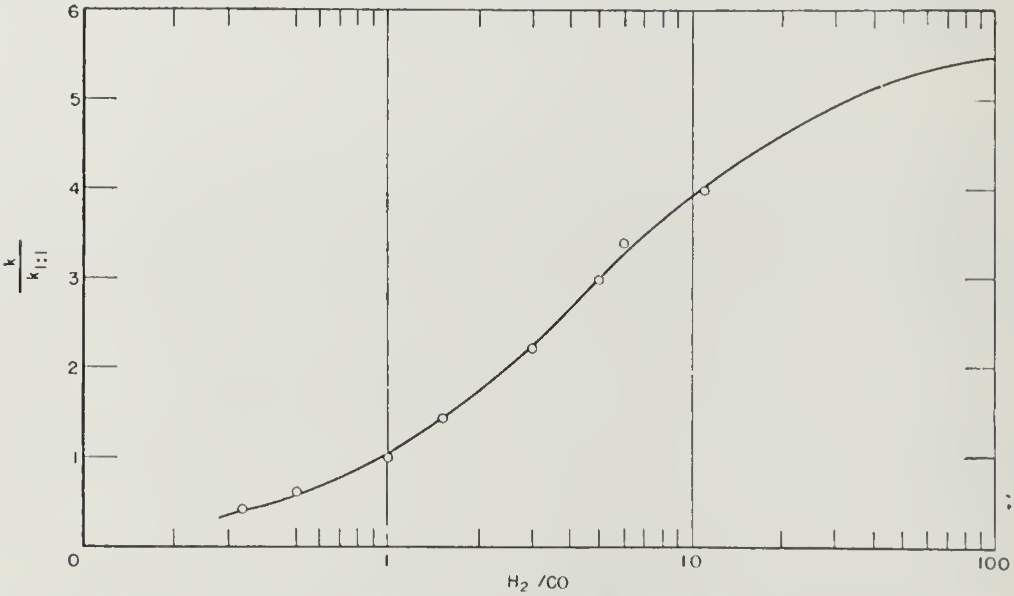


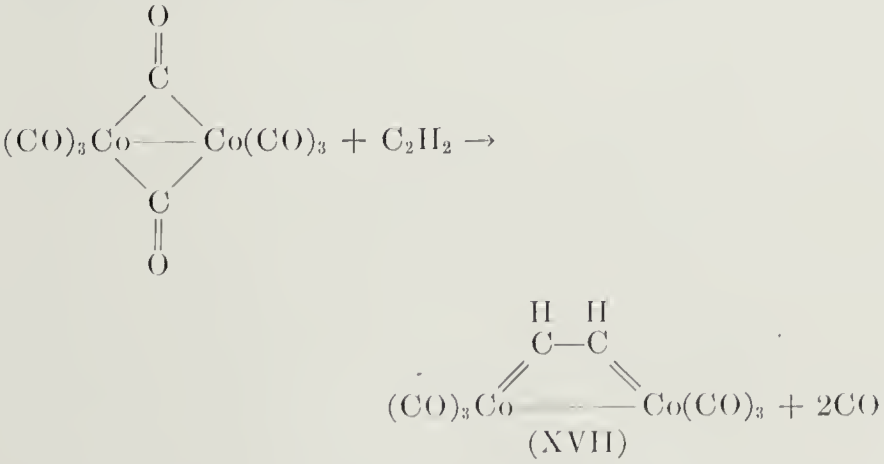
Figure 4. Comparison of specific reaction rate constants (k) for cyclohexene at any H_2:CO ratio. Curve calculated from Martin's equation.[45] ○ experimental points.[78]

plotted against the ratio of CO to H_2. That this is the case is shown in Figure 3; the data in this figure were obtained by Wender, Metlin, Ergun, Sternberg and Greenfield using cyclohexene[84]. Figure 4 was obtained by plotting the specific reaction rate constants obtained at various ratios of hydrogen to carbon monoxide in the synthesis gas over the rate constant obtained with equimolar ratios of the gases against the hydrogen to carbon monoxide ratio. This curve indicates that the maximum possible increase in rate over that at 1:1 synthesis gas in going to higher ratios of H_2/CO is about 6.

This mechanism assigns no role to cobalt hydrocarbonyl. Martin suggested that reaction (35) might occur in more than one step, but stated that there appeared to be no reason why this reaction is not as simple as the equation indicates. There are cogent reasons, however, for believing that (XV) must react to form another complex, (XVI), which then rearranges to give aldehyde and cobalt tricarbonyl. The complex or intermediate (XV) is a large molecule, and it is unlikely that it will split a molecule of hydrogen and then undergo the complex molecular rearrangements necessary to form aldehyde and tricarbonyl in one step. It is reasonable to postulate that (XV) reacts with hydrogen in the following manner before aldehyde is formed:[84]

$$\underset{\text{(XV)}}{Co_2(CO)_7 \cdot C_6H_{10}} + H_2 \rightarrow \underset{\text{(XVI)}}{[Co_2(CO)_7 \cdot C_6H_{10} \cdot 2H]} \qquad (37)$$

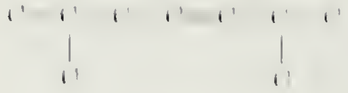
An idea of the structure of (XV) may be gained by an examination of the complex obtained from the reaction of acetylene with dicobalt octacarbonyl[25, 76]. The stoichiometry of this reaction indicates that the acetylene complex, (XVII), is formed in the following manner:



(38)

The analytical, spectroscopic, magnetic, and dipole moment data are compatible with the structure written for (XVII). It is reasonable to assume

TABLE 13. EFFECT OF OLEFIN STRUCTURE ON RATE OF HYDROFORMYLATION AT 110°C

Olefin	Specific Reaction Rate, $10^3 k$, min^{-1}
C–C–C–C–C=C	66
C–C–C–C=C–C	18
C–C–C–C=C–C–C	19
 $C{-}\underset{\mid \atop C}{C}{-}C{-}C{=}C{-}\underset{\mid \atop C}{C}{-}C$	6.2
 $C{-}C{-}C{=}\underset{\mid \atop C}{C}{-}C$	4.0
 $C{-}\overset{C \atop \mid}{\underset{\mid \atop C}{C}}{-}C{=}\underset{\mid \atop C}{C}{-}C$	2.6
 $C{-}\underset{\mid \atop C}{C}{=}\underset{\mid \atop C}{C}{-}C$	1.4

that an olefin, RCH=CHR', displaces only one mole of carbon monoxide, so that the olefin carbonyl complex (XV) probably has the following structure:[34]

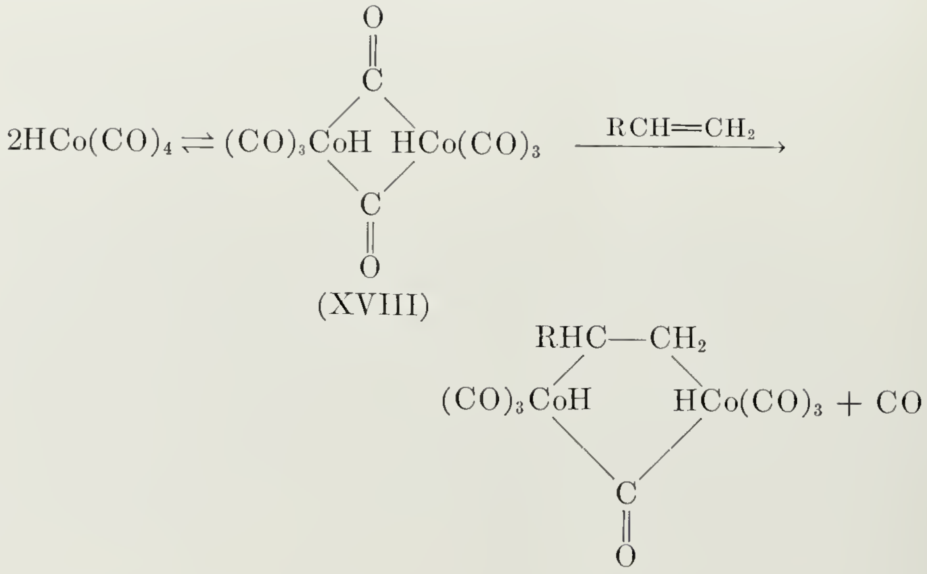
(XV)

One might expect that the ease of formation of (XV) (or any similar complex) would be influenced by the steric requirements of the olefin and that the rates of reaction of various olefins would depend on the configuration about the double bond. This effect has been observed and is illustrated in Table 13.

The straight chain terminal olefin is least hindered and reacts most rapidly; the corresponding internal olefins react at about one-third this rate. However, the position of the double bond, as long as it is internal, has no effect upon the rate. Although 2,6-dimethyl-3-heptene is doubly branched and has a double bond far removed from the terminal position, it reacts more rapidly than olefins lower in the table, because there are no substituents at the double bond to offer steric interference to complex formation with the carbonyl. It is seen that the other olefins offer increased steric hindrance at the site of reaction and react at correspondingly decreased rates.

The fact that a minimum in the rate of reaction of the cyclic olefins (Table 14) occurs at the C_6 ring may also be explained in terms of complex formation with a carbonyl. Traynham[91] has calculated that cyclopentene has a strain energy of 1.1 kcal/mole relative to cyclohexene and that cycloheptene has a strain energy of 1.1 kcal/mole relative to the same olefin. Both cyclopentene and cycloheptene have larger tendencies to form complexes with silver ion than does cyclohexene. Traynham has pointed out that in all cases reported the more strained is a cyclic compound, the more reactive is it in electron donating roles. Cyclopentene and cycloheptene may thus react so rapidly in the hydroformylation reaction because of their great tendency to form complexes with either $Co_2(CO)_8$ or with $HCo(CO)_4$.

The formation of (XVI) has been postulated above to explain the dissolution of hydrogen by the catalyst. There is independent evidence for the existence of a complex such as (XVI). It has been shown that cobalt hydrocarbonyl, $HCo(CO)_4$, reacts with olefins at room temperature (in the absence of synthesis gas) to form aldehydes[93]. Since cobalt hydrocarbonyl is the source of both hydrogen and carbon monoxide in this reaction, at least two molecules of hydrocarbonyl must react with one of olefin. Either a termolecular reaction between two molecules of hydrocarbonyl and one of olefin, or two consecutive bimolecular reactions must occur (Eq. 39) to furnish the aldehyde; the latter is the more likely occurrence. It is therefore likely that both the runs with stoichiometric amounts of cobalt hydrocarbonyl and the autoclave runs with catalytic amounts of dicobalt octacarbonyl proceed via the same intermediate (XVIII). Cobalt hydrocarbonyl may not be present under hydroformylation conditions because of its rapid reaction with olefins according to Eq. (39).



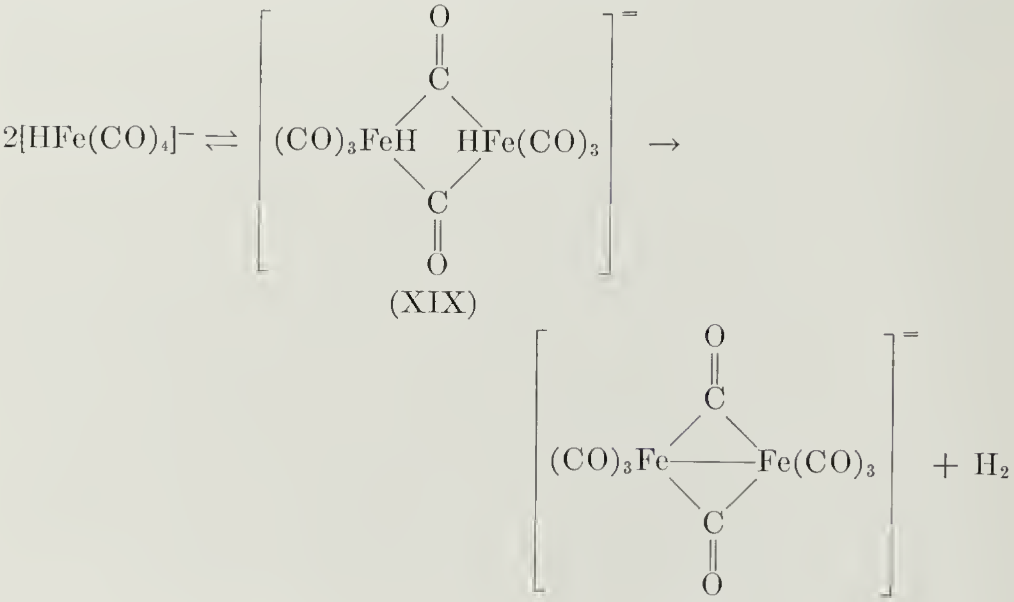
(XVIII) (39)

(XVI)

Recent work by Sternberg, Markby, and Wender[78] on the course of the reaction discovered by Reppe and Vetter[68]

$$H_2C{=}CH_2 + 3CO + 2H_2O \xrightarrow[Fe(CO)_5]{NaOH} CH_3CH_2CH_2OH + 2CO_2 \qquad (40)$$

has shown that aldehydes are the primary products of this reaction and that the same type of intermediates (dimeric metal hydrocarbonyls) are involved. The intermediate complexes are anions, however, formed from the $HFe(CO)_4^-$ ion in alkaline solution:



(XIX)

(XX)

The monosodium salt of (XX) (the analog of dicobalt octacarbonyl) has been isolated and shown to be catalytically active at room temperature for the isomerization of terminal olefins to internal olefins.

Natta, Ercoli, and Castellano[54] have written two other mechanisms for the oxo reaction. The first involves the formation of a complex from cobalt hydrocarbonyl and the olefin:

$$HCo(CO)_4 + C_6H_{10} \rightleftharpoons HCo(CO)_3 \cdot C_6H_{10} + CO \tag{41}$$

$$\underset{\text{(XXI)}}{HCo(CO)_3 \cdot C_6H_{10}} + HCo(CO)_4 \xrightarrow{\text{slow}} C_6H_{11}CHO + [Co(CO)_3]_2 \tag{42}$$

$$2[Co(CO)_3]_2 \rightleftharpoons [Co(CO)_3]_4\text{, etc.} \tag{43}$$

It is interesting that the composition shown on the left hand side of Eq. (42) corresponds to the complex (XVI), which may be postulated as an intermediate in this case also. The variation in rate of reaction of cyclohexene at 120°C with the partial pressure of CO at constant hydrogen pressure was found to agree satisfactorily with theoretical curves based on a calculation involving the assumption of an equilibrium constant for Eq. (27). To date, however, not even approximate data for this equilibrium are available. The agreement was not so good for the experimental points obtained at 110°C.

The second mechanism involves the formation of the complex (XV) according to Eq. (44) and resembles

$$[Co(CO)_3]_2 + C_6H_{10} + CO \rightleftharpoons Co_2(CO)_7 \cdot C_6H_{10} \tag{44}$$

a scheme proposed earlier[53]. This mechanism assigns no role to cobalt hydrocarbonyl and does not appear to fit all the kinetic data.

The Nature of the Olefin in the Intermediate Complexes

Although some double bond isomerization occurs under oxo conditions, the rate of isomerization is relatively slow[24, 84]. Goldfarb and Orchin attempted to discover whether the facts that 1-pentene absorbs synthesis gas 3 to 3.5 times as fast as 2-pentene and both isomers were reported to give the same products, might not result from 2-pentene isomerizing to 1-pentene in a slow step. Accordingly, they performed a series of experiments in which they treated 1- and 2-pentene under oxo conditions and interrupted the reaction at various stages of completion. The unconverted olefin was recovered and analyzed and the products were also recovered and analyzed. The following simple scheme was used to test the data:

$$\begin{tikzcd}
\text{1-pentene} \arrow[r, shift left, "k_1"] \arrow[d, "k_2"] & \text{2-pentene} \arrow[l, shift left, "k_4"] \arrow[d, "k_3"] \\
\text{aldehydes} & \text{aldehydes}
\end{tikzcd}$$

From the literature data on pentene equilibria, it is known that $k_1 = 20\ k_4$. If one considers the slow step in the hydroformylation of 2-pentene to be its prior isomerization to 1-pentene, then the measured rate constant for the 2-pentene reaction is k_4 and the rate of isomerization of the 1-isomer to the 2-isomer should be twenty-times this value. However, k_1 was found to about seven times as fast as k_2 and were the above scheme correct, then appreciable quantities of 2-pentene should have appeared as the reaction of 1-pentene proceeded. This was found experimentally not to be the case. The difference in measured rates of gas absorption of the two isomers was not large enough to be accounted for by the isomerization rates and accordingly it is unlikely that 2-pentene isomerizes to 1-pentene, prior to reaction. The data are more consistent with the slow step being the formation of a common intermediate from both isomers, with each isomer forming the intermediate at different rates. It was also found that the product distribution from each isomer remained essentially constant all during the conversion of the olefin, and this finding again argues for a common intermediate. The fact that slightly different product distributions were secured from each isomer is not entirely consistent with the common intermediate explanation. Perhaps the major portion of the reaction proceeds through such an intermediate and a relatively minor fraction proceeds directly from the olefin.

TABLE 14. PRODUCT DISTRIBUTION FROM ISOMERIC PENTENES

Catalyst	Temp. (°C)	Pressure, (atm.)	Products					
			Hexanol (%)		2-methyl-1-pentanol (%)		2-ethyl-1-butanol (%)	
			from 1-pentene	from 2-pentene	from 1-pentene	from 2-pentene	from 1-pentene	from 2-pentene
Reduced cobalt[41]	120–160	100–200	50	55	40	35	10	10
Reduced cobalt[46]	145–155	80–180	48	44	46	46	6	10
$Co_2(CO)_8$[46] (in benzene)	145–150	80–180	67	52	30	39	3	9
$Co_2(CO)_8$[24] (in hexane)	112	210–220	80	70	17	27	3	3

Although internal olefins are thermodynamically more stable than terminal olefins under reaction conditions, the products obtained in the hydroformylation reaction are largely derived by addition to the terminal carbons. Three papers have appeared on the product distribution obtained from the isomeric pentenes; the results are summarized in Table 14. Although the results are difficult to compare because the experiments were not carried out under identical conditions and the analyses were made in a different manner in each case, some conclusions may be drawn from the data. With reduced cobalt catalysts, approximately equal amounts of alcohols derived by addition to the first and second carbon atoms are secured. When dicobalt octacarbonyl is used, the straight chain alcohol is obtained in preponderant amounts from both 1- and 2-pentenes. Two interpretations of the data are possible: (1) Essentially the same products are obtained from both of the isomeric pentenes and (2) the product distribution from 1-pentene is significantly different from that obtained with 2-pentene. Although Goldfarb and Orchin[24] favor the latter conclusion the work of Keulemans, Kwantes, and van Bavel[41] lends credence to the first interpretation; these workers obtained the same distribution of products from the isomeric methyl-butenes:

$$\left.\begin{array}{l}\text{2-methyl-1-butene}\\ \text{2-methyl-2-butene}\\ \text{3-methyl-1-butene}\end{array}\right\} \rightarrow \begin{array}{l}55\%\ \text{4-methyl-1-pentanol}\\ 45\%\ \text{3-methyl-1-pentanol}\\ 5\%\ \text{2,3-dimethyl-1-butanol}\end{array}$$

The results in Table 14 indicate that lower temperatures favor the production of straight rather than branched alcohols. This view is supported to some extent by the work of Schreyer[70] who prepared a mixture of butyl and isobutyl acetates by treating propylene with 1:1 synthesis gas at 250°C and 700 atmospheres pressure in the presence of acetic acid. The reaction conducted under these conditions gave 72 per cent of isobutyl acetate and only 28 per cent of butyl acetate.

A recent paper by the group at the Bureau of Mines[84] has offered the following explanation for the distribution of products in the oxo reaction based on the conclusion that the isomeric olefins considered yield essentially the same products. Because of steric hindrance, 2-pentene reacts with dicobalt octacarbonyl to form a complex more slowly than 1-pentene, and this accounts for the differences in rates observed with these olefins. It appears that the energy required for the rearrangement of the complex subsequent to its initial formation is small; one may therefore conclude that essentially the same complex is obtained from both terminal and internal olefins. The structure given for the olefin-carbonyl complex, (XV), probably represents the complex as it initially forms from either a terminal or internal olefin. It is not possible at present to write an adequate structure for the olefin-carbonyl complex as it exists a moment later, for the position of attachment of the unsaturated entity to the carbonyl is probably not fixed.

Some mechanism must exist for the facile movement of hydrogen in these complexes. Hydrogens are probably transferred from one part of the chain to another by interaction with the cobalt atoms. This idea is supported by the observation that allenes with at least one hydrogen atom ($R_2C{=}C{=}CHR$) are polymerized by dicobalt octacarbonyl at room temperature[27]. Similarly acetylene, or any acetylene of the formula RC≡CH, is polymerized by the acetylene-cobalt carbonyl complex (XVII) at room temperature; complexes derived from acetylenes with no hydrogen atom (RC≡CR) do not catalyze these polymerizations[79].

While the intimate mechanism of the hydroformylation reaction waits further study, the course of the reaction and the nature of the intermediates seem fairly well defined. The concept that a carbonyl-olefin complex such as (XVI) is the only immediate source of hydrogen and carbon monoxide and that the transfer of hydrogen and carbon monoxide to the olefin takes place within this complex is an aid in our understanding of the nature and the role of intermediates in catalytic reactions.

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CHAPTER 3

DIRECT CATALYTIC SYNTHESIS OF HIGHER ALCOHOLS FROM CARBON MONOXIDE AND HYDROGEN

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INTRODUCTION

In Volume III Chapter 8 of this treatise the catalytic synthesis of higher alcohols from CO and H_2 with the use of modified methanol catalysts was not considered, although ordinarily this synthesis of higher alcohols is believed to be closely related to that of methanol. However, the difference in the mechanisms of the two reactions and the existence of several other processes for the synthesis of higher alcohols justify a separate treatment.

The problem of obtaining higher alcohols by a catalytic process has been approached by many authors from a number of different angles. The synthesis has been performed by several methods. This, and the lack in the literature, of a sufficient number of detailed research results which could have served as a basis for the clarification and the understanding of this matter, make it very difficult to review this field. The authors of this chapter have attempted a systematic treatment of the subject but wish to point out that the scarcity of experimental work has made it almost impossible to present a unified picture of the problems involved in the catalytic synthesis of higher alcohols.

The various processes for obtaining higher alcohols from CO and H_2 may be schematically divided into three groups:

(1) Synthesis by processes and catalysts derived from those used in the synthesis of hydrocarbons (Fischer-Tropsch, Synthol, isosynthesis, Synol).

(2) Synthesis with modified methanol catalysts.

(3) Synthesis from CO, H_2 and olefins (oxosynthesis).

The processes belonging to the first group are closely connected with the Fischer-Tropsch process and with isosynthesis. This is clear particularly if the types of catalysts used, the reaction pressures, and the supposed reaction mechanisms are considered. It is obvious that a detailed discussion of higher alcohol synthesis by these processes cannot be separated from that of the synthesis of hydrocarbons from CO and H_2. The authors are therefore referring the reader to the various chapters on Fischer-Tropsch synthesis and isosynthesis in Volume IV of this series of books on "Catalysis" for related information on the formation of higher alcohols.

The synthesis of higher alcohols in the presence of modified methanol catalysts is a more definite process, which therefore lends itself to a more complete treatment. In particular, this chapter will consider the catalysts containing:

(1) a component which is selective for the synthesis of methyl alcohol;

(2) one or more promoters or activating agents specific for the synthesis of higher alcohols and, possibly,

(3) one or more stabilizing agents, whose presence in the catalyst structure increases the catalyst life.

The oxo synthesis was originated in Germany during World War II as a process for the production of higher alcohols[60]. The first catalysts used were similar to the cobalt-base catalysts commonly employed in the Fischer-Tropsch hydrocarbon synthesis. The process for the production of higher alcohols was practically divided into two consecutive stages, namely, the direct synthesis of aldehydes from CO, H_2 and olefins, and the hydrogenation of the aldehydes to alcohols[60]. Later, with the general use of catalysts composed of cobalt carbonyl compounds, oxosynthesis has been directed toward the production of many classes of organic compounds, and is actually such a fundamental process as to require a separate treatment. For a discussion of the synthesis of higher alcohols by this process, reference should be made to Chapter 2 of this volume.

Among the proposed methods for the synthesis of alcohols from olefins, the Ziegler process has assumed recently a considerable interest. This process[65] is based on the addition of oxygen by metal-alkyl compounds to form alcoholates[59], which react with water to give the corresponding alcohols. Such alkyl-metallic compounds, and particularly alkyl-aluminum, may be prepared through exchange reactions between triethylaluminum or tri-isobutylaluminum and the olefins produced from CO and H_2 with the Fischer-Tropsch process. The alcohols obtainable with this process are different from those obtained through the hydration of olefins in the presence of acid catalysts, because these latter are secondary alcohols, whereas the Ziegler process leads to primary alcohols.

This process for the production of alcohols is closely connected with the other Ziegler-type catalytic processes, and therefore will not be considered in this chapter.

HISTORICAL REVIEW

At the beginning of this century, Sabatier and Senderens published the results of their first experiments on the catalytic synthesis of methane from CO and H_2[49]. Several years later the Badische Anilin und Soda Fabrik patented its process of catalytic hydrogenation of carbon monoxide[1]. While Sabatier and Sanderens had worked with reduced nickel or cobalt oxides as catalysts, the B.A.&S.F. catalysts consisted of alkalized oxides of cobalt or osmium. With these catalysts, in experiments performed at 100 to 200 atm. and 300 to 400°C, a prevailingly liquid product is obtained, which is a mixture of alcohols, aldehydes, ketones, acids and other organic compounds.

While the research work of the B.A.&S.F. was later developed toward the synthesis of methanol, progress in the synthesis of higher alcohols was noticeable in 1923–24 when Fischer and Tropsch developed their "Synthol" process[13, 14, 15, 16]. The reaction between CO and H_2 was performed at pressures ranging from 100 to 150 atm. and at temperatures of 400 to 450°C, in the presence of an alkalized iron oxide catalyst. The product was a mixture of alcohols, aldehydes, ketones, acids and other compounds.

These early results disclosed the wide field of the different organic syntheses from CO and H_2. This subject was later developed along three distinct lines, namely, the synthesis of hydrocarbons, the synthesis of alcohols, and oxo synthesis.

The scientific and industrial importance of this matter was so clearly appreciated that in many laboratories experimental research on the subject was undertaken. Some interesting results have, accordingly, been achieved in the interpretation of the reaction mechanisms and in the understanding of this type of heterogeneous catalysis. The industrial development of the synthesis, however, initially proceeded rather slowly; significant progress could be achieved from the industrial point of view only after the solution of the many difficulties involved, such as the separation of the reaction products, and above all the preparation of highly selective and durable catalysts.

The discovery of the ZnO and Cr_2O_3 base catalysts represents a decisive step in the selective synthesis of alcohols from CO and H_2. The first high yields in the synthesis of methanol from CO and H_2 were obtained at relatively high pressures in the presence of catalysts of this type[2]. It was soon learned that these catalysts, when modified through the addition of salts or oxides of alkaline metals, brought about the formation of liquid end-products, consisting mainly of aliphatic alcohols[8, 17, 18, 30]. From this point on, the industrial synthesis of higher alcohols from CO and H_2 and that of methanol have followed two different paths, with the latter assuming a more important position than the synthesis of higher alcohols.

The direct synthesis of higher alcohols assumed considerable importance in Europe in the period 1935–1945. In fact, while with the more frequently used process of olefin hydration only secondary alcohols are obtained, the direct synthesis from CO and H_2 gives a mixture of primary alcohols, most of which are of the non-linear type. Primary isobutylalcohol, which is the main product of the synthesis, has been used in Germany for the production of pure isobutylene, which in turn is an interesting intermediate of the syntheses of isooctane and of *Oppanol* elastomers[60].

Recently, the extensive development of oxo synthesis has brought to the front the industrial synthesis of alcohols through the hydrogenation of aldehydes. The direct catalytic synthesis of alcohols from CO and H_2 has thus lost much of its original interest. A reason for this is to be found in the fact that, while the products of the reaction of oxo synthesis from olefinic hydrocarbons are mainly the isomeric aldehydes containing one carbon atom more than the original hydrocarbon, the synthesis of alcohols from CO and H_2 leads to complex mixtures of alcohols and it is very difficult to direct the reaction toward the formation of a few special end-products. Therefore it may be concluded that the high cost of the separation and purification processes has been responsible for the slowness of the industrial development of the direct synthesis of higher alcohols from CO and H_2, after the development of oxo synthesis. Nevertheless in the last part of World War II and in the years which followed, the I.G. Farbenindustrie and the Ruhrchemie in Germany succeeded in the realization of the "Synol" process[63], which substantially represents a last stage in the evolution of the synthesis of primary linear higher alcohols from CO and H_2[60]. However, it must be pointed out that the low pressures of synthesis and the type of catalysts used for the synol process place it closer to the Fischer-Tropsch hydrocarbon synthesis than to the classical high pressure synthesis of alcohols from CO and H_2 with zinc or chromium-base catalysts.

THERMODYNAMIC CONSIDERATIONS

The following over-all reactions may be considered, which lead to the formation of alcohols starting from CO and H_2:

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n - 1)H_2O \qquad (1)$$

$$(n + 1)H_2 + (2n - 1)CO = C_nH_{2n+1}OH + (n - 1)CO_2 \qquad (2)$$

The free energy variation of Eq. (1) in the temperature range of 600 to 1500°K may be calculated from the following equation:

$$\Delta G_1^\circ = -38.386n + 11.098 + \frac{(5.982n - 0.144)}{100} T \text{ Kcal/mole} \qquad (3)$$

In Figure 1 the values of $\Delta G^\circ/n$ are reported as functions of the absolute

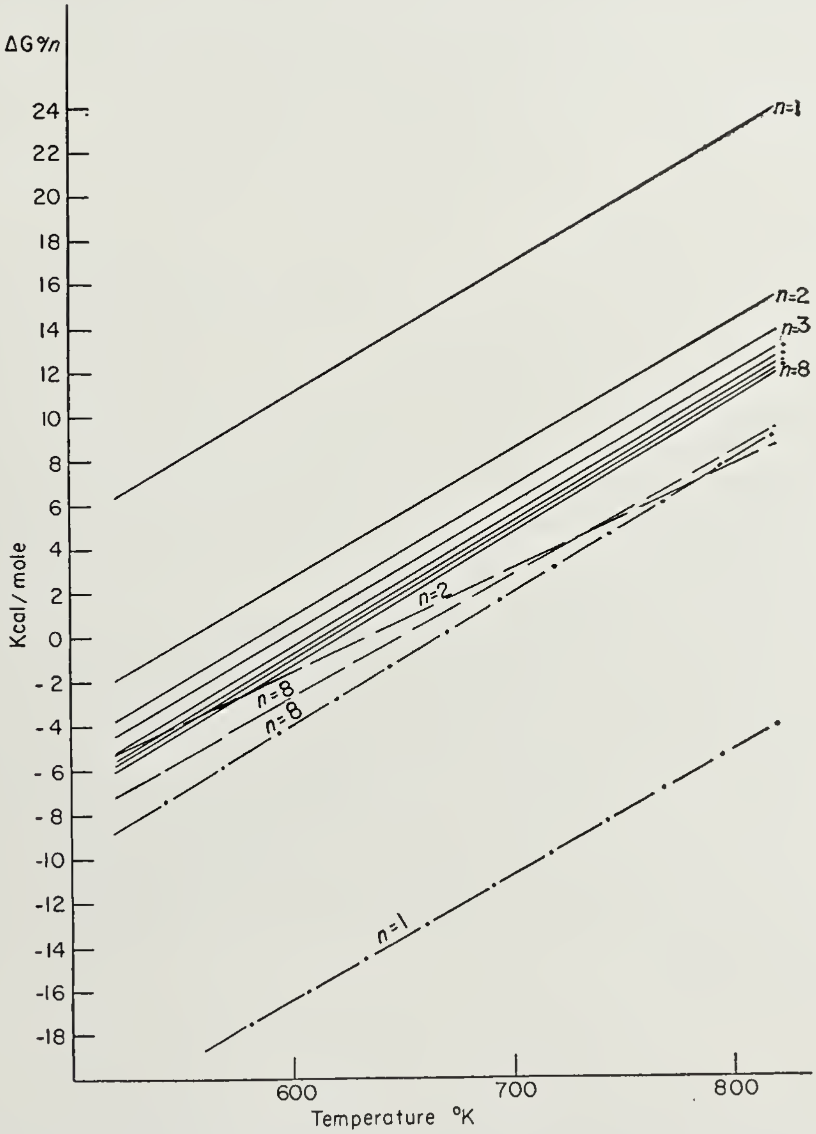

Figure 1. Free energy variation with temperature for the synthesis of alcohols, αn-olefins, and n-paraffins from hydrogen and carbon monoxide.

———— reactions leading to alcohols $n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}$
— — — — " " " αn olefins $n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
— · — · — " " " n paraffins $n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$

temperature, for several fixed values of n. The calculation of such values for $n > 1$, has been made according to the group contributions method, using the values reported by van Krevelen and Chermin[61]. The results which are generally obtained with this method are accurate within ±0.6 Kcal/mole. The degree of accuracy in our specific reactions is certainly much higher.

The free energy variations for reaction (2) may be readily calculated from Eq. (3), adding to the ΔG° of reaction (1), for any given value of n, the ΔG° of the conversion reaction (4), multiplied by $(n - 1)$:

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

$$\Delta G^\circ_{(4)} = -8.514 + 0.771T \times 10^{-2} \text{ Kcal/mole}$$

for $600°K < T < 1500°K$.

Since the free energy of reaction (4) is negative in the temperature range of the higher alcohols synthesis, reaction (2) is thermodynamically favored with respect to reaction (1) (Figure 2).

It may be deduced from the curves of Figures 1 and 2 that at a given temperature the stability of higher alcohols increases with the number of carbon atoms in their molecules. From the above reported data it may be calculated that the temperatures at which the free energies are zero, range respectively from 555 to 620°K for reaction (1), and from 590 to 700°K for reaction (2) for each value of n higher than 1.

With alkalized methanol catalysts the synthesis of higher alcohols occurs generally at temperatures above 400°C. It is therefore necessary in view of the considerable volume contractions of reactions (1) and (2) to operate the synthesis under high pressure.

Such simple considerations are obviously not sufficient to justify the experimental conditions under which the synthesis of higher alcohols is performed. In fact, several possible reactions between CO and H_2, competitive to the synthesis of higher alcohols, have lower ΔG° values in the temperature range of interest. This is particularly true for the Fischer-Tropsch synthesis:

$$2nH_2 + nCO = C_nH_{2n} + nH_2O \tag{5}$$

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O \tag{6}$$

In fact, from the data given by van Krevelen and Chermin, the following formula may be deduced in the case of reaction (5) leading to α-n-olefins:

$$\frac{\Delta G^\circ_{(5)}}{n} - \frac{\Delta G^\circ_{(1)}}{n} \text{ Kcal/mole} = \frac{6.547}{n} - \frac{3.290}{n} \text{T}.10^{-2}$$

This difference becomes zero for T = 200°K, while for temperatures above 200°K, $-\Delta G^\circ_{(5)}/n$ is higher than $-\Delta G^\circ_{(1)}/n$.

Similarly, it may be calculated, for reaction (6) leading to n-paraffins:

$$\frac{\Delta G^\circ_{(6)}}{n} - \frac{\Delta G^\circ_{(1)}}{n} = \frac{24.06}{n} + \frac{0.03}{n}\,T.10^{-2}$$

These considerations are sufficient to make necessary the use of highly selective catalysts in the synthesis of higher alcohols.

It should be pointed out that reactions (1) and (2), which lead to higher alcohols, occur with volume contractions which are slightly higher than

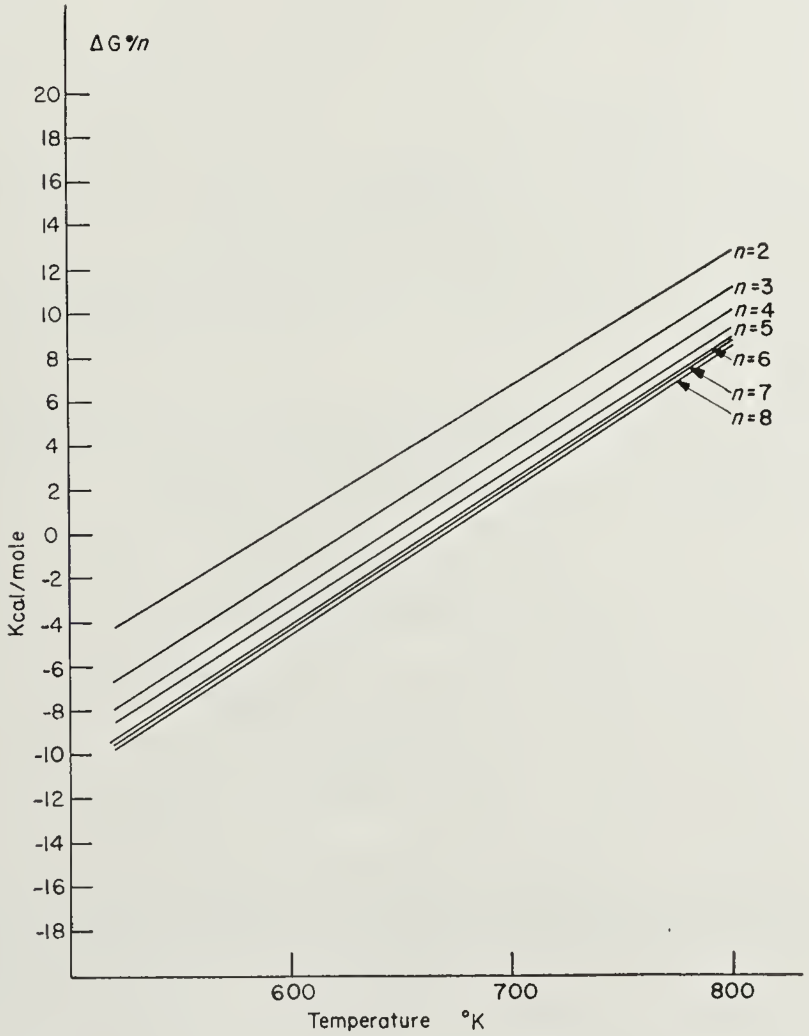

Figure 2. Variation with temperature of $\frac{\Delta G^0}{n}$ for the reaction

$(n + 1)H_2 + (2n - 1)CO \rightarrow C_nH_{2n+1}OH + (n - 1)CO_2$

those of reaction (5) and (6), leading to hydrocarbons. In fact the volume contraction for reactions (1) and (2), expressed as volume ratio between the reactants and products, is equal to 3, while those of reactions (5) and (6) are respectively equal to $3n/(n + 1)$ and $(3n + 1)/(n + 1)$, which are both lower than 3.

As will be shown in the following paragraph, the various processes for the synthesis of higher alcohols lead to the exclusive formation of certain types of alcohols with linear or branched structures. Not even in this respect may any conclusion from general thermodynamic considerations be drawn. It is, in fact, known that the variations of standard free energy for a typical isomerization reaction (7) have very low values:

$$CH_3 - (CH_2)_{n-2}\text{—}CH_2OH = (CH_3)_2CH\text{—}(CH_2)_{n-4} - CH_2OH \quad (7)$$

$$\Delta G^\circ_{(7)} = -1.355 + 0.258 . T . 10^{-2} \,*$$

The ΔG° of reaction (7) assume the following values: $T = 525°K$, $\Delta G^\circ = 0$; $T = 600°K$, $\Delta G^\circ = +0.195$; $T = 700°K$, $\Delta G^\circ = +0.455$; $T = 800°K$, $\Delta G^\circ = +0.705$ Kcal/mole.

The low value of the slope $d(\Delta G^\circ)/dT$ for reaction (7) prevents one from calculating with sufficient precision the temperature at which one isomer becomes stable with respect to another, until very accurate data become available.

As far as the other possible reactions are concerned between CO, H_2 and their reaction products, we shall consider in this paragraph only those that will be involved in the reaction mechanisms proposed†.

$$CH_3OH + CO \rightarrow CH_3COOH \quad (8)$$

$$\Delta G^\circ_{(8)} = -33.23 + 3.69 . T . 10^{-2}$$

$$CH_3OH + CH_3OH \rightarrow C_2H_5OH + H_2O \quad (9)$$

$$\Delta G^\circ_{(9)} = -16.18 - 0.014 . T . 10^{-2}$$

$$CH_2O + CH_2O \rightarrow CH_2(OH) - CHO \quad (10)$$

$$\Delta G^\circ_{(10)} = -16.88 + 2.95 . T . 10^{-2}$$

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* This formula is approximate. In this respect it is sufficient to point out that such a formula may be applied to any isomerization reaction of the following type:

$$CH_3\text{—}CH_2\text{—}CH_2\text{—}\ldots\text{—}CH_2\text{—}X \rightarrow CH_3\text{—}CH_2\text{—}\ldots\text{—}CH(CH_3)\text{—}\ldots\text{—}CH_2\text{—}X$$

or also:

$$CH_3\text{—}CH_2\text{—}CH_2\text{—}\ldots\text{—}CH_2\text{—}X \rightarrow CH_3\text{—}CH_2\text{—}\ldots\text{—}CH(X)\text{—}\ldots CH_2\text{—}CH_3$$

† The ΔG° values for methanol have been calculated from references 25, 51, and 66.

$$CH_3(CH_2)_{n-2} - CHO + H_2 \rightarrow CH_3(CH_2)_{n-2} - CH_2OH \qquad (11)$$

$$\Delta G^\circ_{(11)} = -17.24 + 2.99.T.10^{-2}$$

In Figure 3 the values of ΔG° for these various reactions are plotted as a function of absolute temperature.

In the temperature range 600 to 800°K the reaction free energies are negative for reactions (8) and (9), and slightly positive for reactions (10) and (11). However, since the latter reactions occur with volume contractions, these too may be considered as possible when operations are carried out at high pressure.

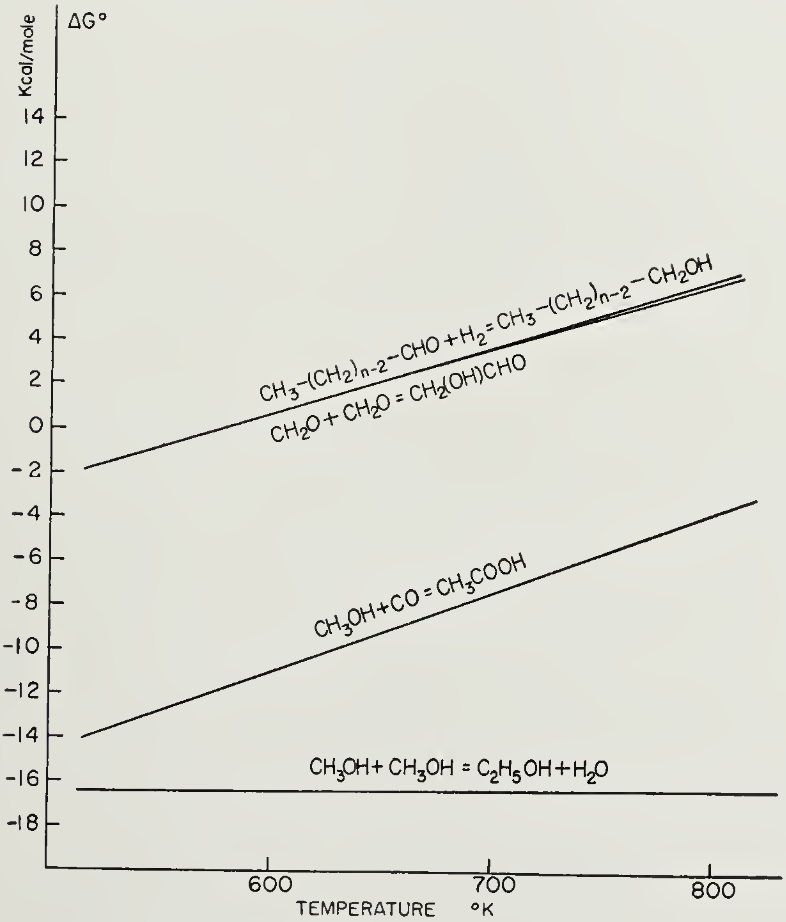

Figure 3. Variation with temperature of ΔG^0 for some reactions involved with or competitive to the synthesis of higher alcohols.

As a conclusion, it may be stated that both the nature and distribution of products obtained in the synthesis of higher alcohols depend mainly upon the particular characteristics of the catalysts employed and upon kinetic factors. Therefore, these general thermodynamic considerations are not sufficient to establish the possible steps of this synthesis.

REMARKS ON THE CATALYTIC SYNTHESIS OF HIGHER ALCOHOLS FROM CO AND H_2

When the synthesis of methanol from CO and H_2 is performed with a normal selective catalyst, the formation of low quantities of higher alcohol may be noticed. The concentration of these higher alcohols varies according to the type of catalyst used and to the physicochemical conditions under which the reaction is operated. Means for inhibiting the formation of higher alcohols include the use of very pure ZnO catalysts (as, for example, ZnO from zinc acetate obtained by solution of pure Zn in acetic acid) and operation at low temperatures and high space velocities. Under such conditions the formation of higher alcohols is negligible[40]. If, instead, the catalyst is prepared by precipitation with alkali of zinc hydroxide or of basic zinc and chromium carbonates, the formation of much higher quantities of higher alcohols is noticed. This is probably to be attributed to the promoting action of the traces of alkaline ions adsorbed on the surface of the catalyst and not entirely eliminated in the filtration and in the washing of the precipitates[54].

Another way of enhancing the formation of higher alcohols is the use of substantial amounts of strongly basic substances. If, for example, ZnO is treated with a solution of potassium dichromate, a catalyst is obtained after reduction of chromium to Cr^{+++} containing potassium zincate and potassium chromite which promote the synthesis of higher alcohols[33].

A considerable production of higher alcohols is obtained as a rule when a catalyst selective for the synthesis of methanol is activated with a promoter containing cations of strongly basic character. Also, the alkalization of certain catalysts originally non-selective for the synthesis of methanol leads to the formation of higher alcohols from CO and H_2. This is shown in the synthesis of higher alcohols with alkalized iron or iron oxide catalysts, which are initially selective for the synthesis of hydrocarbons[52]. In the synthesis of hydrocarbons with the Fischer-Tropsch process, during operations at temperatures over 200°C and at high or medium pressures with iron-base catalysts, small amounts of oxygenated compounds, including higher alcohols, are obtained[52].

The formation of higher alcohols, mainly of the branched type, is observed when the high-pressure synthesis of hydrocarbons is performed at relatively low temperatures with thorium oxide-base catalysts (isosynthesis)[43, 44]. More recently the Badische Anilin and Soda Fabrick has introduced the use of a catalyst consisting of a mixture of alkalized titanium and zirconium oxides[3]. With this latter catalyst a liquid reaction product is obtained, containing 20 to 25 per cent isobutyl alcohol together with other higher alcohols. Other types of catalysts employed in the synthesis of higher alcohols from CO and H_2 will be considered in the following paragraphs.

The mechanism of the synthesis of higher alcohols appears to be extremely complicated, and possibly connected with a series of reactions consecutive to the synthesis of methanol. This side of the synthesis will be discussed in detail in the course of this chapter.

Effect of the Nature of Promoters

From the consideration of the data available in the literature, concerning the influence of the alkaline promoters upon the activity of the catalysts used for the synthesis of higher alcohols, it may be concluded that the relative influence of the various promoters is practically independent of the type of the catalysts used. The activating character of such promoters appears to be rather a function of their basicity*. This behavior is shown particularly by the cations of the metals belonging to the first semigroup of group 1 of the periodic system; their promoting activity is closely related with their basicity, which increases with an increase in the atomic weight.

Fischer and Tropsch[10, 11, 14] were probably the first authors who pointed out that the yield of higher alcohols in the synthesis from CO and H_2, performed with alkali-activated iron-base catalysts, increases with the basic character of the promoters. In the following years Natta and Strada[31] obtained similar results in the higher alcohols synthesis with ZnO-base catalysts, and found that the highest yields of alcohols were obtained by the use of catalysts containing potassium, rubidium or cesium ions[32]. A few years later Morgan and his co-workers performed a systematic investigation of the quantitative influence of the addition of five different alkali ions to a chromium oxide-manganese oxide catalyst employed in the synthesis of alcohols[28]. The results obtained by these workers are shown in Table 1. It may be observed that the presence of Li^+, Na^+ or K^+ (added as hydroxides) leads to a decrease of the over-all reaction yield (expressed as per cent of converted gas in each passage through the catalyst), whereas this is not observed when Rb^+ or Cs^+ are present.

A consideration of the content, in the reaction product, of compounds insoluble in $CaCl_2$ solutions indicates that the concentration of higher alcohols, in the liquid end products, increases with the addition of alkaline promoters in the order: Li, Na, K, Rb, Cs. The best catalyst among those tested by Morgan and his co-workers contains 9.8 per cent Rb^+. A further increase in the rubidium content of this catalyst does not appear to bring a substantial variation of the yield. These results were confirmed later by Taylor[58], who worked with a Cr_2O_3-MnO catalyst, and found that the best yields in higher alcohols were obtained when the catalyst was pretreated with RbOH.

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* It is therefore obvious that the cations used as promoters should not be easily reducible to metals, because such reduction would destroy their basic character.

Table 2 shows some recent interesting results obtained by Runge and Zepf, who studied the effects of alkaline promoters upon the performance of a ZnO-Cr_2O_3 catalyst[48]. The data reported in Table 2 were obtained, with each catalyst under the best tested conditions of pressure and temperature. According to these authors, the sodium-activated catalyst appears to be slightly superior to that containing potassium. This apparent discordance with the above mentioned alkalinity rule is probably to be related to the higher water content in the product obtained with the sodium activated catalyst.

TABLE 1. INFLUENCE OF THE ADDITION OF ALKALI IONS UPON THE PERFORMANCE OF A CHROMIUM OXIDE-MANGANESE OXIDE CATALYST[28]

Alkali added as oxide	Weight per cent of added alkali	Per cent gas conversion at each passage through catalyst	Over-all conversion yield (g/h)	Methanol in reaction product (%)	Per cent carbon converted into compounds other than MeOH	Amount of carbon in compounds other than MeOH (g%)	Volume percentage of material insoluble in $CaCl_2$ soln. (cc/100 g)	Yield material insoluble in $CaCl_2$ soln. (cc/h)
—	—	3.5	6.2	80.5	2.8	13.0	0.3	0.2
Li	3.4	2.7	47	76.9	3.8	21.7	3.55	1.7
	6.7	2.6	45	73.7	3.2	20.3	6.26	2.8
	10.1	2.3	40	71.7	3.6	24.9	4.42	1.8
Na	2.8	2.4	43	63.9	5.0	32.9	12.8	5.5
	6.3	1.2	21	55.0	2.6	37.9	14.4	3.0
	9.8	1.0	17	50.1	2.1	39.4	14.05	2.4
K	1.5	2.7	47	81.8	2.8	16.4	0.63	0.3
	3.9	2.2	39	60.8	5.5	38.4	12.80	5
	4.9	1.9	33	50.7	5.9	48.6	21.50	7.1
	5.7	1.6	29	53.0	4.3	42.9	18.60	5.4
	8.4	1.4	24	52.2	3.6	43.4	17.50	4.2
	11.9	1.5	27	49.0	4.3	46.3	23.00	6.2
Rb	2.3	3.4	61	75.5	5.2	23.1	4.65	2.8
	4.4	3.5	62	67.2	7.7	33.1	17.8	8.8
	9.8	3.0	53	49.7	8.4	46.0	28.7	15.2
Cs	1.8	3.5	62	79.5	3.6	16.2	1.53	1.0
	3.8	3.0	53	82.1	3.8	18.8	1.58	0.8
	8.9	3.3	58	63.7	8.3	37.5	16.4	9.5

As has already been pointed out, the various investigators who studied this field agree substantially in concluding that the most active promoters for the production of higher alcohols are Cs^+, Rb^+, K^+. From a practical point of view, the high cost of rubidium and cesium has prevented their employment in the industrial processes: therefore almost all the catalysts used for the industrial synthesis of higher alcohols from CO and H_2 contain potassium.

A generalization of the basicity rule could lead to useful conclusions concerning the possible employment of other metals as promoters for the higher alcohol synthesis. In these reactions for which dry catalysts are used, it is preferable to refer the basic strength to the dissociation heat of

TABLE 2. EFFECT OF ALKALINE PROMOTERS UPON THE PERFORMANCE OF A ZnO-Cr_2O_3 CATALYST EMPLOYED IN THE SYNTHESIS OF ALCOHOLS[48]

Fractions Obtained in the Distillation of Product**	Catalyst activated with*				
	Li	Na	K	Rb	Cs
Tops CH_3OH C_2	$\left.\begin{matrix}0.9\\40.4\\4.6\end{matrix}\right\}45.9$	$\left.\begin{matrix}0.6\\44.6\\4.6\end{matrix}\right\}49.8$	$\left.\begin{matrix}0.4\\53.5\\3.5\end{matrix}\right\}57.4$	$\left.\begin{matrix}0.5\\46.6\\3.8\end{matrix}\right\}50.9$	$\left.\begin{matrix}0.8\\47.4\\4.0\end{matrix}\right\}52.2$
C_3	0.5	0.9	0.8	1.6	1.0
Isobutylalcohol (primary)	8.1	12.5	10.3	15.2	15.6
C_5 (amyl alcohols)	0.6	0.9	1.1	1.7	1.3
Intermediates C_6 C_7 Residue	$\left.\begin{matrix}0.3\\0.5\\0.8\\0.5\end{matrix}\right\}2.1$	$\left.\begin{matrix}0.5\\1.2\\1.3\\2.5\end{matrix}\right\}5.5$	$\left.\begin{matrix}0.9\\1.0\\1.2\\2.3\end{matrix}\right\}5.4$	$\left.\begin{matrix}1.6\\1.3\\2.3\\4.1\end{matrix}\right\}9.3$	$\left.\begin{matrix}1.1\\1.6\\2.0\\4.5\end{matrix}\right\}9.2$
Intermediates 2,4 + distillation loss	1.7	1.7	1.7	2.5	2.4
H_2O	41.1	28.7	23.3	18.8	18.3
Yield, expressed in liters per hour per liter of catalyst	0.585	0.985	0.882	0.980	1.102

* The compositions of the catalysts, expressed in weight percentages, before the reduction of CrO_3 to Cr_2O_3, were the following:

$ZnO:CrO_3:Li_2O = 55.0:36.1:0.32$
$ZnO:CrO_3:Na_2O = 56.1:34.1:0.59$
$ZnO:CrO_3:K_2O = 55.5:35.6:0.96$
$ZnO:CrO_3:Rb_2O = 55.0:35.5:1.90$
$ZnO:CrO_3:Cs_2O = 54.5:33.7:2.20$

As it may be noticed, the alkali contents are equal in all catalysts, if measured in moles.

** The concentrations of reaction products are expressed in weight per cent.

the carbonates into CO_2 + oxides. This criterion is justified considering that in the conditions of the synthesis of higher alcohols, uncombined hydroxides are certainly not present in the catalysts. In Table 3 the ionization potentials of the corresponding metals are also indicated. These values are closely related with the reducibilities of the oxides.

A more complete and correct comparison of the activities of catalysts activated with the different promoters should take into consideration the differences in reducibility of metal oxides and their selectivities for the various reactions (dehydrogenation, dehydration, hydrocarbon synthesis, etc.). However, if only the alkaline and alkaline earth metals are considered, their promoting activity for the synthesis of higher alcohols may be considered as closely connected with their basic strength. The low basic strength of ZnO and Cr_2O_3 is probably the cause of the almost complete absence of higher alcohols in the synthesis of methanol with ZnO or ZnO-Cr_2O_3 base catalysts free from alkali. It can be assumed that chromium oxide, Cr_2O_3, presents a lower basic strength than ZnO, since the neutral chromium carbonate, $Cr_2(CO_3)_3$, is not known. The other metal oxides listed in Table 3 exert a relatively favorable influence for the formation of higher alcohols. From a qualitative point of view, this influence seems to depend upon their basic strength. This assumption is corroborated by the conclusion of Strada[53, 54] that magnesium oxide is a more effective promoter for a zinc-oxide catalyst than manganese oxide.

TABLE 3

Metals	Ionization Potentials (Electron-Volts)*	Carbonates	Dissociation Heat (Kcal/mole)
Li	5.36	Li_2CO_3	54.1
Na	5.12	Na_2CO_3	76.9
K	4.32	K_2CO_3	93.5
Rb	4.16	Rb_2CO_3	96.7
Cs	3.87	Cs_2CO_3	99.5
Mg	7.61	$MgCO_3$	29.0
Ca	6.09	$CaCO_3$	42.5
Ba	5.19	$BaCO_3$	63.9
Cu	7.68	$CuCO_3$	11.1
Zn	9.36	$ZnCO_3$	17.1
Mn	7.41	$MnCO_3$	27.9
Fe	7.83	$FeCO_3$	21.0
Co	7.81	$CoCO_3$	21.5
Cr	6.74	—	—

* The ionization potential values were taken from the book "Spectrochemical Procedures" by C. E. Harvey (A. R. L. Glendale, Calif. 1953)—The values of dissociation heats were taken from reference 47.

A differentiation of the various promoters according to their basic strength does not appear to be valid for certain catalysts of slightly basic character which, however, favor the formation of higher alcohols without the aid of alkaline promoters. A striking example of this kind of catalyst is offered by thorium oxide, the well known catalyst of isosynthesis[43, 44, 45]. The basic strength of ThO_2 is very low: the corresponding neutral carbonate is not stable and only the acid carbonate is known[20]. It may be convenient to note at this point that the activating influence of alkaline metals in the synthesis of higher alcohols is probably associated with an analogous promoting action upon the conversion of water gas[19]:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 .$$

Activated zinc oxide (particularly if obtained by decomposition of the neutral zinc carbonate, smithsonite) can also be considered a catalyst for the conversion of water gas. However, its activity for this reaction grows when it is pretreated with alkali (particularly with K_2CO_3)[35].

From the data given by Morgan and his co-workers[28] with an alkali-activated Cr_2O_3-MnO catalyst, it may be concluded that the yield in higher alcohols increases, up to a certain limit, with the amount of alkali present in the catalyst. This is particularly true with a rubidium or cesium-activated catalyst. The results of Morgan and co-workers were substantially confirmed by other authors who tested different catalysts. For example, the already mentioned catalysts tested by Natta and Strada show yields of higher alcohols increasing with the content of the alkali acting as promoter.

Frolich and Lewis[18], working with potassium-activated chromium steel catalysts, have reached conclusions in disagreement with those of the above mentioned authors. In Figure 4 the production curves obtained by Frolich and Lewis are reported as functions of the K_2O content in the catalysts. It may be seen that the yields of higher alcohols present a minimum for a K_2O content of 5 per cent, and that the best yields are obtained with catalysts containing small amounts of K_2O. The apparent singularity in the behavior of these catalysts may be considered as due to differences of constitution and probably differences in the mechanisms of the reactions.

In conclusion, it has to be pointed out that the method of preparation of the catalysts appears to be very important for their evaluation in the synthesis of alcohols. Therefore the results obtained by different investigators cannot be strictly correlated. This limitation has to be kept in mind when, for example, the relatively high yields of higher alcohols obtained by Runge and Zepf[48] with ZnO-Cr_2O_3 catalysts containing small amounts of alkali oxides are considered.

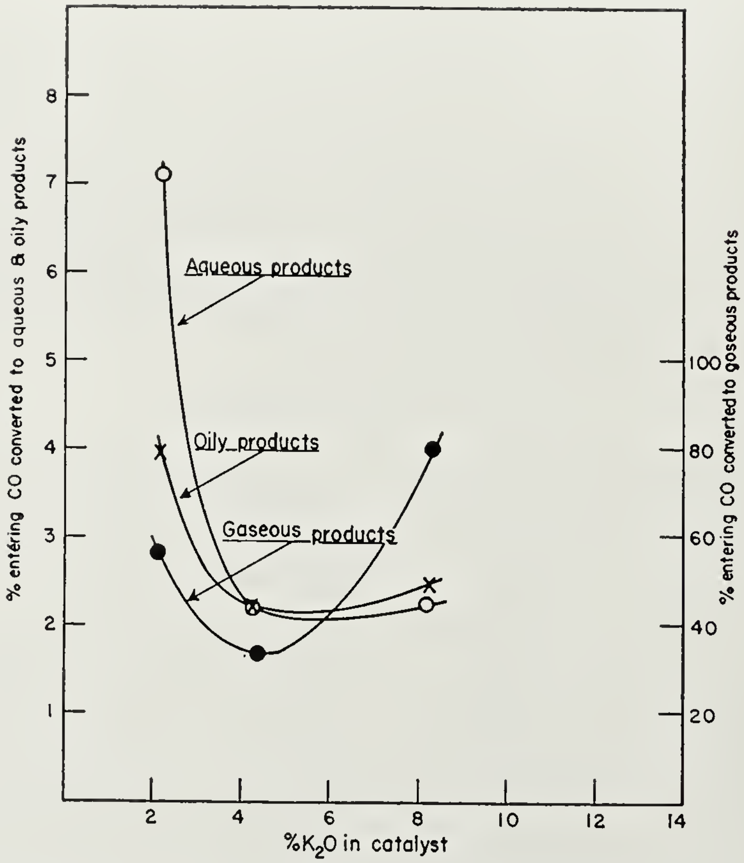

Figure 4. Influence of the amount of promoter (K_2O) present in a catalyst upon the yields in gaseous, aqueous, and oily products (From Ref. 18).
Catalyst = chromium steel turnings
Temperature of synthesis: 330°C
Pressure of synthesis: 254 atm.
Gas composition: $CO/H_2 = 40:60$
Space velocity: 400–2000

REVIEW OF THE CATALYSTS PROPOSED FOR THE SYNTHESIS OF HIGHER ALCOHOLS

The data available in the literature are indeed very scarce. Furthermore, it has to be pointed out that all the experiments reported in the literature, and particularly those published before 1950, were performed in apparatus in which probably a good constancy of the temperature in all the parts of the catalyst was not obtainable because of the difficulty of obtaining isothermal conditions for highly exothermic reactions operated under pressure. As may be seen from the work of Natta and co-workers[38] a constancy of temperature (within 2°C) along all the catalyst is obtainable only with relatively limited space velocities and with very low ratios of catalyst volume to the area of the surface of the surrounding thermostat walls.

ZnO-Base Catalysts with Alkaline Promoters

Pure zinc oxide, with the addition of only alkaline compounds, is not suitable for the preparation of durable catalysts for the synthesis of higher alcohols. The reasons for this are quite obvious when one bears in mind what is already known on the aging of ZnO employed for methanol synthesis[40]. This oxide, however, being a base for most of the catalysts used in alcohol synthesis, has a paramount importance in this field.

Natta and Strada[33], examining some ZnO catalysts, found that those obtained from calcined smithsonite* were very active catalysts, both in the synthesis of methyl alcohol and higher alcohols. Calcined iron-free smithsonite, when operating at high pressures and at temperatures not exceeding 380 to 390°C, on mixtures of CO and H_2, produces by itself only MeOH. If, however, the synthesis is operated at temperatures over 400°C, this catalyst also produces small amounts of water and of methyl ether, resulting from the dehydration of methanol. When the reaction is performed in the same experimental conditions, but at slightly higher temperature ($t =$ 390 to 420°C), after the catalyst has been impregnated either with alkali hydroxide or with other salts of alkaline metals, a mixture of alcohol is obtained. Impregnation of the catalyst is carried out very easily by soaking the calcined smithsonite, whose porosity is very high, with a solution of the alkaline salt.

As already stated, Natta and Strada[33, 53] have studied the activity of zinc oxide from smithsonite, impregnated with variable amounts of some potassium salts (Figure 5). From the careful examination of the products obtained with the use of such catalysts, these authors concluded that the average composition of the reaction product after the first few hours of performance does not substantially depend upon the kind of tested anion combined to the alkali metal (hydroxide, carbonate, organic salts). Operation with such a catalyst at 400°C, 250 atm. with a $CO:H_2$ ratio of 1:2 yielded a raw product with about 20 per cent of higher alcohols, the principal component of which was isobutanol.

ZnO and Cr_2O_3 Base Catalysts with Alkaline Promoters

In this group may be found the catalysts which have been mostly applied not only for the synthesis of methanol from CO and H_2 but also for the synthesis of higher alcohols. Frolich and Lewis[18] studied several catalysts, composed of oxides of the following elements: Cr-K; Fe-Cr-K; Zn-Cr-K, Ba-Cu. These authors noticed that the best results are obtained with Zn-Cr-K catalysts; in particular they have found that the best yields of higher alcohols were obtained with a catalyst prepared by reduction of a

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* Smithsonite is neutral $ZnCO_3$ mineral, containing other divalent metal oxides as impurities in solid solution.

mixture of zinc oxide, ammonium dichromate, and potassium carbonate. Operating with such a catalyst at 490°C, 240 atm. with a space velocity of 2000, they reported obtaining a raw product having the following volume composition: methanol 17.8%, ethanol 2.3%, propionic alcohols 33.4%, butyl alcohols 2.5%, amyl alcohols 9.0%, and water 35.6%. However, owing to the fractionation method used by these authors, the above data should not be considered as completely reliable.

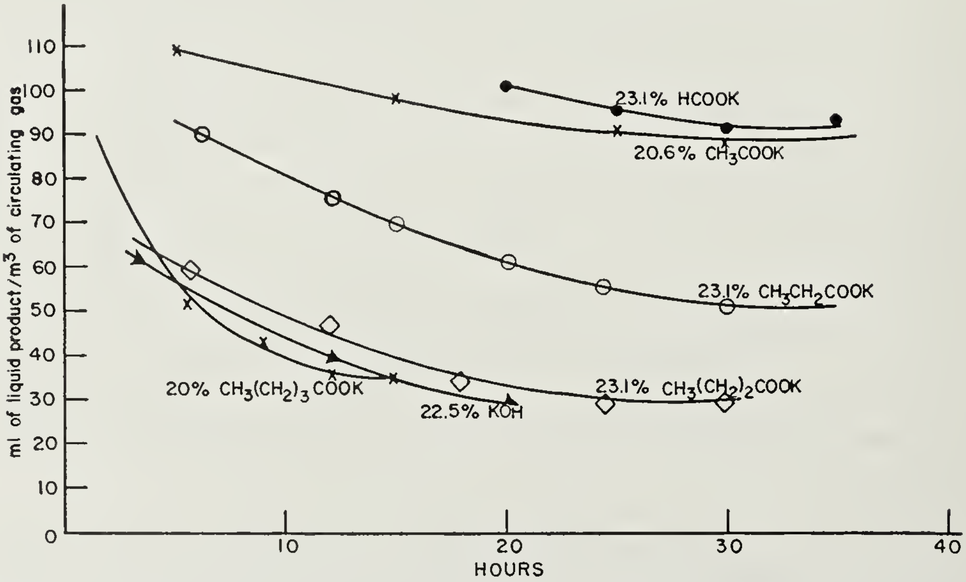


Figure 5. Influence of the anion bonded to the alkaline promoter upon the conversion of carbon monoxide and upon the stability of the catalysts employed in the synthesis of higher alcohols. (From Refs. 33 and 53)

Catalyst: ZnO from calcined smithsonite
Temperature of synthesis: 400°C
Pressure of synthesis: 250 atm.
Gas composition: $CO/H_2 = 1/2.2$

The data obtained by Runge and Zepf[48] who experimented with catalysts impregnated with the different alkaline components, have already been mentioned. The best results (see Table 2) were obtained by these authors in experiments carried out at a temperature of 440 to 445°C, with a pressure of 250 atm. and a space velocity of 20,000. The composition of the input gas was approximately 5:1 H_2:CO.

It is to be noticed that such experimental conditions correspond closely to those which may be deduced from the operating data of an industrial plant set up in Germany by the I.G. Farbenindustrie for the synthesis of isobutanol[60].

Catalysts Containing Oxides of Zinc, Manganese, Chromium Activated with Alkaline Promoters

From the examination of seventeen types of catalysts, Frolich and Cryder[19] noticed that the best performances were given by catalysts obtained through reduction of mixtures of basic carbonates of zinc, chromium, and manganese containing potassium carbonate. The molar composition of such catalysts was as follows:

$$Zn:Mn:Cr = 1.00:1.10:1.03.$$

The activity of such catalysts was very high and uniform even in long tests and the products obtained contained low amounts of acids and aldehydes. The composition of the products obtained varied considerably according to the space velocity of the feed gas. The values for the individual productions of C_1-C_4 alcohols are not reported here because of the very low separating power of the fractionation methods then used.

Catalysts Containing Cu, ZnO, Cr_2O_3 Activated with Alkaline Promoters

The presence of Cu requires, for maintaining the life of the catalyst, that the synthesis be operated at temperatures lower than when ZnO-Cr_2O_2 catalysts are employed. Pospechov[46] has studied a catalyst having the following molar composition: 82% Cu, 16% ZnO, 2% Cr_2O_3. Such a catalyst was prepared through the reduction of a mixture of the hydroxides, obtained by reaction of the nitrates with NaOH. The addition of 0.1 to 5.0 mole per cent of K_2O imparts to the catalyst a very remarkable activity. Pospechov has obtained at a temperature of 200°C and a pressure of 100 atms. with a catalyst of this type activated with 0.1 mole per cent of K_2O a mixture of alcohols containing up to 22.3 per cent by weight of ethanol. It should be pointed out that, contrary to what occurs for the catalysts so far examined, in this case the production of relatively high amounts of ethanol is observed. This result may be connected with the relatively low temperature of synthesis. A similar result is reached with the use of a CuO-MgO (or ZnO) catalyst[9] when employed at temperatures above 100°C and pressures above 10 atm.

Another catalyst of this type, prepared by slowly heating (from 100 to 400°C) an equimolecular mixture of $Zn(OH)_2$, $Cu(OH)_2$ and $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ was reported to be very durable and active for the synthesis of isobutanol[41]. The yield of isobutanol obtained with this catalyst was 30 per cent, while the over-all yield of other higher alcohols was 15 per cent, when it was operated at 400°C and at 150 atm. According to Sueta and Niwa[55] the activity and durability of this catalyst may be considerably improved through the addition of small amounts of CaO.

Catalysts Containing Copper and Oxides (or Salts) of Zinc, Chromium, Manganese, Calcium, Lead, Aluminum, Thorium, etc. Activated with Alkaline Metals

Several types of catalysts were proposed, containing two or more of the above listed metallic oxides. One such catalyst may be prepared by adding CaC_2 to a mixture of ZnO and Cr_2O_3. Such a catalyst was employed by Nagishi[29] who obtained a liquid product containing higher alcohols. The addition of small quantities of ThO_2 increases the yield of butanol up to values over 18 per cent of the total liquid product, without, however, varying the amount of methanol obtained. A catalyst having essentially the same properties may be conveniently prepared by melting a mixture of ZnO and $CaCr_2O_7$[23].

As was previously mentioned, the Cr_2O_3-MnO-base catalysts, which were also proposed by the I.G. Farbenindustrie[24], were particularly studied by Morgan and his co-workers[28]. These authors determined experimentally the influence of the five alkaline metals upon a catalyst of this type. The best results were obtained when the catalyst was activated with 9.8 per cent or more rubidium. In particular, the product obtained with the catalyst containing 15 per cent Rb had the following composition (expressed in percentage, as referred to the initial carbon): 42% methanol; 38% higher alcohols; 15% aldehydes, acetals (and probably ketones); 1% acids; 2% methane; 2% carbon dioxide.

A catalyst containing Cu, Cr, K, whose composition was Cu:Cr:K = 1:4:1.97, examined by Tahara and co-workers[56, 57], who operated at 490°C and 180 atm., with gases having a $CO:H_2$ volume ratio of 1:2 flowing at the rate of 700 l/h over 80 ml of catalyst, was reported to give yields of isobutanol as high as 37 per cent of the total liquid reaction product. This appears to be amazingly high. However, due to the high temperature of synthesis, the catalysts of this type show a poor resistance to aging.

Bocherova, Dolgov and co-workers[4, 5, 6] have studied the influence of the presence, in ZnO-base catalysts, of the oxides of lead, aluminum, vanadium, etc. These authors operated, in general, in the following experimental conditions: temperature, 350 to 450°C; pressure, 150 to 250 atm.; gas composition, $CO:H_2 = 1:1$; space velocity, 5–6000. They operated with the following catalysts:

(1) $4ZnO.PbO$; $PbO.Zn(OH)_2$; $4ZnO.PbO.0.2Zn(OK)_2$; $4ZnO.PbO$ $0.2Zn(OK)_2CdO$

(2) $4ZnO.V_2O_5.KOH$; $8ZnO.V_2O_5.KOH$

(3) $ZnO.Al_2O_3.KOH$

(4) Alkali zincate with the addition of Sb_2O_5 ; V_2O_5 ; $Ca(OH)_2$; MnO_2
(5) $8ZnO.Al(OK)_3.0.1V_2O_5$
(6) $Ca(OH)_2 + KOH$
(7) $8ZnO.Al(OH)_3.0.1V_2O_5.0.1MoO_3.3KOH$.

The catalysts of group (1), containing PbO, have given very low yields of higher alcohols, at all the temperatures tested, as could be predicted from the ease with which the lead oxides reduce.

The alkali vanadates of group (2) have given higher yields than the catalysts of groups (3), (4) and (6), but lower than those of groups (5) and (7). The catalyst $8ZnO.Al(OK)_3.0.1V_2O_5$ has given a production of 225 ml of liquid compounds per cubic meter of gas. The total yield in alcohols is 60 per cent, with a concentration of 35 per cent of higher alcohols in the condensate product, along with 60 per cent of methanol. The condensate was, as usual, present in two strata, one of which was aqueous, the other, oily. Qualitatively the aqueous condensate consisted of MeOH, EtOH, and isopropanol, while the oily condensate contained a mixture of propanol with butanols (mainly with primary isobutanol).

Among the several other catalysts which have been proposed by the various investigators for the synthesis of higher alcohols from CO and H_2, the following should be mentioned:

(1) The catalysts containing ZnO-CuO-K_2O proposed by Patart[42]

(2) A catalyst consisting of equal weights of K_2CO_3, V_2O_5, and CuO, which has yielded at 480°C a product containing 40% MeOH, 25% isobutanol, 20% H_2O, and 15% other higher alcohols and esters[23].

(3) The catalysts containing large amounts of one or more components which act as hydration catalysts rather than as hydrogenation catalysts. An example of this class of catalysts is the catalyst CdO-Cr_2O_3[24].

Catalysts Containing Cobalt

Such catalysts differ from those mentioned above because they contain a metal of the iron group and because of the fundamentally different nature of the products obtained. While the modified methanol catalysts lead mainly to the formation, among the other higher alcohols, of primary isobutanol, the catalysts containing Co give rise to the formation of high amounts of ethanol, even if the synthesis is operated at high temperatures. Taylor[58] was probably the first investigator who observed the formation of substantial amounts of ethanol when using a catalyst containing Cu, Mn and Co. The highest yields in ethyl alcohol (up to 22 per cent with respect to the condensate product) were obtained by Taylor with a catalyst prepared by adding 0.1 g eq. of CoS to a mixture of 1 g eq. CuO + 1 g eq. MnO. The reaction was operated at 40°C and 200 atm. with a space velocity of 200,000.

High yields in ethanol (20 per cent of the total condensate product) were also obtained with the use of a catalyst prepared from $Co(NO_3)_2$, $Zn(MnO_4)_2$ and $KMnO_4$. With this group of catalysts the higher alcohols obtained are prevailingly of the linear type, whereas with modified methanol catalysts they appear to have mainly branched molecules.

Klyukvin and his co-workers[26] have obtained very high yields of ethanol operating with a catalyst composed of $ZnO:CoO = 3:1$. In fact, when the reaction was performed at 320 to 330°C and 120 atm., yields of ethyl alcohol were obtained up to 39 per cent of the condensate products.

TABLE 4. PERFORMANCE OF AN ALKALI-ACTIVATED* ZnO-Cr_2O_3 CATALYST AS A FUNCTION OF TIME

Temperature of synthesis: 400°C
Pressure of synthesis: 400 atm
Space velocity: 29,000
Feed gas composition: $CO = 15$–20%; $H_2 = 52$–60%; $CH_4 = 18$–22%; $CO_2 = 2$–4%

	Total Production (kg per 100 liters catalyst)	Density of Production	Per cent Alcohols in Product	Per cent Acids in Product	Per cent Esters in Product	Per cent Water in Product
1st Day of performance	1630	0.850	78.0	0.4	2.2	18.5
16th " " "	1580	0.855	75.0	0.4	1.8	21.0
31st " " "	1420	0.865	72.6	0.2	1.7	24.0

* The catalyst was impregnated with 12% by weight of potassium acetate.

RESISTANCE OF THE CATALYSTS TO AGING AND POISONS

While the catalysts employed in the industrial synthesis of methanol have a life which may reach one year or more of actual performance, those employed for the synthesis of higher alcohols are not very resistant to aging, and their activity decreases rapidly with time. Natta tested several alkali-activated methanol catalysts for the synthesis of higher alcohols, and noticed that their activity decreased remarkably with time. A typical example of this behavior is given by a ZnO-Cr_2O_3 catalyst activated with 12 per cent by weight of potassium acetate. This catalyst has shown a higher resistance to aging with respect to analogous catalysts activated by different potassium compounds (K_2CO_3 or KOH); however, its activity decreased considerably with working time.

In Table 4 some unpublished data obtained by Natta are given, concerning the performance of a plant which had been designed for the synthesis of methyl alcohol, but which for a certain period was used for the synthesis of higher alcohols. In such experiments the production of methanol was still as high as $\frac{2}{3}$ of the over-all alcohol production. The amount of isobutanol produced was about 50 per cent of the total production of higher alcohols.

The low resistance to aging of certain catalysts which have been employed[56, 57] for the synthesis of higher alcohols in a rather high temperature range has already been pointed out.

Natta and Strada[33, 53] have studied the influence of the type of anion bonded to the promoting alkaline metals upon the resistance to aging of the catalysts for higher alcohol synthesis. These authors have tested in particular a series of ZnO catalysts prepared from calcined smithsonite, activated with different potassium salts, such as KOH, K_2CO_3, HCOOK, CH_3COOK, C_2H_5COOK, C_3H_7COOK, C_4H_9COOK. The experimental results obtained by these authors are reported in Figure 5. It is clear that the resistance to aging is not uniform for the catalysts having different promoters. The catalysts activated with potassium formate or acetate are more durable than those activated with potassium hydroxide or carbonate. We shall consider later on the possible causes for this lower resistance of the catalysts activated with KOH or K_2CO_3. The catalysts activated with either C_2H_5COOK, C_3H_7COOK, C_4H_9COOK show a limited resistance to aging; their durability is lower the longer the carbon atom chain.

TABLE 5. AMOUNTS OF FATTY ACIDS CONTAINED IN HIGHER ALCOHOL CATALYSTS FROM CALCINED SMITHSONITE, REFERRED TO THE CATALYSTS' WEIGHTS.
Working temperature: 400–420°C

Type of Promoter	Per cent Promoter in Catalyst	Carbonic Acid	Formic Acid	Higher Fatty Acids	Nature of Most Abundant Fatty Acids
KOH	17.5	3.34	3.91	4.24	acetic, propionic
K_2CO_3	28.5	6.65	1.92	7.89	acetic, propionic
HCOOK	23.1	5.70	0.51	4.77	acetic, propionic
CH_3COOK	20.6	1.59	2.40	10.90	propionic
C_2H_5COOK	23.1	2.55	0.62	13.05	propionic, butyric
C_3H_7COOK	32.1	4.50	0.31	2.32	butyric, valeric

In general, it may be stated that the low melting points of most of the alkaline salts favor the recrystallization of the ZnO. This appears to be one of the causes of the generally low aging resistance of the higher alcohol catalysts. Another factor which seems to contribute to the low durability of higher alcohol catalysts is the filling of the catalyst pores by high molecular weight reaction products.

Natta and Strada[33] have reported that ZnO catalysts contained, after a normal performance, relatively high amounts of fatty acids. In Table 5 are indicated the amounts of the different fatty acids contained in a series of higher alcohol catalysts prepared from calcined smithsonite impregnated with different potassium salts.

It may be of some interest to point out that Natta and Strada did not notice the presence of fatty acids in catalysts that had operated at 430 to 450°C.

Other authors[12, 50] reported the gradual elimination by thermal decomposition of formic acid from the catalysts activated with alkaline formates.

In catalysts activated with alkaline salts of fatty acids, the formation of fatty acids with higher molecular weights than the starting ones has been noticed. The formation of such acids on the catalyst is probably one of the main reasons for the aging of the catalysts activated with KOH or K_2CO_3. Let us consider for example a typical KOH-activated methanol catalyst. Owing to the reaction

$$ZnO + 2KOH \rightarrow ZnO_2K_2 + H_2O$$

the ZnO at its surface is transformed into potassium zincate. The consecutive formation of the organic potassium salt takes place through the zincate, with the formation of ZnO.

The transformation of K_2O into organic potassium salts is accompanied by a volume increase of about 156 per cent. The organic salts thus formed have, on an average, the molecular weight of the potassium acetate; their formation results in a reduction of the pore volume. The activation of ZnO with K_2CO_3 leads to catalysts which are more active and resistant than those activated with KOH. According to Natta and Strada[33], a similar cause is responsible for the stronger promoter action of the potassium acetate when used as activator for ZnO catalysts.

Several factors may influence this effect: the type of ZnO used, the possible presence of other promoters, the pore size distribution and the mechanical behavior of the catalyst.

It has already been mentioned that the copper-containing catalysts have a lower resistance to aging than ZnO catalysts.

Tahara and his co-workers[56, 57] have tested a copper-chromium catalyst activated with K_2CO_3, and having the composition:

$$CuO:Cr_2O_3:K_2CO_3 = 1:4.72:2.80.$$

At 490°C they noticed a considerable reduction with time of the amount of liquid reaction products obtained. After 48 hours of performance such volume was only 43 per cent as large as initially. In the same test, the isobutyl alcohol concentration in the liquid dropped from 37 to 30 per cent after 10 hours, and to 24 per cent after 100 hours, with a corresponding increase of the methanol concentration.

Effect of the Composition of Reacting Gases

Stoichiometrically, the synthesis of higher alcohols requires two volumes of hydrogen for one volume of carbon monoxide, according to the reaction:

$$nCO + 2nH_2 = C_nH_{2n+1}OH + (n + 1)H_2O \qquad (1)$$

It is, however, obvious that the volume ratio $CO/H_2 = \frac{1}{2}$ must not be presumed to be the optimum, either for the input gas or the circulating gas. During the reaction the concentration of H_2 in the gas increases as a result of the carbon monoxide conversion reaction brought about by the water formed in reaction (1):

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

The occurrence of reaction (2) is particularly evident when the reaction is performed continuously with recycle of the reacting gases.

If reactions (1) and (2) are combined, the following equation is obtained for the higher alcohol synthesis:

$$(2n - 1)CO + (n + 1)H_2 = C_nH_{2n+1}OH + (n - 1)CO_2 \qquad (3)$$

The carbon dioxide formed in reaction (3) is very soluble in the liquid reaction products; therefore, the hydrogen concentration in the gaseous phase increases. This is shown, for example, by the performance data of an I.G. Farbenindustrie isobutanol plant, in which the H_2/CO ratio varies from 1.8 in the input gas to 2.6 in the circulating gas[60].

While in the above mentioned isobutanol plant the input gas composition corresponds to a H_2/CO ratio of 1.8, in the Synol process the same ratio is approximately 1.0. Since the reaction is heterogeneous, the rate of the over-all process of higher alcohol formation depends mainly on the concentration of the reactants adsorbed by the catalyst. It is obvious that the concentrations in the adsorbed phase do not necessarily follow the stoichiometric ratios of the reactants in the gas phase.

Only few data are available concerning the influence of the $CO:H_2$ ratio upon the higher alcohols synthesis with modified methanol catalysts. On the contrary extensive studies have been reported for the synthesis of methanol[38, 39]. Bocharova and co-workers[5] studied the synthesis of higher alcohols with a catalyst of the following composition: $8ZnO.Al(OK)_3.0.1V_2O_5$. They reported that the CO-H_2 ratio of 1:1 is the most satisfactory. Such a conclusion is, from a qualitative point of view, in agreement with the results obtained by Natta and Rigamonti[34], who reported that the best yields of higher alcohols are found when the $CO:H_2$ ratio in circulating gases is higher than the stoichiometric ratio.

It appears clear that a high partial pressure of carbon monoxide favors the formation of high molecular weight compounds. This matter will be discussed more thoroughly in the paragraph concerning the mechanism of the synthesis of higher alcohols.

The presence of inert gases exerts an influence due to the decrease in the partial pressures of the gases participating in the reaction.

A more remarkable influence is ascribed to the presence in the synthesis gas of compounds which may take part in the reaction. One such compound is, of course, water, which inhibits the formation of higher alcohols. An excess of CO, which removes the water with the formation of CO_2, is very favorable to the reaction. On the other hand, it should be noted that the synthesis of higher alcohols may be also performed starting from hydrogen and carbon dioxide[6, 27].

When the synthesis of higher alcohols is performed with the preliminary addition of methanol, the results are practically identical to those obtained when the reaction is operated with only CO and H_2. This is true also when the synthesis of higher alcohols is realized by the use of CO and methanol as the sole components of the starting gas. In the aforementioned I.G. plant, methanol is recycled and is computed in the balance as $CO + 2H_2$[60]. Such a way of operating the higher alcohol synthesis makes it possible to direct the reaction toward the formation of larger amounts of higher alcohols with respect to methanol, as a consequence of the mass action effect of this compound. It is possible to work under such conditions that the amount of methanol produced is equal to that which is converted to higher alcohols in the consecutive reactions.

An analogous influence is exerted by the presence of higher alcohols in the starting gas used for their synthesis. For example, the presence of propyl alcohol in the input gas increases considerably the yield of isobutanol[3]. The presence of olefins in the reaction gas has a favorable effect on the formation of higher alcohols. This seems to be attributed to the following factors:

(1) A mass-action effect, as olefins are produced in the secondary dehydration reaction of higher alcohols;

(2) A more direct effect, because olefins may participate in the mechanism of the higher alcohol formation.

In this connection, it has been claimed[7] that the yields of higher alcohols can be increased up to 145 per cent by the addition of as little as 1.2 per cent (by volume) of ethylene to the input gas, when the synthesis is performed with cobalt-base catalysts.

The presence, in the reaction gas, of other compounds, such as propionic aldehyde or acid, seems to lead to a higher yield of isobutanol. This has been noticed with the use of alkalized $ZnO\text{-}Cr_2O_3$ catalysts, operating in the usual conditions of reaction (300 atm., 430°C)[3].

EFFECT OF SPACE VELOCITY

In the synthesis of methanol, the purity of the product may be increased by operating the reaction with increased space velocities. This is to be attributed to a negative effect on possible consecutive reactions which lead to products other than methanol. The synthesis of higher alcohols has to be operated with lower space velocities, in order to obtain sufficiently high concentrations of the desired products. This is due to the fact that the for-

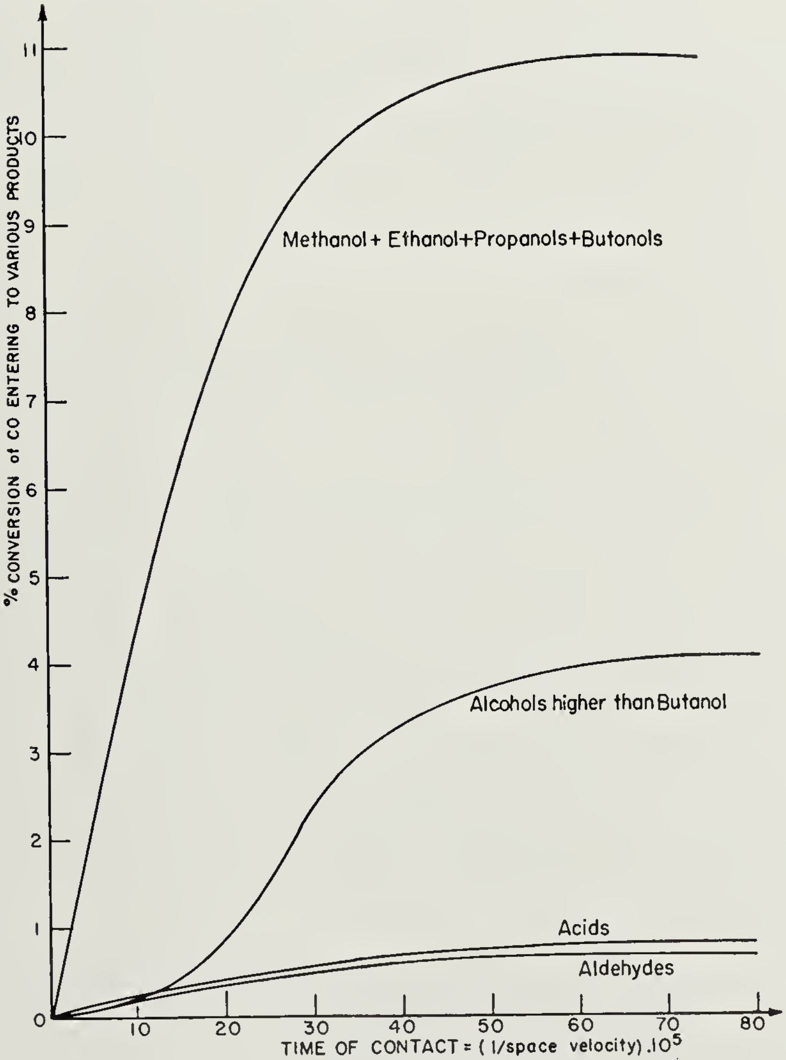


Figure 6. Effect of contact time upon the conversion of carbon monoxide to alcohols, acids and aldehydes. (From Ref. 19)

Catalyst: ZnO-MnO-Cr_2O_3-K_2O
Temperature of synthesis: 400°C
Pressure of synthesis: 204 atm.
Gas composition: $CO/H_2 = 0.84$

mation of higher alcohols takes place through reactions consecutive to the synthesis of methanol.

The results obtained by Frolich and Cryder[19] are shown as an example in Figure 6. These authors worked with a $ZnO\text{-}MnO\text{-}Cr_2O_3\text{-}K_2O$ catalyst and with a H_2:CO ratio in the circulating gas of 1.18. It may be further observed that the concentration ratio between higher alcohols and methanol in the reaction product increases with the contact time, although the yield in methanol is higher than the yields of its homologs.

However, considerations of a different nature have played an important role in the choice of the space velocity for the synthesis of higher alcohols. We have already mentioned the experiments of Runge and Zepf[48] who operated with a space velocity as high as 20,000. In the most recent industrial plants[60] the space velocities employed are of this order.

Effects of Temperature and Pressure

The synthesis of methanol from CO and H_2 is ordinarily operated at temperatures of the order of 350 to 400°C with the most active catalysts, and at even lower temperatures with such catalysts as CuO or CuO-ZnO.

The synthesis of higher alcohols with modified methanol catalysts takes place to an appreciable extent only when the reaction is operated at higher temperatures. Some temperature data concerning the synthesis of higher alcohols with modified methanol catalysts have already been reported in this chapter. It may be here pointed out that, from a practical point of view, the synthesis has to be performed at temperatures higher than 400°C, owing to the increase, with an increase in temperature, of the yield of higher alcohols with respect to methanol. The catalytic synthesis of alcohols from CO and H_2 leads mainly to methanol when temperature is maintained below a certain limit; above this limit there is a sharp increase with temperature of the concentration of higher alcohols in the reaction products. For example, for alkalized $ZnO\text{-}Cr_2O_3$ catalysts, this characteristic temperature at which the concentration of higher alcohols is sharply increased is about 390°C[19].

Composition of the Product of the Direct Synthesis of Higher Alcohols

It may be stated that, when the synthesis is operated with alkalized methanol catalysts, the production of a relatively high amount of methyl alcohol cannot be avoided. In general, primary isobutanol is predominant among the higher alcohols, while the concentrations of ethanol, propanols, and other higher alcohols, are much lower.

Detailed analyses of the product of this synthesis were performed by several authors, but in most of the cases the complexity of the reaction product was such as to prevent the obtaining of precise, complete results. The problem is further complicated by the influence upon the nature and distribution of reaction products exerted by the type of catalyst, and by the type and the amount of promoters employed. The composition of the reaction products obtained with a given catalyst varies with the physicochemical conditions of the synthesis, particularly with temperature, space velocity and gas composition.

Natta and Rigamonti[34, 35] have reported the analytical data for the raw product obtained on industrial tests performed with the use of a catalyst prepared from calcined smithsonite activated by impregnation with potassium acetate. The following higher alcohols were found in this product:
Normal alcohols: methanol, ethanol, 1 propanol, 1 amyl alcohol
Branched alcohols: isobutanol, 2-methylbutanol, 2-methylpentanol, 2-methylhexanol, 3-methylpentanol, isoamyl alcohol, 2,3-dimethylbutanol
Secondary alcohols: isopropanol, ethyl isopropylmethanol, diisopropylbutanol, propyl-isopropylcarbinol
Tertiary alcohols: tertiary butyric and amyl alcohols.
As far as the relative amounts of alcohols produced, the analysis of Natta and Rigamonti shows that methanol is the most abundant, and that isobutanol is the principal higher alcohol, followed by *n*-propanol, 2 methylbutanol, ethanol, isopropanol, *n*-butanol, 2-methylpentanol.

The amount of isobutanol plus *n*-propanol is as high as 65 per cent of the over-all higher alcohols production.

In Table 6 the relative amounts of the individual higher alcohols produced are shown, referred to the total production of higher alcohols, as reported by Natta and Rigamonti[35].

The relative amounts of alcohols produced in the two different tests are substantially identical. It should be further observed that among the branched alcohols those with a methyl group in the 2-position are predominant. The higher content of this type of branched alcohols had also been observed by Morgan and co-workers[28] and by other investigators.

Tertiary alcohols seem to be present in extremely low amounts in the synthesis product. In fact, Natta and Rigamonti have noticed only qualitatively the presence of tertiary butyl and amyl alcohols.

The data found by the above mentioned authors are in good agreement with the results obtained by Morgan and co-workers[28], who operated the synthesis of higher alcohols with catalysts containing only oxides of manganese, chromium, and alkaline metals. The following alcohols were identified by these investigators: methanol, ethanol (traces), propanol, isobutanol, 2-methylbutanol, 2-methylpentanol, 2,4-dimethylpentanol.

The analytical data concerning the product obtained by Graves[21] show the presence of an amazingly high amount of secondary alcohols (Table 7).

However, Graves does not indicate the nature of catalyst, the apparatus used for the synthesis nor the concentration of lower alcohols (methanol, ethanol, propanol).

TABLE 6. COMPARATIVE PRODUCTIONS OF INDIVIDUAL HIGHER ALCOHOLS[35] WITH ALKALIZED ZnO CATALYSTS*

Alcohols	Production	
	Test 1	Test 2
Ethanol	4.16%	3.33%
n-propanol	11.59%	13.12%
isopropanol	3.69%	2.62%
n-butanol	1.99%	1.78%
isobutanol	46.65%	51.37%
2 methylbutanol	4.79%	4.93%
higher alcohols (b.p. <107°C)	4.25%	3.61%
higher alcohols (107°C $<$ b.p. $<$ 180°C)	15.10%	14.98%
higher alochols (b.p. $>$ 180°C)	7.78%	4.26%

* These tests were performed under the following conditions:

Test 1: Catalyst, calcined smithsonite, activated with potassium acetate (9.3% K_2O); space velocity, 17,000; gas composition, $CO/H_2 = 4$; temperature, 400–420°C; pressure, 400 atm.

Test 2: Catalyst, calcined smithsonite, activated with potassium acetate (13.7% K_2O); space velocity, 10,000; gas composition, $CO/H_2 = 4$; temperature, 400–420°C; pressure, 350–400 atm.

TABLE 7. HIGHER ALCOHOLS IDENTIFIED BY GRAVES[21] IN THE REACTION PRODUCT

Primary alcohols: 48.5%	Secondary alcohols: 51.5%
Propanol	Isopropanol
Isobutanol	
2-methylbutanol	3-methyl-2-butanol
2-methylpentanol	2,4-dimethyl-3-pentanol
2,4-dimethylpentanol	3-pentanol*
2-methylhexanol	2-pentanol*
2,4-dimethylhexanol*	2-methyl-3-pentanol*
2-methylheptanol*	

* Products whose identification was uncertain.

The results obtained by the various investigators show clearly that both the nature and the amount of secondary reaction product depend upon the type of catalyst employed in the synthesis and upon the physicochemical conditions of the reaction.

In general, several types of oxygenated compounds are present among the reaction products: water, aldehydes, ketones, esters, acids. However, while Morgan and co-workers[28] obtained over 13 per cent of aldehydes plus ketones with an alkalized Mn-Cr catalyst, Natta and Rigamonti[35] found only 1 per cent of such compounds, with traces of ethers and hydrocarbons and with higher concentration of esterified fatty acids.

Morgan and co-workers have identified in the reaction products formaldehyde, propionic aldehyde, and both hydroxyaldehydes and unsaturated aldehydes.

Strada[54] has obtained in the higher alcohol synthesis a raw product with 1.08 per cent of free acidity and 1.58 per cent of fixed acidity (expressed as propionic acid). This investigator has separated a continuous series of fractions boiling up to 285°C. His results show that acetic acid was present in a lower concentration (2.20 per cent of total acids) than butyric acid (9.20 per cent of total acids).

MECHANISM OF THE SYNTHESIS OF HIGHER ALCOHOLS

Several hypotheses have been proposed to explain the mechanism of this synthesis. The first of them is probably that of Fischer and Tropsch[13], who suggested that higher alcohols are formed from methanol through the following consecutive reactions:

$$CH_3OH + CO \rightarrow CH_3COOH \tag{1}$$

$$CH_3COOH + H_2 \rightarrow CH_3CHO + H_2O \tag{2}$$

$$CH_3CHO + H_2 \rightarrow C_2H_5OH \tag{3}$$

and so forth for primary linear higher alcohols.

The acetic acid produced from methanol in reaction (1) is partly transformed into acetone, which in turn undergoes reduction to isopropylalcohol:

$$2CH_3COOH \rightarrow (CH_3)_2CO + H_2O + CO_2 \tag{4}$$

$$(CH_3)_2CO + H_2 \rightarrow (CH_3)_2CHOH. \tag{5}$$

A further addition of CO and H_2 to isopropylalcohol leads to the formation of isobutylalcohol.

Another interesting hypothesis was formulated by Natta[32, 36], whose starting point was the consideration that the formation of alkali salts of fatty acids on the catalysts may be explained by their direct participation in the mechanism of the synthesis. This hypothesis differs from that given by Fischer and Tropsch because it implies that the catalysts play a fundamental role in the formation of these intermediate fatty acid salts.

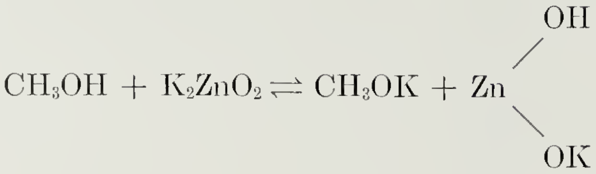
According to Natta, the synthesis of higher alcohols takes place in the following consecutive steps:

(1) Synthesis of methanol, catalyzed by ZnO:

$$CO + 2H_2 \rightarrow CH_3OH$$

(2) Formation of potassium methylate, by reaction of methanol with alkali or with alkali zincate*:

$$CH_3OH + KOH \leftrightharpoons CH_3OK + H_2O$$



$$CH_3OH + K_2ZnO_2 \rightleftharpoons CH_3OK + Zn\begin{matrix} \diagup OH \\ \diagdown OK \end{matrix}$$

(3) Reaction of alkali methylate and CO with the formation of alkali acetate:

$$CH_3OK + CO \rightarrow CH_3COOK$$

(4) Hydrogenation of alkali acetate to alkali ethylate:

$$CH_3COOK + 2H_2 \rightarrow H_2O + C_2H_5OK.$$

The water formed in the above written reactions provokes the hydrolysis of the alcoholates, thus regenerating potassium hydroxide and giving rise to the formation of ethanol. The portion of potassium ethylate which is not hydrolized may react with carbon monoxide and give rise to the formation of potassium propionate, which in turn is easily reduced to potassium propylate, by a reaction analogous to reaction (4). The formation of isopropyl alcohol is explained by admitting a thermal decomposition of potassium acetate to give acetone, the reduction of which then leads to isopropyl alcohol. The formation of acetone is catalyzed by zinc oxide.

Several authors have noticed the presence of acetone, which is found in higher concentrations when the reaction is performed with an excess of carbon monoxide. Similarly, the formation of secondary butylalcohol is assumed to take place through that of methyl-ethylketone.

According to this mechanism, primary linear higher alcohols could be

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* The formation of alkali zincate takes place in the temperature range of the synthesis, in the reaction between ZnO and KOH or K_2CO_3 :

$$ZnO + 2KOH \rightarrow K_2ZnO_2 + H_2O$$

$$2ZnO + K_2CO_3 \rightarrow K_2ZnO_2 + ZnCO_3 \text{ (or } ZnO + CO_2)$$

formed by the direct hydrogenation of the salts of the corresponding fatty acids. However, the slowness with which these salts are reduced makes it possible that primary linear alcohols be formed at least partially by the reduction of aldehydes, which are produced in the thermal decomposition of mixtures of alkali formate and alkali salts of fatty acids:

$$\mathrm{HCOOK} + \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{COOK} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{CHO} + \mathrm{K_2CO_3} \qquad (1)$$

$$\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{CHO} + \mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{CH_2OH} \qquad (2)$$

The hypothesis proposed by Natta is corroborated by the following experimental data:

(1) When the higher alcohol synthesis is performed with ZnO catalysts activated with potassium formate or potassium acetate, the formation of considerable amounts of methyl, ethyl and isopropyl alcohols is noticed. Much smaller amounts of isopropyl alcohol are formed when the synthesis is performed with ZnO catalysts activated with potassium carbonate[32].

(2) At temperatures lower than 400°C and at high pressures, carbon monoxide and hydrogen may be fixed by alkali activated ZnO-base catalysts containing alcoholate, to give salts of fatty acids[32].

(3) Above 400°C, alkali salts of fatty acids are rapidly decomposed, in the presence of hydrogen, according to the following reactions:

$$\mathrm{CH_3COOK} + 2\mathrm{H_2} \rightarrow 2\mathrm{KOH} + \mathrm{CH_3CH_2OH}$$

$$2\mathrm{CH_3COOK} \rightarrow \mathrm{K_2CO_3} + \mathrm{CH_3COCH_3}$$

$$2\mathrm{CH_3COOK} + \mathrm{H_2} \rightarrow \mathrm{K_2CO_3} + \mathrm{CH_3CHOHCH_3}$$

(4) Higher alcohol catalysts tested by Natta and co-workers were found to give optimum yields at about 400°C. This temperature value is higher than the corresponding optimum temperature in the synthesis of methanol. It is interesting to note that the temperature of 400°C corresponds to effective equilibrium conditions between the formation and decomposition of fatty acid salts on the catalyst surface.

(5) Alkali carbonates adsorbed by ZnO or $\mathrm{ZnCO_3}$ are partly reduced by high pressure hydrogen, to alkali formates[32].

(6) Alkali hydroxides react with carbon monoxide to give formates. These alkali formates are easily reduced by high pressure hydrogen to give methylates and methanol. The alcoholates react readily with carbon monoxide, thus forming the salts of higher fatty acids. In the specific case of methanol, its reaction with CO to give acetic acid in the presence of certain oxides or carbonates has been reported by several authors[64].

(7) The decomposition of alkali salts of fatty acids explains the forma-

tion of ketones and the production of secondary alcohols, such as, for example, isopropyl and isobutyl alcohol.

The following reactions, which are assumed to take place with the participation of alkali formate, explain the formation of aldehydes and of primary alcohols:

$$HCOOK + CH_3COOK \rightarrow K_2CO_3 + CH_3CHO$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$

It has been reported that the production of aldehydes and ketones is particularly high when the reaction is operated with a low concentration of hydrogen.

(8) Zinc oxide appears to be a very good catalyst for the following reactions:

$$2CH_3COOH \rightarrow H_2O + CO_2 + CH_3COCH_3$$

$$CH_3COOH + HCOOH \rightarrow CH_3CHO + H_2O + CO_2$$

(9) In the reaction products, practically all the acids corresponding to the alcohols formed in the synthesis[53, 54] are present.

The hypothesis of the formation of higher alcohols through the direct reduction of fatty acids is apparently unable to explain the fact that in the higher alcohols synthesis only low amounts of ethanol are produced. This could be explained by claiming that acetic acid, rather than reacting with hydrogen to give ethanol, tends to react with other acids to give ketones or acetaldehyde. Experimental evidence for this behavior of acetic acid is lacking.

A satisfactory hypothesis concerning the mechanism of the higher alcohol synthesis should explain the fact that the main reaction products, other than methanol, are isobutyl alcohol and *n*-propyl alcohol. If, according to the above mentioned hypothesis, one assumes that these alcohols are formed through the corresponding acids, one should conclude that secondary alcohols are adsorbed by the catalyst more readily than primary alcohols or branched alcohols. Also, one should assume that isopropyl alcohol (formed in the reduction of acetone) reacts promptly with carbon monoxide to give isobutyric acid, which in turn undergoes reaction with alkali formate and hydrogen to yield isobutyl alcohol.

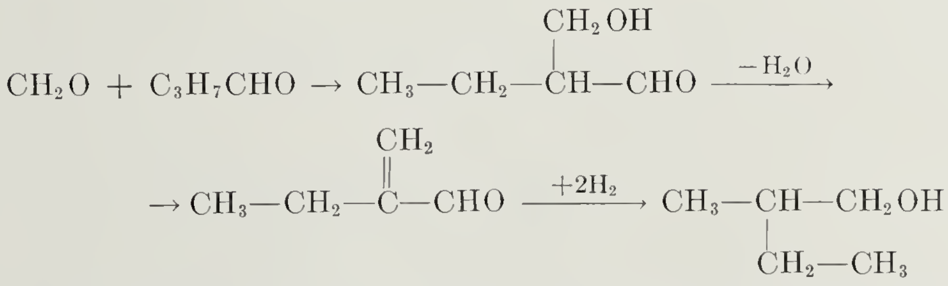
It may be convenient at this point to note that also in "isosynthesis," which is operated with thorium-base catalysts (not necessarily alkali-activated) there is a similar reaction product distribution, with low concentration of ethanol and relatively high concentration of isobutanol. The possible absence of alkali in the isosynthesis catalysts is in apparent contrast with the hypothesis that assumes a direct participation of alkali salts in the reaction mechanism. However, the structural differences between the ThO_2 catalysts for "isosynthesis" and the alkali-activated ZnO catalysts make a direct comparison of these catalysts rather unreliable. It is, however, interesting to refer to the hypotheses which have been proposed for the mechanism of isosynthesis discussed in Chapter 5, Volume IV of the present series of books on "Catalysis."

An interesting hypothesis concerning the mechanism of the higher alcohols synthesis was proposed by Morgan, Hardy and Procter[28]. These investigators suppose that the formation of higher alcohols takes place through an aldolic condensation of formaldehyde, according to the following scheme:

$$RCHO + R'CH_2CHO \rightarrow RCH(OH)CHR'CHO \xrightarrow{-H_2O}$$
$$RCH{=}CR'{-}CHO \xrightarrow{+H_2} R{-}CH_2{-}CHR'{-}CHO \xrightarrow{+H_2}$$
$$R{-}CH_2{-}CHR'{-}CH_2OH$$

These authors base their hypothesis upon the fact that, among the condensation products obtained from CO and H_2 in the higher alcohols synthesis, they have identified a number of aldehydes, including unsaturated and hydroxyaldehydes*. The scheme proposed by Morgan and coworkers is able to explain the formation of those primary alcohols, which have actually been found among the products of the synthesis. In fact, it is possible to determine theoretically, from the above scheme, which of the alcohols with 5, 6, 7, 8 or 9 carbon atoms may actually be formed in the reaction.

For example, the following reactions explain the formation of the two alcohols with 5 carbon atoms which have actually been observed among the products of the synthesis:



$$CH_2O + C_3H_7CHO \rightarrow CH_3{-}CH_2{-}\overset{\displaystyle CH_2OH}{\overset{|}{C}}H{-}CHO \xrightarrow{-H_2O}$$
$$\rightarrow CH_3{-}CH_2{-}\overset{\displaystyle CH_2}{\overset{\|}{C}}{-}CHO \xrightarrow{+2H_2} CH_3{-}\underset{\underset{\displaystyle CH_2{-}CH_3}{|}}{C}H{-}CH_2OH \qquad (1)$$

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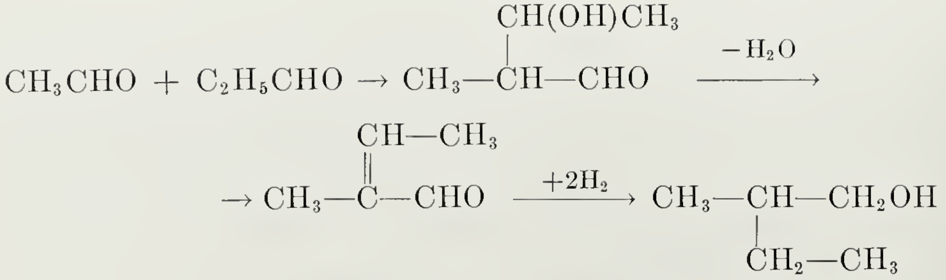
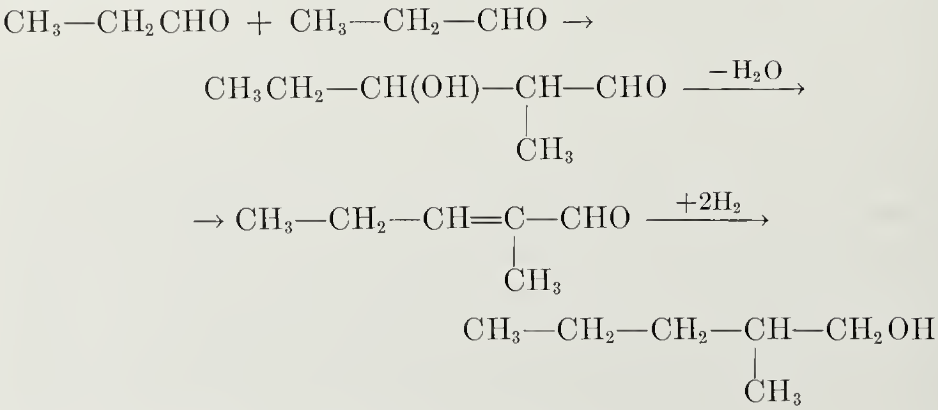
* Such hydroxy-aldehydes are probably not of the linear aliphatic type, but rather of the type $R{-}C_6H_3(OH)CHO$. However, the product obtained by Morgan had properties different from those of hydroxybenzaldehyde.



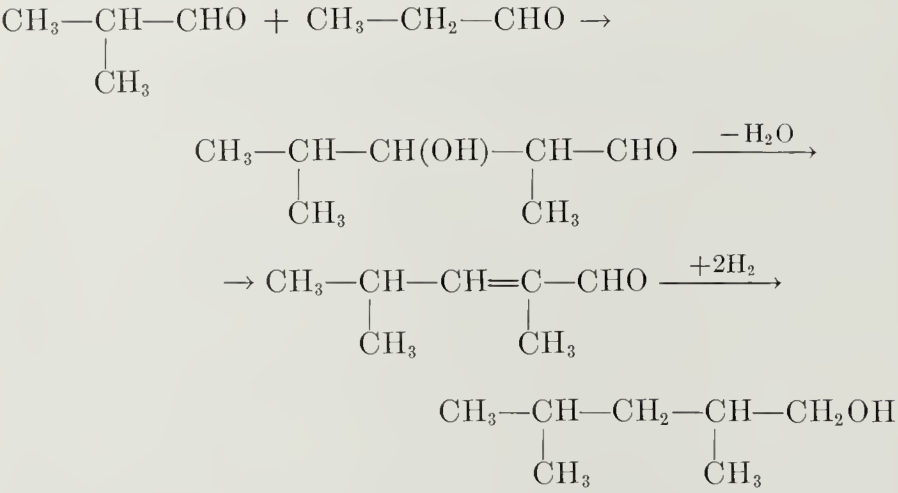
$$CH_3CHO + C_2H_5CHO \rightarrow CH_3-\overset{\overset{\displaystyle CH(OH)CH_3}{|}}{C}H-CHO \xrightarrow{-H_2O} \rightarrow CH_3-\overset{\overset{\displaystyle CH-CH_3}{\|}}{C}-CHO \xrightarrow{+2H_2} CH_3-\underset{\underset{\displaystyle CH_2-CH_3}{|}}{C}H-CH_2OH \qquad (2)$$

$$CH_3CHO + C_2H_5CHO \rightarrow C_2H_5CH(OH)CH_2CHO \xrightarrow{-H_2O} \rightarrow C_2H_5CH{=}CHCHO \xrightarrow{+2H_2} C_2H_5CH_2CH_2-CH_2OH \qquad (3)$$

Similarly, 2-methylpentanol and 2,4-dimethylpentanol may be produced in the reactions:



$$CH_3-CH_2CHO + CH_3-CH_2-CHO \rightarrow CH_3CH_2-CH(OH)-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CHO \xrightarrow{-H_2O} \rightarrow CH_3-CH_2-CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}-CHO \xrightarrow{+2H_2} CH_3-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2OH \qquad (4)$$



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CHO + CH_3-CH_2-CHO \rightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH(OH)-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CHO \xrightarrow{-H_2O} \rightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}-CHO \xrightarrow{+2H_2} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2OH \qquad (5)$$

This mechanism is able to explain the formation of compounds with 3 or more carbon atoms. However, this picture fails to explain the mechanism of the initial chain growth, starting from methanol. In fact, while it is known that the reaction:

$$CH_2O + CH_2O \rightarrow CH_2OH{-}CHO$$

takes place in appropriate conditions, it seems very unlikely that this reaction may occur under the conditions of the higher alcohol synthesis (high temperature and very low partial pressure of CH_2O). Moreover, this mechanism does not consider the formation of isopropyl alcohol and of secondary butyl alcohol, which are always present in the reaction products. In order to take into account the presence of such secondary alcohols, this mechanism would have to assume the isomerization of normal alcohols.

The $CO:H_2$ ratio in the input gas has an influence upon the synthesis of higher alcohols. Such influence is not fully understood if only the equilibrium:

$$\text{alcohol} \rightleftarrows \text{aldehyde} + \text{hydrogen}$$

is considered. In this case a slight increase in the temperature would be sufficient to compensate for a diminution of the $CO:H_2$ ratio and thus give an equivalent equilibrium composition for the system aldehyde-alcohol. While this mechanism is not satisfactory for the formation of higher alcohols, it seems likely that the formation of certain aldehydes takes place through an aldolic condensation. An example of this is given by crotonic aldehyde, whose methylacetal was identified by Natta* in the top fraction of the methanol rectification. Such aldehyde should be considered as formed by the aldolic condensation of acetaldehyde.

An interesting hypothesis for explaining the mechanism of higher alcohols formation is that of the condensation of lower alcohols. An hypothesis of this type was first advanced by Guerbert[22] who advanced it to explain the condensation of alcohols to give higher alcohols in the presence of alkali metals, in liquid phase.

The presence, in the products of higher alcohols synthesis, of certain primary and secondary alcohols, and the exclusion of others which instead may be formed in this type of condensation, was explained by Graves[21] who assumed that:

(1) Higher alcohols may be formed in the intermolecular dehydration between pairs of lower alcohol molecules.

(2) Such dehydration may involve even a hydrogen atom bonded to the carbon atom of methanol. However, the rate of this dehydration is lower than the dehydration rate involving a hydrogen atom bonded to a secondary carbon.

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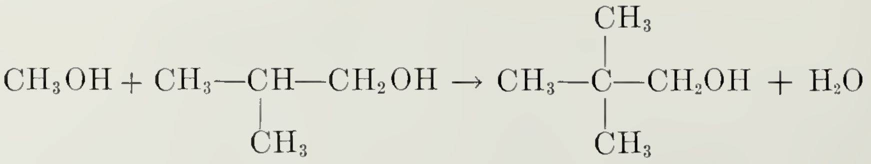
* Unpublished results.

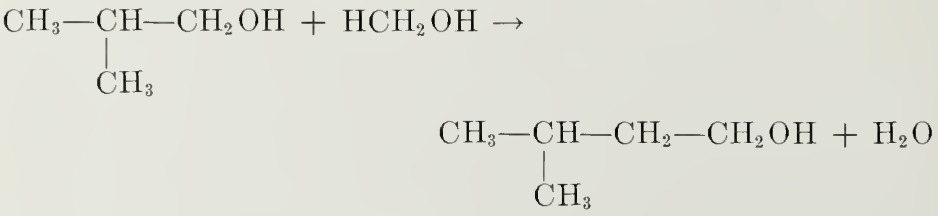
(3) The condensation takes place with difficulty on methyl groups and does not take place in CH groups. The majority of alcohols result from a condensation on methylenic groups.

More recently, Nagishi[29], after a thorough evaluation of the several hypotheses advanced for explaining the mechanism of formation of higher alcohols, considers the direct condensation hypothesis as the most reliable, with the assumption that the methylic hydrogen reacts more readily when the CH_3 group is in α-position. Another assumption of this author concerns the possibility of an aldolic condensation between aldehydes and ketones which are formed in the higher alcohol synthesis through secondary reactions.

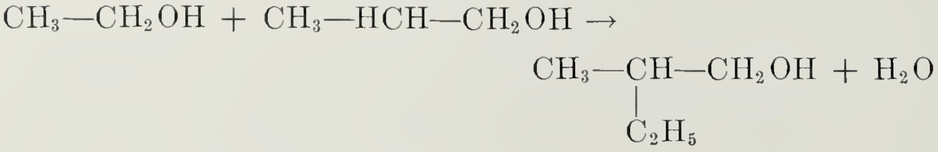
The first assumption made by Nagishi may be justified if the possible reactions of condensation between two alcohols (chosen among methanol, ethanol, n-propanol, isobutanol) are considered, which give rise to the formation of amyl alcohols:



$$CH_3OH + CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_2OH \rightarrow CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}CH_2OH + H_2O \tag{1}$$



$$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_2OH + HCH_2OH \rightarrow CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_2\text{—}CH_2OH + H_2O \tag{2}$$



$$CH_3\text{—}CH_2OH + CH_3\text{—}HCH\text{—}CH_2OH \rightarrow CH_3\text{—}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{—}CH_2OH + H_2O \tag{3}$$

$$CH_3\text{—}CH_2\text{—}CH_2OH + HCH_2\text{—}CH_2OH \rightarrow CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2OH + H_2O \tag{4}$$

If the amyl alcohols which are actually produced in the synthesis of higher alcohols are considered, the prevalence of 2-methyl-1-butanol (reaction 3) is noticed, as well as the almost complete absence of n-amyl alcohol (reaction 4), *tert*-butylcarbinol (reaction 1) and isoamyl alcohol (reaction 2). It may therefore be concluded in agreement with the condensation hypothesis, that the H atoms of CH_3 and CH radicals react with more difficulty than those of CH_2 radicals. With this assumption Graves is able to explain the prevalent formation of those primary alcohols identified among the products of higher alcohols synthesis, up to octyl alcohols.

In a similar way the formation of the observed secondary higher alcohol may be explained by the assumption that the condensation takes place with the preferential loss of a hydrogen atom bonded to an α carbon; when this condensation occurs with the participation of secondary higher alcohols, they lose their hydroxyl rather than their hydrogen.

This hypothesis is, however, in disagreement with the fact that higher alcohols have never been obtained through the condensation of methanol. The first step of the condensation hypothesis is thus missing:

$$CH_3OH + CH_3OH \rightarrow C_2H_5OH + H_2O$$

The presence, among the synthesis products, of a low concentration of ethanol does not appear to be a sufficient proof for the hypothesis of condensation of methyl alcohol.

The views of Graves are in substantial agreement with the earlier results of Frolich and Cryder[19], who studied the behavior of the following gas mixtures under the conditions of higher alcohol synthesis:

$$CH_3OH + H_2\ ;\ CH_3OH + CO;\ C_2H_5OH + H_2\ ;\ CH_3OH + C_2H_5OH + H_2\ ;$$

$$(C_2H_5)_2O + H_2\ ;\ CH_3COOH + H_2\ ;\ (CH_3)_2CO + H_2\ ;\ CH_3CHO + H_2\ ;$$

$$CH_3OH + H_2O + H_2\ ;\quad CH_3OH + H_2O + CO.$$

These authors have obtained the following important results:

(1) The mixtures $CH_3OH + CO$ and $H_2 + CO$ have equivalent behaviors;

(2) When the reaction is operated with methanol-hydrogen mixtures less satisfactory results are obtained, because of the formation of large amounts of water;

(3) The amounts of acid formed do not depend upon the presence of CO in the initial mixture;

(4) Water acts as an inhibitor toward the synthesis of higher alcohols;

(5) The mixture ethanol-hydrogen gives rise to butanol + water, with partial dehydration of ethanol to ethylene;

(6) When the reaction is performed with methanol-ethanol mixtures, higher alcohols are obtained with a predominance of propanol;

(7) Dimethylether may not be formed starting from methanol alone;

(8) The mixture diethylether + hydrogen gives rise to the formation of higher alcohols, with a predominance of ethanol and butanol.

From these data Frolich and Cryder have reached the following conclusions:

(1) Methanol is an intermediate product in the synthesis of higher alcohols.

(2) The formation of higher alcohols takes place predominantly through the condensation of lower alcohols, with the following rate controlling reaction:

$$2CH_3OH \rightarrow C_2H_5OH + H_2O.$$

(3) Ethers do not appear to be intermediate products.

(4) The formation of esters takes place presumably through the condensation of aldehydes.

(5) Acids may be involved in the mechanism of the synthesis.

(6) The type of mechanism may be affected by the nature of catalyst, and by other experimental conditions, such as $CO:H_2$ ratio, pressure, etc.

However, bearing in mind the conditions of the experiments carried out by Frolich and Cryder, one is not able to exclude the possibility that the decomposition of the reacting gases under the synthesis conditions leads to results which are not essential in the mechanism of this synthesis.

Several other hypotheses have been formulated by various investigators, but none of them appears to be entirely satisfactory. For example, Fischer and Tropsch have supposed in one interesting paper[13] that the formation of "Synthol" compounds is due to hydrogenation of formaldehyde condensation products. These authors presume that formaldehyde is the first compound formed in the reaction of hydrogen with carbon monoxide when metals are present as hydrogenation catalysts. This assumption is corroborated by the actual presence of such compounds in the reaction products when the synthesis is accomplished with iron-containing catalysts at relatively low pressures. However, this hypothesis does not seem to be valid in the case of catalysts not containing iron or other elementary metals. A mechanism has been proposed, according to which free methylene radicals are formed, in the hydrogenation of carbon monoxide. These radicals would easily condense to form olefins. The formation of higher alcohols would take place through the hydration of these olefins. As pointed out by Fischer and Tropsch, such an hypothesis appears to be very involved, considering also the nature of alcohols which would be formed in this case. The hypothesis of higher alcohol formation through the homologation of methanol should be seriously considered after the interesting experimental work of Wender, Levine and Orchin[62], who synthesized ethyl alcohol from methanol, hydrogen and carbon monoxide:

$$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$$

This hypothesis is limited by the following experimental data:

(1) The homologation reaction has been accomplished only with cobalt-base catalysts (carbonyl-cobalt).

(2) The fact that methyl alcohol has a greater tendency than ethanol

towards homologation should agree with a relatively high concentration of ethanol in the reaction products, but this is in contrast with experimental evidence. Among the several other hypotheses which have been proposed for this synthesis, attention should be given to the mechanism of higher alcohol formation with a reaction analogous to that of oxosynthesis. This hypothesis was originated by the actual presence of traces of olefins in the products of higher alcohol synthesis.

Natta and Ercoli[37] have shown that methyl alcohol may participate in oxosynthesis reactions. In fact, these authors have produced acetaldehyde from methanol, carbon monoxide and hydrogen, operating the reaction in a temperature range (120°C) lower than that of the experiments of Wender, Levure and Orchin[62]. It should be noticed that this synthesis could be considered as belonging to the oxosynthesis type, if the formation of free methylene radical through dehydration of methanol is assumed.

This hypothesis is limited by the two considerations which were listed above for the homologation of methanol. In fact, oxosynthesis reactions require the presence of cobalt-containing catalysts. Moreover ethyl alcohol is practically absent from the reaction products of higher alcohol synthesis. This latter circumstance might be explained by postulating a rapid dehydration of ethanol in the physicochemical conditions of the synthesis and the consecutive formation of higher molecular weight products from ethylene. There is still another evidence against this hypothesis. In the oxosynthesis of propylene, over a relatively large temperature range, *n*-butyric aldehyde is formed as the principal product rather than isobutyric aldehyde, whereas isobutyl alcohol is one of the main products of higher alcohol synthesis.

CONCLUSION

From this review of the results achieved by the various investigators in the direct synthesis of higher alcohols from hydrogen and carbon monoxide, the following considerations can be made:

(1) The synthesis of higher alcohols is always to be related to the presence of strongly basic substances.

(2) When the reaction is operated at temperatures above 400°C with ZnO-base catalysts, higher alcohols may be produced together with methanol. Among the higher alcohols, isobutanol and *n*-propanol are formed in relatively high proportions.

(3) When the synthesis is performed with catalysts containing certain transition metals (in particular, metals of the iron group) the formation of higher alcohols takes place at temperatures considerably below 400°C. With catalysts containing Fe, Co, or Cu, the formation of higher alcohols with an unusually high content of ethanol has been noticed.

(4) When the reaction is performed with catalysts containing metals of

the iron group (or with ThO_2) hydrocarbons are formed together with higher alcohols. When, on the contrary, ZnO-base catalysts are employed, in the absence of iron group metals and of a dehydrating catalyst (like Al_2O_3), the formation of hydrocarbons is almost totally prevented.

From the above statements it may be concluded that different reaction mechanisms are to be considered for various possible cases:

(a) When iron group metals (or ThO_2) catalysts are employed, the presumable reaction mechanism is strictly connected with the Fischer-Tropsch synthesis*, and the reaction goes probably from the formation of methylene groups to that of olefins and to aldehydes through oxo reactions on these olefins. Alcohols could then be formed through the reduction of aldehydes.

(b) When ZnO-base catalysts are employed the production of alcohols is not connected with the formation of hydrocarbons. In these circumstances, the necessity of using strongly alkaline promoters is a decisive factor in favor of the reaction mechanisms by which the catalytic action of alkali plays a decisive role. The reactions of aldolic condensation, and perhaps the condensation of alcohols with aldehydes are also possible for the conditions under which the synthesis is usually performed. However, the presence of salts of fatty acids in catalysts preemployed in the synthesis of higher alcohols and the results obtained in the hydrogenation of such fatty acid salts with alkalized ZnO catalysts are in favor of the reaction mechanism proposed by Natta.

It should be noted that the temperature range of the higher alcohols synthesis with ZnO-base catalysts (400 to 450°C) represents the limit for the stability of the majority of oxygenated organic compounds. This affects undoubtedly the equilibrium of many of the reactions involved in the mechanism and probably favors some isomerization reactions. Under these conditions, the thermodynamic factors probably play a more important role than at lower temperatures, and therefore they may exert a considerable influence on the composition of the end product.

The possibility should be considered, that the presence of relatively high amounts of branched compounds, which is noticed in the synthesis of higher alcohols, as well as in the isosynthesis process for the production of hydrocarbons, is partly due to the fact that many isomerization equilibria are shifted at higher temperatures towards the formation of branched molecules.

While in the industrial synthesis of methanol it is possible, with the use of highly selective catalysts, to obtain a pure compound as end-product with very high yields, this is not feasible in the direct synthesis of higher alcohols from CO and H_2. The formation of alcohols is due to a chain of reactions which cannot practically be arrested at a definite step. There is

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* For a thorough treatment of this subject, see Chapter 3, Vol. IV of this treatise, written by Dr. R. B. Anderson.

therefore the formation of a complex mixture of reaction products, among which primary alcohols are predominant but not the only ones present. This is the main reason for the gradual decrease of interest in the industrial synthesis of higher alcohols from CO and H_2 compared to other processes such as, for example, those derived from oxosynthesis or from the aldolic condensations followed by hydrogenations.

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CHAPTER 4

THE CATALYTIC HYDROGENATION OF AROMATIC COMPOUNDS

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INTRODUCTION

The study of the addition of hydrogen to organic compounds received little attention prior to the twentieth century. In the early nineteen hundreds, Sabatier and Senderens[320, 321] became interested in catalytic hydrogenation over reduced nickel. Most of their work was carried out at atmospheric pressure by passing organic vapors in a stream of hydrogen over the catalyst in a heated tube. Shortly thereafter, Ipatieff[151] made the first studies of the hydrogenation of organic compounds in the liquid phase under pressure of molecular hydrogen thus disproving earlier ideas that catalysis proceeds only when the vapors of organic materials come into contact with the catalyst. Ipatieff subsequently performed a large number of catalytic experiments with organic compounds using hydrogen under pressure. His many experiments are summarized in his book on catalytic reactions at high temperatures and pressures[147].

Since the early work of Sabatier and of Ipatieff, extensive investigations have been made dealing with the hydrogenation of organic compounds. The many experiments of Adkins and co-workers[6] on nickel and copper chromite catalysts and of Adams and co-workers on platinum oxide[3] did much to establish catalytic hydrogenation as an important tool in present-day organic chemistry. This process is now used not only as a synthetic method, but also as a means of analysis for unsaturation and as a means of proof of structure. Not only are simple unsaturated carbon to carbon linkages subject to saturation with hydrogen, but virtually all aromatic systems as well as many groups such as carbonyl, carboxyl, cyano, nitro, etc., may be reduced quantitatively[253].

Catalysts, Apparatus and Methods

In the earliest work, Sabatier and Senderens used nickel as a catalyst. The nickel was formed by reduction of the oxide (supported on kieselguhr) by hydrogen at 300 to 400°C. The reduced nickel was pyrophoric. Cobalt, copper, platinum and palladium were also found to be active catalysts when formed under similar conditions. This work has been summarized by Sabatier[318]. At the present time, the most useful catalysts for the hydrogenation of organic compounds are undoubtedly Raney nickel[302] and Adams platinum oxide[3]. For both of these, the exact nature of the catalytic material is not clearly understood. Raney nickel is prepared by reaction of the aluminum in a finely powdered nickel-aluminum alloy with sodium hydroxide solution. The products of the reaction are washed away from the finely-divided porous nickel. The temperature of reaction and of subsequent digestion, the method of washing the catalyst, and even the type of vessel used in the preparation have been thoroughly investigated by Adkins and co-workers, who designate a series of catalysts of different activity depending on the particular conditions used[7, 11, 250, 281, 282]. There is some evidence, however, that the relative activity of various preparations depends on the reaction used as a test[11, 359]. The composition of the catalyst is also in doubt. Adkins and Billica[7] reported that the very active W-6 nickel contained about 11 per cent aluminum, the remainder being nickel. Ipatieff and Pines[155], on the other hand, reported that this catalyst contained 77 per cent nickel, 21 per cent alumina, and 1.4 per cent aluminum. Watt and Parker[437] claim that the maximum alumina content is less than 1 per cent, and that the alumina reported by Ipatieff and Pines was formed during analysis of the sample. Whatever the situation, if alumina is adsorbed on the catalytic surface, it undoubtedly influences its activity.

In the reaction of Raney alloy with alkali, a considerable amount of hydrogen is formed. The amount and nature of the hydrogen associated with the catalytic nickel has been the subject of some controversy. Raney[301] describes the catalyst as a hydride of the formula NiH_2. He reports that a catalyst which has been dried in acetone will decompose with a flash when warmed gently. Vandael[414] has measured the quantity of hydrogen liberated from the hot leaching bath, and also claims that Raney nickel is a hydride of formula NiH_2.

Freidlin and Ziminova[105, 107] found 95.3 ml of hydrogen contained in 1 gram of Raney nickel. This corresponds to about one-half atom of hydrogen per atom of nickel. Of this quantity, approximately one-fourth is attributed to adsorbed hydrogen and the remainder is dissolved hydrogen. The catalyst possesses no activity when all of the hydrogen is removed. Freidlin and Ziminova do not subscribe to the hydride theory; they conclude that the catalyst is skeletal nickel promoted with hydrogen. These same authors also found that the quantity of adsorbed hydrogen is related to the amount of remaining dissolved hydrogen in a linear fashion[106], but that it is difficult to replace the dissolved hydrogen during the course of a catalytic hydrogenation reaction[103]. They postulate that the loss of activity of the catalyst under the usual hydrogenation conditions is due to the destruction of active surface by chemical reaction with hydrogen on the nickel surface, and blocking of active spots[104].

Aubry[29] claims that the high activity of Raney nickel is due to adsorbed or absorbed hydrogen, and that the catalyst acts as a reversible electrode to hydrogen as platinized platinum does[29]. In the pH range from 5 to 14, Raney nickel follows the potential variations of a reversible hydrogen electrode[395]. It has also been found that most (95 per cent) of the original hydrogen in Raney nickel may be replaced with deuterium when a dioxane-deuterium oxide suspension of the catalyst is saturated with deuterium gas[174].

Adams platinum oxide is made by fusion of a mixture of platinic chloride and sodium nitrate. The platinic nitrate formed decomposes to give platinum oxide. The melt containing the suspended oxide is dissolved in water and the catalyst washed until free from nitrates (as evidenced by colloid formation or nitrate test)[4]. In the process of fusion, a certain amount of the nitrate is decomposed and 2 per cent or more of sodium is left in the catalyst; the alkali is presumably in combination with the platinum since tests for chloride and nitrite or nitrate are negative[173], although in Adams' original report the sodium present was referred to as "alkali salts[2]." The X-ray powder diffraction photographs of Adams' fusion product show several distinct lines which duplicate those reported for PtO_2 [62, 173, 431]. It appears that neither the alkali nor the water (Adams and Shriner originally suggested that the catalyst was $PtO_2 \cdot H_2O$) is part of the compound which gives the characteristic X-ray pattern of PtO_2 observed for the catalyst.

When the platinum oxide is exposed to hydrogen it is quickly reduced. The alkali content is no longer associated with the platinum catalyst itself, and its presence may prevent or at least influence a hydrogenation reaction. The usual procedure of using an acid solution as a solvent in the hydrogenation of aromatic compounds is undoubtedly of considerable importance in this respect[173].

In addition to Raney nickel catalyst, nickel is often used supported on kieselguhr or alumina. Platinum also is often used supported on such materials as charcoal or barium sulfate.

Other catalyst such as cobalt, rhodium, palladium, etc., have been employed to some extent in the hydrogenation of aromatic compounds. Recent summaries of catalysts and their preparation include those of Ciapetta and Plank[69], de Cat[81], and Komarewsky and Riesz[180]. The uses of Raney nickel have been summarized by Lieber and Morritz[191].

The design of apparatus to be used for hydrogenation of aromatic hydrocarbons will depend largely on the purpose of the experimenter. Primarily the types may be classed as flow systems, low or high pressure constant volume systems, and constant pressure apparatus. Flow systems consist primarily of a tube packed with granular or supported catalyst through which a mixture of hydrogen and an organic vapor is passed. Consideration must be given to the packing of the catalyst bed and the dissipation of the heat of reaction resulting from hydrogenation of aromatic compounds. This general type is useful in commercial installations. It has also received considerable attention in tests for activity of a catalyst. For this purpose, the aromatic hydrocarbon, usually benzene, is conducted in a stream of hydrogen through the catalyst bed at known space velocities and for known contact times. The activity of the catalyst is measured by the fraction of the benzene converted to cyclohexane.

The majority of research dealing with the reduction of aromatic compounds by hydrogen is carried out in constant volume systems. The course of the reaction is followed by pressure changes. Low pressure systems are particularly useful for reductions over platinum or palladium. Such an apparatus consists in a bottle containing the aromatic compound, generally in a solvent, connected by means of thick-walled rubber tubing to a reservoir of hydrogen. The bottle is attached to a cradle which is mechanically shaken. Pressures up to 60 psi are readily obtainable. The pressure drop accompanying the hydrogenation process is determined by the hydrogen uptake of the aromatic compound together with the volume of the system.

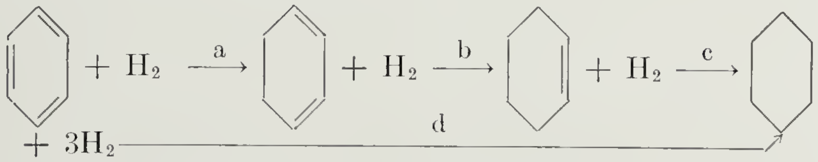
This low-pressure apparatus is little used when aromatic compounds are reduced over catalysts less active than platinum since its pressure and temperature ranges are quite limited. For nickel or similar catalysts it is usually necessary to employ pressures considerably above atmospheric as well as temperatures of the order of 150°C or higher. Such experiments require metal bombs. The problems connected with the design of closures, valves, pressure gages, temperature controls and stirring devices for high pressure hydrogenation apparatus as well as materials of construction have received a great deal of attention. Summaries of design and construction of high-pressure hydrogenation apparatus include those of Adkins[6], Meigs[229], Komarewsky and Riesz[180], and deCat[81]. High pressure reductions are very useful in organic synthesis. Reactions which will take place immeasurably slowly at room temperature even in the presence of a catalyst may be made to proceed at a very satisfactory rate at elevated temperatures and pressures. The same materials may react in various ways depending on the catalyst employed, as well as on temperature and pressure.

Constant pressure systems are useful mainly in analytical procedures where the volume of hydrogen taken up by a known quantity of material must be determined. Many catalysts themselves take up, by reaction and adsorption, a considerable quantity of hydrogen when in use, and this must be reproducible. Good agitation is of secondary importance as compared to reproducible volume measurements. Satisfactory forms of apparatus for this purpose have been described by Joshel[164] and by Noller and Barusch[260].

Resonance and Geometry

One of the important characteristics of aromatic compounds is their resonance stabilization. While most of the studies relating to this phenomenon are confined to benzene, they apply at least in part to other aromatic nuclei. Kistiakowsky[177] and co-workers measured the heats of hydrogenation of benzene and of its partially hydrogenated products. According to their data, the heats of hydrogenation at 355°K for cyclohexene, 1,3-cyclohexadiene and benzene are −28.59, −55.37 and −49.80 kcal per mole. From these figures one can see that the addition of 1 mole of hydrogen gas to benzene to form cyclohexadiene would be endothermic by 5.6 kcal. Taylor[388] calculated the free energy for the hydrogenation of benzene to cyclohexane at 600°K to be +10.2 kcal, while for cyclic systems with little or no resonance energy (as cycloheptatriene) the value of ΔF is negative by about the same amount.

Janz[159] calculated the free energy changes involved in the hydrogenation of benzene for the steps indicated below.



The tabulated free energies for these steps are as follows:

T(°K)	ΔF (kcal)			
	a	b	c	d
298.16	13.2	−17.9	−18.7	−23.4
400	15.7	−14.8	−15.2	−14.35
550	19.6	−10.2	−9.4	0.00
700	23.5	−5.5	−4.4	13.62
1000	31.3	4.2	6.5	41.97

Voitekhoff[418a] studied the equilibrium between benzene, hydrogen and cyclohexane, and obtained a value of 7.36 for Kp at 256°C. The free energy change calculated from this value is −2100 calories, a figure which is in very good agreement with the calculations of Janz.

From these values it is evident that cyclohexadiene would be an unstable intermediate over the entire temperature range studied. Such calculations also indicate that hydrogenation of benzene, and presumably other aromatic systems as well, is less favored thermodynamically than hydrogenation of non-resonating unsaturated systems.

Smith and Meriwether[367] determined the heats of activation for the hydrogenation of cyclohexene, the cyclohexadienes and benzene on platinum under conditions where the heats of adsorption of these compounds would not be included in the apparent activation heats. They concluded that the resonance energy of benzene must be destroyed on the catalyst. The heat of activation for the hydrogenation of benzene (7.4 kcal) was very close to the endothermicity (5.6–7.4 kcal) which is the minimum activation energy required for the hydrogenation of benzene to a cyclic diene. Kagan and Friedman[167] point out that in the adsorption on a catalyst the π bonds are ruptured. As a result, the rearrangement accompanying chemisorption of benzene is accompanied by a loss of some 34 kcal per mole as compared with the loss for chemisorption of an olefin, and this loss of energy is sufficient to explain the difficulty of hydrogenation of benzene. Similar arguments may be applied to other aromatic systems, thus explaining the fact that many catalysts which are active in the hydrogenation of ethylenic linkages are inactive in the hydrogenation of aromatic nuclei.

A different explanation for the inactivity of many catalysts toward the hydrogenation of benzene is based on a geometric factor. The idea that the hydrogenation of benzene and the reverse dehydrogenation reaction could take place only on catalysts in which the atoms at the crystal faces had satisfactory spacings is embodied in the multiplet theory of Balandin[37, 38, 39]. The postulated mechanism involves the flat adsorption of benzene on the octahedral faces of certain crystal lattices. Reduction then proceeds by addition of hydrogen adsorbed on neighboring sites. Much evidence can be given to support such a hypothesis. A thorough discussion of Balandin's contribution to heterogeneous catalysis has been published by Trapnell[394]. This theory has been sharply criticized by Taylor[388] on the basis of thermodynamic calculations which can equally well explain many of the results. Kagan[166] points out that the multiplet theory for hydrogenation of benzene and the reverse dehydrogenation of cyclohexane is in violation of the principle of microscopic reversibility. Balandin's theory calls for the simultaneous addition or removal of all six hydrogen atoms, contrary to the observation[168] that in the presence of a platinum catalyst, the first stage in cyclohexane dehydrogenation is the formation of cyclohexene which rapidly disproportionates to form benzene and the initial cyclohexane. Furthermore Kagan finds that an active copper catalyst which, on the basis of the multiplet theory, should catalyze the hydrogenation of benzene and the reverse dehydrogenation process is actually inactive toward these reactions. It does, however, catalyze both the hydrogenation and dehydrogenation of cyclohexene. According to Kagan, the important factor is not the geometry as proposed by Balandin, but the energy factor due to resonance stabilization.

Hill and Selwood[137] studied the structure and activity of nickel catalysts supported on alumina. Their results indicated that, in agreement with Balandin's theory, a minimum aggregation of nickel atoms is required in order to catalyze the hydrogenation of benzene. It is apparent that the situation is not settled. While most of the arguments concerning this theory have been centered on benzene, similar considerations may be applied to other aromatic compounds. The present status of this as well as of several other theories is discussed by Tolpin, John and Field[392].

Kinetics of Hydrogenation of Aromatic Compounds

A considerable amount of attention has been given to the study of the kinetics of hydrogenation of aromatic organic compounds. Such information is of importance in the evaluation of catalyst activity, in the determination of the mechanism of catalysis, and in the investigation of the influence of structure on the course and velocity of hydrogenation reactions.

In 1928, Adams and Marshall[1] studied the hydrogenation of aromatic hydrocarbons on platinum-oxide platinum black. They determined the times necessary to reduce thirteen such compounds in acetic acid solution at room temperature under a hydrogen pressure of 2 to 3 atmospheres. Other workers have also followed this early procedure. Such methods are very approximate, and often lead to erroneous results. Rates of catalytic reactions, in addition to being sensitive to conditions of temperature and pressure or concentration, are highly susceptible to influences of small amounts of impurities. They may also depend on diffusion of the hydrogen or of the aromatic compound to the catalytic surface and to the variations in activity of catalyst samples.

One of the first reliable kinetic studies dealing with the catalytic hydrogenation of aromatic compounds was reported by Lozovoy and Dyakova[89, 210, 211, 212, 213], who investigated the hydrogenation of aromatic hydrocarbons over a nickel-alumina catalyst. These workers established the order of the reaction, the influence of pressure (up to 250 atmospheres) and temperature (up to 230°C), as well as the influence of substituents. The hydrogenations were carried out in an autoclave rocked in such a manner as to give good agitation. The bomb was equipped with a needle valve through which samples could be withdrawn periodically and analyzed by refractive index methods.

A somewhat simpler method was developed by Smith and co-workers in a series of studies dealing with the kinetics of hydrogenation of aromatic compounds[112, 357, 358, 364, 366, 368, 369, 370, 371, 372]. In this method, the rate of hydrogenation over Adams platinum catalyst was determined by following the pressure drop in a constant volume system. Considerable attention was paid to reproducibility of catalyst samples, purification of aromatic compounds, control of temperature, and balance between catalyst weights and agitation conditions so that equilibrium conditions were maintained on the catalyst; thus the rate which was measured was characteristic of the reaction studied rather than of diffusion. In both of these studies, the reactions were found to be, in general, first order with respect to hydrogen pressure but zero order with respect to the concentration of aromatic compound. For compounds with one aromatic nucleus, no interference was found from the hydrogenated products. It was noted that over a nickel catalyst the order with respect to hydrogen changes from zero order (below 110°) to first order (above 200°) as the temperature is increased[3]. The kinetic laws applicable to surface catalysis and their general interpretation have been summarized by Laidler[188] and by Schwab[333].

It should be emphasized that much of the confusion caused by conflicting data in the catalytic literature results from failure of the experimentalist to pay adequate attention to some of the factors previously indicated. This is particularly true when aromatic compounds are involved, for the more complex ones are often difficult to purify from small traces of materials which are selectively adsorbed on catalytic surfaces, and which may completely halt a hydrogenation. When freed from such impurities these compounds may undergo catalytic reduction with relative ease. Many investigators have paid relatively little attention to the maintenance of equilibrium conditions on a catalytic surface and hence have reported as characteristic of a given reaction, rate constants which are dependent on the individual apparatus employed for experimental measurements.

Stereochemistry of Catalytic Hydrogenation of Aromatic Compounds

While the importance of a geometric factor of the type suggested by Balandin[39] in the hydrogenation of aromatic compounds may be open to criticism, there is no doubt that the product of such a reaction may be predominantly a single geometric isomer when this type of isomerism is possible. Furthermore, this is usually a *cis* isomer which from the standpoint of thermodynamics is not the most stable form. Thus *cis*-1,2-dimethylcyclohexane may be obtained from *o*-xylene[67, 225, 238, 460], *cis*-1,3-cyclohexane dicarboxylic acid from isophthalic acid[187, 362, 448], *cis*-decalin from naphthalene[142, 450] and saturated glycols of *cis-syn-cis* configuration from phenanthraquinone[205], all by processes of catalytic hydrogenation. Since conversion from *cis* to the *trans* forms may take place under the conditions of the hydrogenation reaction[53, 54] a mixture of isomers is often obtained, and the composition may vary from predominantly *cis* to predominantly *trans* forms; the latter configuration is usually in excess in an equilibrium mixture of the two. Thus napthalene yields mainly *trans*-decalin when catalytically reduced at 160°C[143, 450]. At the present time, catalytic hydrogenation is the most useful method for obtaining the thermodynamically unstable isomers of compounds containing reduced aromatic nuclei.

It is usually assumed that the aromatic compound is adsorbed so that the unsaturated ring is flat against the catalytic surface. The zero order kinetic behavior of the material undergoing hydrogenation is generally interpreted as indicative of strong adsorption. Numerous experiments by Linstead and co-workers[78, 79, 193, 200, 201, 202, 203, 204, 205, 206, 207] indicate that the course of the reaction and the nature of the hydrogenation products is influenced by substituents which may prevent such flatwise adsorption. These workers believe that the hydrogen is also adsorbed on the catalytic surface and becomes attached to the aromatic nucleus from the catalyst side. On the other hand, the first order kinetic dependence usually found for the hydrogen indicates the possibility that the hydrogen approaches the unsaturated nucleus from the side opposite to the catalyst. This is in line with the van der Waals-chemisorbed layer interaction theory advanced by Rideal[94, 304, 305]; according to this theory, only one reactant is chemisorbed, with the other interacting from the van der Waals layer. In any case, the predominance of *cis* forms in the products indicates attack by the hydrogen from one side only. Kogure[179] has recently reviewed the various theories of the stereochemistry of catalytic hydrogenation of aromatic compounds.

In recent years a number of physiologically active compounds containing saturated ring systems have been prepared. For this reason, the hydrogenation of aromatic systems has received a great deal of attention by the synthetic organic chemist.

THE HYDROGENATION OF THE BENZENE NUCLEUS

Benzene

Benzene undergoes hydrogenation over a variety of catalysts, and this reaction makes a very convenient test for catalytic activity. The hydrogenation proceeds cleanly to cyclohexane unless elevated temperatures (above 350°C) are employed; then cracking and rearrangement into a variety of products occurs[44, 268, 291]. At room temperature benzene may be reduced over platinum, palladium and similar catalysts. An acid solvent is usually necessary[1, 173, 368]. In general, elevated temperatures are required for reduction of benzene with hydrogen over such materials as nickel, copper and cobalt[153, 197, 257, 328, 379, 386, 387, 400]. The purity and method of preparation of the catalytic material is of great concern. For example, Sabatier and Senderens[319] originally claimed that benzene could not be hydrogenated over copper, but some years later Pease and Purdum[283] successfully reduced benzene to cyclohexane over this metal. Ipatieff, Corson and Kurbatov[153] also found that benzene could be hydrogenated over copper at 225 to 350°C and 100 kg/cm^2 hydrogen pressure provided the copper was pure and finely divided. Above 350°C, the copper becomes less active. Zelinskii and Turova-Pollak[462] studied under a variety of conditions the hydrogenation of benzene over nickel, platinum, iridium, ruthenium and palladium.

Amano and Parravano[18a] studied the vapor phase hydrogenation of benzene over ruthenium, rhodium, palladium and platinum catalysts supported on alumina at one atmosphere hydrogen pressure and temperatures from 25 to 225°C. They found the reaction to be essentially first order with respect to hydrogen and zero order with respect to benzene. They also found the order of catalytic activity to be $Rh > Ru > Pt > Pd$. They find that the activation energy for the reaction over the first three catalysts was approximately 12 kcal per mole. The activity of the palladium catalyst was too low to allow determination of activation energy under their experimental conditions. This is presumed to be caused by hydride formation on the catalyst surface. They state that the order of catalytic activity of the rhodium, ruthenium and platinum is related to the per cent *d*-character of the metal bond. This is at variance with the results of Anderson and Kemball[19a] who employed evaporated metallic films as catalysts. Minachev, Shuikin, and Rozhdestvenskaya[240] found that ruthenium or rhodium catalysts (1 per cent) supported on either alumina or carbon were almost as active as platinum in promoting the hydrogenation of benzene.

Komarewsky and Miller[179a] found that cyclohexane could be produced from benzene and hydrogen at 475°C and 115 atmospheres pressure over vanadium oxide. The catalyst was inactive for this reduction at 400°C and atmospheric pressure. They were unsuccessful in attempts to hydrogenate benzene over chromium oxide both at atmospheric and superatmospheric pressures.

Recently a number of studies of benzene hydrogenation has been made over catalytic metals of varying crystal sizes. Rubinshtein[308] studied the hydrogenation of benzene at 155–175°C on nickel crystals with dimensions of 49 to 102Å. He found the highest yield of cyclohexane with the more disperse catalyst. He also found an increase in the activation energy from 3100 to 10,450 calories per mole as the crystal size was increased from 49 to 102Å. In further work, a series of platinum catalysts on charcoal was investigated by Rubinshtein, Minachev and Shuikin[310]. As the platinum content was decreased by steps from 20 to 0.1 per cent these authors found systematic disappearance of high index reflections. With increasing dilution of the metal, the (2,2,2) plane disappeared first followed by the

(0,2,2), (1,1,3) and (0,0,2) reflections. The reflection from the (1,1,1) plane persisted throughout the series, and was only weakened at the lowest platinum content. The activity of this series was measured in terms of the percentage hydrogenation of benzene to cyclohexane. The percentage of conversion remained constant with 4–1 per cent platinum and decreased only slightly (still 90 per cent as effective) when the catalyst of 0.1 per cent platinum content was tested.

These results are claimed to be evidence that the catalytic activity of platinum on carbon depends primarily on the presence of (1,1,1) planes, with higher index planes playing minor roles in hydrogenation of benzene. Furthermore, these findings are consistent with the location by Balandin of the hydrogenation-dehydrogenation activity in the octahedial faces of the catalyst.

These authors also report[311] experiments with even smaller percentages of platinum. For catalysts of 4.0–1.0, 0.5, 0.1, 0.09, 0.06 and 0.03 per cent platinum, the relative activities were 100, 88.5, 88.4, 11.2, 9.0 and 1.0. Thus the curve for the relative fall of activity as a function of decreasing platinum content shows a rapid break below 0.1 per cent. Rubinshtein and co-workers attribute this to blocking of the active centers by decomposition products. It would seem that the isolated monocrystallites found at very low platinum contents are more subject to blocking than the aggregates present at high metal content. X-ray diagrams indicate that the crystal structure of the platinum is preserved even in the most dilute catalyst.

Further studies of benzene hydrogenation on carbon supported nickel catalysts are reported [312, 340]. These catalysts were formed by impregnating active carbon with nickel formate which was subsequently decomposed by heating. These catalysts were satisfactory for hydrogenation of benzene, but their activity was not as great as that of similar platinum catalysts. Maximum activity was found for crystallites of dimensions around 40A. This was similar to results obtained with nickel supported on alumina, so that these authors suggest that the optimum grain size of the catalyzing metal does not depend on the nature of the carrier. Repeated impregnation of the carbon with nickel formate and subsequent decomposition results in the growth of existing nickel grains rather than in the formation of additional crystallites. In general, the activity of the nickel catalysts toward hydrogenation of benzene is inferior to that of the platinum group. Additional work with supported nickel catalysts[339] indicated that iron oxide was an unsatisfactory support. Catalytic activities expressed as the degree of conversion of benzene to cyclohexane with space velocities of 0.3 liters per liter of catalyst per hour are shown in Table 1.

Rubinshtein and co-workers[309] also prepared nickel-alumina catalysts by precipitation from solution of the nitrates. If the mixed oxide precipitates were calcined for 10 to 12 hours at 350 to 425°C and subsequently reduced with hydrogen, no catalytic activity resulted; omission of the calcining gave active catalysts after hydrogen reduction. The calcined catalysts appeared to be amorphous. The authors suggest that the calcining produces $NiAl_2O_4$, and that the isolated nickel atoms resulting from subsequent reduction cannot associate to form the crystals necessary for catalytic activity.

Further work on carbon supported cobalt catalysts[239] indicated that, contrary to earlier findings of Sabatier, finely divided cobalt on active carbon is not inferior to nickel in its catalytic activity. Results with decreasing percentages of metal on the support were similar to those obtained with nickel catalysts. Other experiments were carried out with cobalt catalysts both unsupported, and supported on active charcoal[314]. The cobalt oxide from which the catalyst was formed was reduced at temperatures between 350 and 800°C. Those catalysts reduced around 350° gave hexagonal *alpha* cobalt and were very effective toward the hydrogenation of benzene. Those reduced above 600°C gave almost pure *beta* (cubic) cobalt crystallites, and were ineffective as catalysts. The difference in activity was not due to varying sizes of the crystallites. The authors suggest that the low catalytic activity of the *beta* cobalt may be linked with the unfavorable effect of high temperature of reduction which produces crystallites with few defects.

TABLE 1. INFLUENCE OF CARRIER ON THE HYDROGENATION OF BENZENE OVER NICKEL

Per Cent Ni	Carrier	Per Cent Conversion
14.4	Al_2O_3	100
11.3	ZnO	100
12.6	Cr_2O_3	89.2
16.2	MgO	100
16.9	Fe_2O_3	5.5
19.5	Al_2O_3	100
18.1	ZnO	100
17.0	Cr_2O_3	100
22.0	MgO	100
21.1	Fe_2O_3	5.8

Lihl and Zemsch[197] studied the hydrogenation of benzene over cobalt catalysts prepared by hydrogen reduction of cobalt formate at temperatures from 200 to 700°C. These authors also found that catalytic activity as judged by the production of cyclohexane was good when the cobalt was produced at temperatures below 500°C. Under these conditions hexagonal crystals were formed. At higher temperatures where cubic crystals only were present, the activity was much less. These authors found that the cubic crystals of cobalt could be transformed to the hexagonal form by mechanical rolling, and this process led to higher activities.

Lihl, Wagner and Zemsch[195] found that for equal catalyst weights, cobalt was more active than nickel. Furthermore, the activity of cobalt in creased with time, while that of nickel decreased after the hydrogenation process. These authors also prepared cobalt-nickel and cobalt-iron alloy catalysts from mixed crystals of the salts[196]; they found that for the cobalt-nickel system, the activity toward benzene hydrogenation was a linear function of composition. However, for cobalt-iron, the variation in activity was explainable neither by electron distribution in the alloys nor by a geometric factor. It may be noted that iron usually possesses no catalytic activity for the hydrogenation of benzene.

Lihl and Zemsch[198] also prepared nickel and cobalt catalysts by electrolysis of solutions of nickel and cobalt salts in the presence of a mercury cathode. When the mercury was removed from the nickel, the resulting powder was inactive for the hydrogenation of benzene. However, when the cobalt was recovered by distillation of the mercury or decomposition of the amalgam in air, a very active catalyst for the reduction of benzene was obtained. The cobalt was found to have the hexagonal crystal structure.

Poltorak[284] discusses hydrogenation catalysis from the standpoint of "active ensembles" of surface defects, the surface concentration of which depends strongly on the dimensions and surface energies of crystals. He explains the principal activity of the tetragonal faces of nickel and *alpha* cobalt for hydrogenation catalysis, the existence of maximum activity when reducing crystallite size, as well as the existence of an optimum temperature of catalyst preparation, on the basis of such ensembles.

Shuikin, Minacheff and Rubinshtein[341] also studied the catalytic hydrogenation of benzene on palladium (supported on active charcoal). With space velocities of 0.06 l./hr/l. catalyst at 150°C they found that the percentage conversions of benzene on catalysts containing 2.0, 1.0, 0.25, 0.10 and 0.05 per cent were 90, 76, 54, 36 and 9.4 per cent, respectively. X-ray determination before and after reaction showed that the initial lattice deformation either disappeared completely after the reaction, or at least greatly decreased. There was no evidence of a new phase after the hydrogenations. There was also a gradual fall of activity with time. The authors conclude that the measured differences in activity of these palladium catalysts were due not only to the different palladium contents, but also to differences in structure of the dispersed metal.

Agliardi[14] studied the hydrogenation of benzene over nickel and nickel containing chromium, cobalt and iron each in proportions so small that x-rays showed no modification of the crystal lattice. Pure nickel was the most active catalyst. All of the catalysts showed maximum activity at 220°C. Lihl and Zemsch[197] studied the hydrogenation of benzene over nickel catalysts produced by reduction of the formate, carbonate, oxide, hydroxide and oxalate with hydrogen at temperatures between 200 and 700°C. They found that the initial activity of the nickel depended on the particular compound reduced (oxide and formate yielded most active catalysts) and was greater for lower reducing temperatures. Hill and Selwood[137] tested the activity of nickel catalysts by the reduction of benzene, and concluded that a minimum aggregation of nickel atoms was required for catalytic activity. Mertens[230] investigated the hydrogenation of benzene in a fluidized bed of nickel-alumina catalyst in the form of grains 100 microns in diameter. The rate of hydrogenation was some twelve times greater than with a stationary catalyst.

Studies of benzene hydrogenation have been made with promoted catalysts. Tanida[387] found that molybdenum and tungsten were good promoters for nickel catalysts. Corson and Ipatieff[71, 152] found that small amounts of cobalt and nickel greatly increase the efficiency of copper catalysts for the process of benzene reduction. The promoting effect of copper on cobalt has been linked with the favored formation of *alpha* cobalt in the presence of the copper[239].

Orito and Kawachi[266a] investigated the reaction of hydrogen with benzene in ethanol at 160°C over a nickel-chromium-kieselguhr (1:0.1:1) catalyst. They found that the chromium exerted a promoting action only when it was added to the nickel by coprecipitation. Catalysts prepared by mechanical mixing gave no evidence of promotion.

The poisoning effect of certain materials, particularly thiophene on the hydrogenation of benzene, is well established. Truffault[399] studied the poisoning action of several compounds for the hydrogenation of benzene over nickel at room temperature. He found that with 3 grams of nickel the rate of hydrogenation was decreased 50 per cent by the indicated amounts of each of the following materials:

thiophene	0.6 mg
ethyl bromide	1 mg
chlorobenzene	3 mg
bromobenzene	15 mg
water	100 mg

Roberti[306] found that 0.01 per cent of thiophene in benzene poisoned a nickel catalyst for the vapor phase addition of hydrogen to benzene at 175°C, and that subsequent treatment with hydrogen did not restore its activity. Yoshikawa[455] compared the activities of pure nickel and nickel-copper catalysts by studies of the poisoning action of thiophene in the hydrogenation of benzene. (The more active portions of the catalyst are more easily poisoned than less active areas.) He found that the addition of copper to nickel decreases the more active and increases the less active parts. For a reaction requiring high catalytic activity such as benzene hydrogenation, a nickel copper catalyst is inferior to pure nickel, but where a catalyst of lower activity is satisfactory (as for the hydrogenation of nitrobenzene to aniline) a nickel-copper catalyst has a greater activity than pure nickel.

Rubinshtein and Pribytkova[313] prepared magnesia supported nickel catalysts of different grain sizes and studied the activity of these toward the hydrogenation of benzene and the reverse dehydrogenation of cyclohexane. These authors discovered that when enough thiophene was present to poison completely the ability of the catalyst to promote the hydrogenation of benzene, the nickel was still active toward the reverse reaction. When 3-gram portions of the catalyst were exposed to 10 mg of thiophene in cyclohexane solution, each treatment resulted in the retention of 1.0 mg of sulfur per gram of catalyst. Hydrogenation experiments were carried out at 120, 140 and 160°C while dehydrogenations were studied at 300, 325 and 350°C. Space velocities for both experiments were 1.2 liters liquid per liter of catalyst per hour. With a catalyst containing 24Å nickel crystals and 32.2Å MgO crystals, the hydrogenation reaction dropped from 90 per cent conversion with no sulfur to no conversion when about 3 mg of sulfur per gram of catalyst was present. For the dehydrogenation reaction, much the same activity of the catalyst was found throughout this range of sulfur content. With increasing amounts of sulfur, the rate of the dehydrogenation reaction decreased until with 7 mg of sulfur per gram of catalyst about 20 per cent conversion was obtained.

The authors state that this means that the centers of activation of hydrogen are eliminated exclusively by the first 3 mg of sulfur, and that dehydrogenation centers will be eliminated only after hydrogenation centers have been filled. As the size of the nickel crystals is increased from 24 to 66Å, the amount of sulfur necessary to poison 1 gram of catalyst for hydrogenation decreases from 3 to 0.5 mg, while the amount necessary to reduce the dehydrogenation activity from 63 to 20 per cent decreases from 7 to 0.5 mg of sulfur. Apparently the number of active centers is much greater in the more disperse catalyst.

With increasing sulfur content the activation energy for the dehydrogenation reaction increased showing again that the more active centers are those which are most readily poisoned[307]. The hydrogenation of benzene at 420 and 450°C and pressures of 180 to 220 atmospheres has been studied over a number of oxide and sulfide catalysts[216]. The following showed no activity: SnO_2, TiO_2, V_2O_5, Cr_2O_3, WO_3, Fe_2O_3, Fe, SnS, V_2S_3, FeS, CoS and NiS. MoO_3, MoS_3, MoS_2 and WS_2 showed limited activity.

The mechanism for the hydrogenation of benzene, particularly on platinum and nickel, has been the subject of considerable discussion. In general, the reaction is zero order with respect to benzene and first order with respect to hydrogen either in the gas or liquid phases[98, 118, 147, 367, 368], although exceptions have been reported. For instance Herbo[130] found that with nickel catalysts at atmospheric pressure in a flow system the reaction is zero order with respect to benzene and first with respect to hydrogen up to around 180°C while at higher temperatures the reverse is true. Lozovoy and Dyakova[210, 211] also noted a reversal of order with respect to the benzene and hydrogen with variation in the temperature. This change in order is probably evidence that the benzene molecule is more strongly adsorbed than hydrogen at low temperatures, but this relationship is reversed at higher ones. It has been shown that on nickel and platinum catalysts the conversion of *para* to *ortho* hydrogen takes place readily[95, 98, 141], and that the activation energy for exchange on both catalysts is much lower than for ethylene. These kinetic order changes for hydrogenation, plus the *para-ortho* hydrogen conversion and exchange experiments are all evidence of the fact that benzene adsorption is relatively weak when compared with simple unsaturated molecules such as ethylene. This difference is probably caused by the necessity of overcoming the resonance energy when adsorption takes place[94, 367]

Alchudzhan and Vredenskii[17, 18] studied the hydrogenation of benzene over nickel over the temperature range 100 to 227°C in the vapor state. They found that the rate passed through a maximum around 150 to 170°C. They found that in regions of high benzene vapor pressure (0.5 to 0.8 atm.) the reaction rate is directly proportion to hydrogen pressure and independent of benzene pressure; for low benzene pressures, the kinetic orders are reversed.

These authors also observed that after a change of operating temperature during the hydrogenation of benzene, the activity of the catalyst does not reach its equilibrium value at once, but changes with time till a constant value is reached. Treatment of the catalyst with benzene destroys its activity while treatment with hydrogen causes an increase. In either case, contact with a standard reaction mixture for a sufficiently long time restores the catalyst to standard activity.

It is difficult to distinguish between two possibilities for the mechanism of benzene hydrogenation. According to one mechanism, generally known as the adjacent interaction mechanism[94, 130, 138, 190], two reacting molecules are adsorbed on adjacent sites in a chemisorbed monolayer and, after interaction in the monolayer, the product is desorbed. Herbo[131] interprets the hydrogenation of benzene over a nickel catalyst promoted with zinc oxide and chromium oxide as taking place between adjacent adsorbed molecules, and suggests that these sites are located at the interface between the promoter and the nickel surface. He proposes that the mechanism of the hydrogenation reaction involves the transfer of electrons between the nickel and the oxide promoter. This worker also studied the hydrogenation of benzene over a number of nickel-beryllium oxide catalysts, and suggests that the variation in activity of the catalysts is caused by changes in the number but not the quality of active centers[132].

The second possibility is that one reacting species is chemisorbed on the catalyst surface and molecules of the other species react with it from the gas phase or van der Waals layer. This mechanism has been called the van der Waals-chemisorbed layer interaction[94, 304, 305]. The changes in kinetic order with temperature as well as the hydrogenation of certain nitro compounds[360] and the influence of these on hydrogen-deuterium exchange[199] may be readily explained on the basis of such postulates.

Pullman and Daudel[295] and Maccoll[220] discuss the hydrogenation of benzene in terms of charge distribution. The former workers state that hydrogen will add to the most highly charged bonds of organic compounds. Benzene is stated to have six bonds of low charge, and hence it hydrogenates with difficulty. However, any partially hydrogenated intermediate has more highly charged bonds, and so the hydrogenation of benzene proceeds directly to cyclohexane.

Beeck and Ritchie[49] studied the hydrogenation of benzene over oriented and unoriented films of nickel and iron and reported that the rates were slow and about the same. They further reported that the reaction proceeded through the adsorbed state of benzene without influence by the crystal geometry of the substrate. This is, of course, contrary to the hypothesis of Balandin[39] which has been discussed earlier.

Anderson and Kemball[19a] investigated the catalytic deuteration and exchange of benzene over an evaporated metallic film. Primarily platinum and palladium were used, but some experiments were carried out with nickel, tungsten, iron and silver. These authors state that the deuteration of benzene seems to be limited to the addition of deuterium without additional exchange. This is quite unlike the deuteration of olefins which is accompanied by considerable redistribution of deuterium in the paraffin produced. Furthermore, the activities of various metals for the deuteration of benzene are not at all in the same order as for the hydrogenation of ethylene, and bear no relation to the percentage *d*-bond character of the intermetallic bonds.

Alkyl-substituted Benzenes

The hydrogenation of alkyl-substituted benzenes has received considerable study both from the standpoint of the preparation of cyclohexane derivatives with substituents *cis* to each other and from the standpoint of the influence of alkyl substituents on the rate of hydrogenation of the benzene ring.

In 1922, Skita and Schneck hydrogenated the three xylenes, *p*-cymene and pseudocumene (1,2,4-trimethyl benzene)[353]. They used a colloidal platinum catalyst for the reaction which was performed at 80°C and 3 atmospheres hydrogen pressure. The three xylenes gave predominantly *cis*-dimethylcyclohexanes, the *p*-cymene gave *cis*-*p*-methane, and 1^C, 2^C, 4^C-trimethylcyclohexane was obtained from the pseudocumene. It had been previously shown that reduction of such compounds over nickel at higher temperatures and with 30 kg/cm^2 pressure of hydrogen gave products in the *trans* form. It is not unlikely that the *cis* configurations were also formed over nickel, but underwent isomerization to the thermodynamically more stable *trans* forms at the temperature employed. Dyakova, Lozovoy and Stepantsova[91, 92] hydrogenated the three xylenes, propylbenzene, durene, pentamethylbenzene and hexamethylbenzene with hydrogen pressures of 120 to 230 atmospheres, temperatures of 200 to 240°C and a nickel (introduced as oxide) catalyst. They found that their products were mixtures of *cis* and *trans* forms. Smith and Pennekamp[369] studied the hydrogenation of all possible methyl-substituted benzenes. They used hydrogen at 60–65 psia and worked at approximately 30°C. The boiling ranges of the methylcyclohexanes produced indicated the presence of some *trans* forms in virtually all cases, although the configurations of the products were probably primarily *cis*. Margolis[225] found that hydrogenation of *ortho* and *para* xylenes over osmium (50 to 70°C) yielded *cis*-dimethylcyclohexanes while over nickel the *trans* forms were produced.

Of the studies dealing with the influence of alkyl substituents on the rate of benzene hydrogenation, Lozovoy and Dyakova worked with one of the most complete series of compounds[90, 211]. These experimenters determined the hydrogenation velocities over a nickel alumina catalyst of *n*-alkyl benzenes from toluene to octylbenzene, and showed that the lengthening of the aliphatic side chain had little influence on the velocity with which hydrogen was absorbed. They also found that branching on a side chain had little influence on the hydrogenation velocity. Thus, normal amylbenzene and isoamylbenzene were reduced at identical rates, as were also 1-methyl-4-propylbenzene and *p*-cymene (1-methyl-4-isopropylbenzene). *Ortho*-xylene, tetralin and 1-methyl-2-propylbenzene all underwent hydrogenation at the same rate.

Nikolaeva and Puchkov[259] reported quite different results when they hydrogenated benzene, toluene, ethyl-, propyl-, butyl- and isoamylbenzenes. They used colloidal platinum as catalyst with the solvent acetic acid, room temperature and 4 atmospheres hydrogen pressure. Hydrogenation of all compounds proceeded to completion. These authors concluded that the rate of hydrogenation of the monosubstituted hydrocarbons diminished in the order of increasing molecular weight. Adams and Marshall[1] came to a similar conclusion when hydrogenations were carried out over Adams platinum.

One explanation for the discrepancies found lies in the methods of determining the velocities of hydrogenation. Adams and Marshall, for instance, determined the time necessary for the complete hydrogenation of 0.1 or 0.2 mole of alkylbenzene in 50 cc of acetic acid with 2 to 3 atmospheres hydrogen pressure and 0.2 gram of platinum oxide. For some of the compounds studied it was necessary to use several additional portions of catalyst in order to effect the reduction. Adams and Marshall state that "in general, the rate of reaction of these aromatic compounds seemed to be very dependent on the purity of compounds and reagents." It is apparent that under these circumstances the times for total reduction are not too reliable as far as quantitative estimation of the influence of structure on rate is concerned. Lozovoy and Diakova carried out their studies in a rocking autoclave equipped with a valve through which could be bled off a small sample of the liquid in the apparatus. The composition of this liquid was determined by refractive index measurements. The rate of reaction was determined by periodic sampling of the liquid.

Smith and Pennekamp[368] studied the rates of hydrogenation of monoalkylbenzenes by following the rate of pressure drop when the alkylbenzenes were hydrogenated over platinum oxide catalyst in glacial acetic acid solution with hydrogen pressures of about 4 atmospheres. They showed that the hydrogenation rate was first order with respect to hydrogen pressure, zero order with respect to the concentration of the material undergoing hydrogenation (pure acetic acid was used as solvent) and directly proportional to the amount of catalyst used provided this amount was sufficiently small. If too much catalyst was employed, the rate of the reaction depended on the rate of agitation of the reaction vessel. For low agitation rates or high catalyst weights the rate of hydrogenation was governed by diffusion processes rather than the kinetics of the reaction itself. The activity of each batch of platinum oxide used was corrected to a standard value by measuring the hydrogenation rate for benzoic acid and correcting the catalytic activity accordingly. The standard value for benzoic acid was the average experimental value found with a number of catalyst samples. In general these corrections were less than 5 per cent. The rate constants, all referred to 1 gram of standard catalyst and 1 liter system volume[112, 188], are given in Table 2. It can be seen that increasing the length of the alkyl group causes some dimunition in rate for the first two carbon atoms. Further increase has little influence. The results with branched-chain-substituents indicate that branching influences the hydrogenation rate only when such branching occurs close to the benzene nucleus.

The hydrogenation of polyalkylbenzenes has also been studied by several investigators. Sil'chenko[344] hydrogenated benzene, toluene and xylene at 189 to 190°C at elevated hydrogen pressures over a nickel-cobalt-aluminum catalyst. Mesitylene was hydrogenated to hexahydromesytilene by Turova-Pollak and Sidel'kovskoya[403]. Foresti[102] carried out the hydrogenation of benzene, toluene, *o*-xylene, *p*-xylene, *p*-cymene and mesitylene in solution with a platinum catalyst. He found that the velocity of hydrogenation of these compounds varied with the pH of the media, changing rapidly in acid but slowly in alkaline solutions; in the latter, hydrogenation was quite slow. He calculated a coefficient, K, defined by the equation

TABLE 2. STANDARD HYDROGENATION RATE CONSTANTS FOR MONOALKYLBENZENES ON PLATINUM

Compound	k_{30° (liters grams^{-1} min.$^{-1}$)
Benzene	0.288
Toluene	.178
Ethylbenzene	.130
n-Propylbenzene	.117
n-Butylbenzene	.108
n-Amylbenzene	.117
n-Hexylbenzene	.111
n-Nonylbenzene	.112
i-Propylbenzene	.096
i-Butylbenzene	.067
s-Butylbenzene	.084
t-Butylbenzene	.074
i-Amylbenzene	.121

$$K = \Delta V/V_1\Delta(\text{pH})$$

where ΔV is the change in hydrogenation velocity and V_1 is the maximum velocity. He states that K was, on the average, constant, and attributes this to similar bond characteristics in the benzene homologs. Similar studies with olefinic compounds[102] showed that K for monoolefines was -0.005 to -0.0238, for cyclopentadiene, -0.0389 and for the benzene homologs -0.171. These values reflect the influence of conjugation in double-bond systems.

Ruiter and Jungers[316] studied the hydrogenation in the liquid phase over nickel of a number of compounds including benzene, toluene and mixed xylenes; they observed that the reaction was zero order in alcohol solvents, with activation energies of 8000 to 12,000 calories. They found greater dependence on the hydrogen pressure than on molecular complexity.

Akhmedli[15, 16] hydrogenated benzene, toluene and xylene over nickel and cobalt both free and as supported catalysts, and determined the temperatures for complete reduction. The results are shown in Table 3. This investigator states that the rate of hydrogenation is given by the order

$$C_6H_6 > C_6H_5CH_3 > C_6H_5(CH_3)_2$$

Siegel and Dunkel[342a] studied the hydrogenation of eight isomers of dimethylcyclohexene and of the xylenes over Adams platinum catalyst in glacial acetic acid at room temperature and 35 psi hydrogen pressure and determined the distribution of the resulting dimethylcyclohexanes by two independent methods. They found that the per cent of *cis* isomer from xylene hydrogenation decreased in the order ortho > meta > para, and that the same pattern was followed in the hydrogenation of the isomeric olefins. The *trans* isomer was not formed by isomerization of the saturated *cis* form since more *trans*-1,3-dimethylcyclohexane was produced from *m*-xylene than is present in an equilibrium mixture of *cis*- and *trans*-1,3-dimethylcyclohexane. They conclude that the hydrogenation of the xylenes proceeds through stages, the latter ones in the sequence coinciding with those in the reduction of related olefins. They further conclude that the olefin intermediates must escape from the catalyst surface enough to undergo molecular rotations, though they would probably not be detected due to the fact that they react more rapidly than the xylenes. They claim that this refutes the hypothesis that an aromatic ring is reduced in a single stage[204]. It has already been indicated that free energy calculations indicate the thermodynamic improbability of a cyclohexadiene-type intermediate[159], though a cyclohexene type is possible, and is suggested in connection with phenols where the intermediates may isomerize to ketones. This is discussed in a subsequent section.

TABLE 3. TEMPERATURES FOR COMPLETE REDUCTION OF BENZENE HOMOLOGS

	Benzene	Toluene	Xylene
Pure Cobalt (by reduction of formate)	172°	208°	228°
Co (61.5%) on asbestos	105	100	92
Co (68.75%) on alumina	85	82	41
Co (61.54%) on chromia	42	94	139
Pure nickel (reduced)	92	111	140
Ni on asbestos	76	49	50
Ni on alumina	80	75	68
Ni on chromia	140	135	127

Lozovoy and Diakova[89, 210, 212] made a careful study of the rate of hydrogenation of a number of methyl substituted benzenes over a nickel-alumina catalyst. They suggested that an accumulation of methyl groups hindered hydrogenation, and that the rate could be approximated by the formula

$$V_n = 2^{-n}V$$

where n is the number of substituents and V is the velocity of hydrogenation of benzene. Smith and Pennekamp[369] using platinum catalyst and acetic acid solvent, studied the rate of hydrogenation of all of the methyl-substituted benzenes plus isopropyl benzene and *p*-cymene. The standard rate constants are given in Table 4 together with relative rates of hydrogenation for both the studies of Lozovoy and Dyakova and Smith and Pennekamp. From the data given it is obvious that, while there is a general decrease in rate with an increasing number of substituents, there are also several exceptions. Thus, *p*-xylene with two substituents undergoes hydrogenation more rapidly than toluene with only one; mesitylene (1,3,5-trimethylbenzene) with three substituents is reduced more rapidly than either *o*-or *m*-xylene each with two methyl groups, and durene (1,2,4,5-

TABLE 4. HYDROGENATION RATES FOR THE POLYALKYL BENZENES

Compound	k° liters grams^{-1} min.$^{-1}$ Smith and Pennekamp	Relative Rates		
		Smith and Pennekamp	Lozovoy and Dyakova	Calculated from $V_n = 2^{-n}V$
Benzene	0.288	100	100	100
Toluene	.188	62	50	50
o-Xylene	.092	32	24	25
m-Xylene	.142	49	23	25
p-Xylene	.186	65	31	25
1,2,3-Trimethylbenzene	.041	14		12.5
1,2,4-Trimethylbenzene	.084	29		12.5
1,3,5-Trimethylbenzene	.166	58	10	12.5
1,2,3,4-Tetramethylbenzene	.028	10		6.3
1,2,3,5-Tetramethylbenzene	.033	11		6.3
1,2,4,5-Tetramethylbenzene	.052	18	3.8	6.3
Pentamethylbenzene	.010	3.5	0.5	3.2
Hexamethylbenzene	.006	0.2	too small to record	1.6
Isopropylbenzene	.096	33		50
p-Methylisopropylbenzene	.124	43	33	25

tetramethylbenzene) is hydrogenated more rapidly than hemimellitene (1,2,3-trimethylbenzene). An examination of the structure of these compounds shows that an additional factor besides the number of total substituents influences the rate of reduction, and this factor is apparently symmetry of substitution. Thus, for any given number of substituents, the isomer which is most symmetrically substituted shows the greatest hydrogenation velocity. This is a question of symmetry of substitution and not molecular symmetry itself as is shown by the fact that *p*-cymene (*p*-methylisopropylbenzene) is reduced more rapidly than isopropylbenzene.

There are at least two possible explanations for this phenomenon. It may be that a polymethylbenzene molecule undergoes activated adsorption on the surface of the catalyst in such a manner that the methyl groups tend to be oriented away from the surface, and their presence retards the approach of hydrogen to the benzene nucleus. It may be readily seen that the more symmetrical the substitution, the less interference there would be to the approach of hydrogen if it comes directly from the gas phase. Another possible explanation may be found if it is assumed that the benzene nucleus must be adsorbed so as to "fit" the catalyst in a flat position as suggested by Balandin. The more symmetrically substituted molecules could be expected to make a better fit, and hence undergo more rapid reaction.

Lozovoy and Senyavin[214a] also investigated the addition of hydrogen to alkylbenzenes over tungsten disulfide catalyst at temperatures of 420°C and 200 atm. pressure. They found that benzene was reduced the slowest, and that the order of the reaction was approximately 1.5. Apparent activation energies for benzene and toluene were 21 to 25 kcal. The relative rates of reduction were as follows:

benzene	1
toluene	2.3
m-xylene	3.3
mesitylene	4.3
pentamethylbenzene	6.3
hexamethylbenzene	1.5

It is apparent that the explanations given above for reactions over nickel or platinum are not applicable when tungsten sulfide is the catalyst.

Several studies of hydrogenation of higher alkylbenzenes are reported. Kalsuno and Suwa[170] prepared *tert*-butylcyclohexane and 1,4-di-*tert*-butylcyclohexane by hydrogenation over nickel on kieselguhr of the corresponding benzene derivatives. Octadecylbenzene may be hydrogenated to octadecylcyclohexane at 200 to 260°C over nickel on kieselguhr at high hydrogen pressures[436]. Denisenko and Naber[82a] hydrogenated phenylcyclopentylhexane over platinized charcoal at 230°C to form cyclohexylcyclopentylhexane.

Phenols

When phenol undergoes hydrogenation, the product may be predominantly cyclohexanol, benzene, or cyclohexane, depending on the catalyst employed and the conditions of the reaction. The two courses of the reaction are represented by the equations:

1. $C_6H_5OH + 3H_2 \rightarrow C_6H_{11}OH$

2. (a) $C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$

(b) $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$.

It has long been recognized that cyclohexanone may be isolated during the course of the reaction, and the role of this compound as an intermediate has been investigated.

Vavon and Berton[418] hydrogenated phenol and cresols over platinum black. They isolated cyclohexanone as an intermediate in the reduction of phenol by reaction of the ketone with semicarbazide and isolation of the semicarbazone formed. It was proposed that cyclohexanone is the first product of the reaction and is desorbed. It later returns to the catalyst and there transfers hydrogen to phenol. Grignard and Mingasson[120] studied the hydrogenation of phenol in the solvent cyclohexanol with pumice-supported nickel (from the hydroxide) as catalyst and temperatures up to 300°C. For each pressure investigated they observed a critical temperature at which cyclohexanol is dehydrogenated to cyclohexanone; e.g., 155°C at around 20 mm and 180°C at 760 mm. They suggested that the noncontiguous double linkages of the phenol are first hydrogenated to form the enol of cyclohexanone, and that this enol is tautomerized when cyclohexanone is isolated, but absorbs hydrogen to give cyclohexanol if the hydrogenation is prolonged. If the hydrogenation is carried out above the critical decomposition temperature, cyclohexanone is formed by secondary decomposition.

Ando[21, 22] investigated the formation of various products in the hydrogenation of phenol over nickel. With a 5:1 ratio of hydrogen to phenol and initial hydrogen pressure of 117 atmospheres, the reaction began at 160°C, with cyclohexanol as the main product and cyclohexanone as intermediate up to 260°C. Above 260°C, cyclohexanol decomposed to the intermediate cyclohexene which was reduced to cyclohexane. The latter was stable up to 470°C. In the absence of the catalyst, cyclohexanol and hydrogen with an initial pressure of 49 atmospheres gave little cyclohexane when heated to 389°C, while in the presence of a catalyst, the cyclohexanol was converted (87 per cent) to cyclohexane.

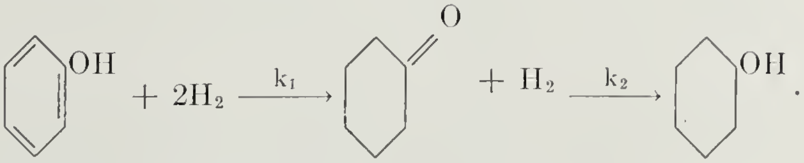
Barney and Haas[47] studied the hydrogenation of thymol over Raney nickel in connection with the synthesis of menthol. They investigated the influence of temperature and pressure on the formation of the ketone intermediate. The results of their studies (Table 5) indicate that both increasing pressure and increasing temperature decrease the per cent of ketones present in the reaction mixture. Higher conversion of the thymol to hydrogenated products increased the reduction of the ketone to alcohol. Whitaker[438] prepared a number of substituted cyclohexanones and cyclohexanols by controlled hydrogenation of polyalkylphenols.

Coussemant and Jungers[72, 165] made a thorough study of the kinetics of catalytic hydrogenation of phenol over Raney nickel. By combining information on hydrogen absorbed plus refractive index, it was possible to ascertain the percentages of phenol, cyclohexanol and cyclohexanone present at any stage of the reaction. Their analytical method was checked by reaction of the ketone with hydroxylamine hydrochloride and titration of the acid liberated.

TABLE 5. INFLUENCE OF TEMPERATURE AND PRESSURE ON HYDROGENATION OF THYMOL

Initial Pressure (psi)	Temperature (°C)	% Ketone	% Alcohol	% Conversion
600	150–160	80	20	65
800	150–160	50	50	70
1000	170–190	30	70	75

The distribution of phenol, cyclohexanone and cyclohexanol at various stages of the reaction is shown in Figure 1. It is readily seen that the cyclohexanone concentration reaches a maximum during the reaction, and that the fraction present at this maximum depends on the temperature. They concluded that the mechanism of the nickel-catalyzed reaction was



By studying the hydrogenation of pure cyclohexanone, the authors found that the activation energy for the reduction of this ketone was 6,500 calories per mole while that for the reduction of phenol to cyclohexanone over the same catalyst was 8,500. The ratio k_2/k_1 was 1.95 at 174°C, and 3.0

at 113°C. This accounts for increased maximum yields of cyclohexanone as the temperature is increased (see Figure 1). These authors made a complete kinetic analysis of this reduction which has general application to two-step catalytic reactions.

If C represents molar concentration, k represents specific reaction rate constant, and b the coefficient of adsorption, while the subscripts 1, 2, and

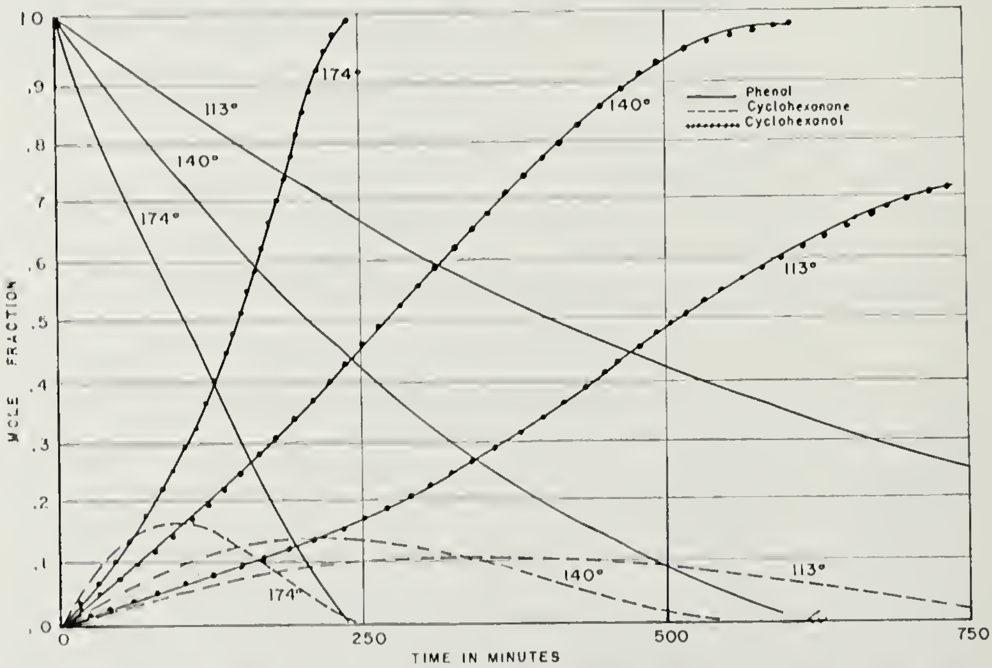


Figure 1. Hydrogenation of phenol over Raney nickel[72]. (From an article by Coussemant and Jungers, Ref. 72)

3 refer to phenol, cyclohexanone, and cyclohexanol, respectively, then

$$-\frac{dC_1}{dt} = k_1 \frac{b_1C_1}{b_1C_1 + b_2C_2 + b_3C_3} \cdot f(\mathrm{H}_2)$$

$$+\frac{dC_3}{dt} = k_2 \frac{b_2C_2}{b_1C_1 + b_2C_2 + b_3C_3} \cdot f(\mathrm{H}_2)$$

$$\frac{dC_2}{dt} = -\frac{dC_1}{dt} - \frac{dC_3}{dt} = \frac{k_1b_1C_1 - k_2b_2C_2}{b_1C_1 + b_2C_2 + b_3C_3} \cdot f(\mathrm{H}_2)$$

By combining these expressions, it can be shown that when the concentration of cyclohexanone is at its maximum value,

$$C_2 = K^{K/1-K}$$

and

$$C_1 = K^{1/1-K}$$

where

$$K = \frac{k_2 b_2}{k_1 b_1}.$$

Since k_1 and k_2 can be evaluated from experimental data, the ratio of the adsorption coefficients b_2/b_1 can be calculated, and was found to vary between 1.8 and 1.6 over the temperature range 113 to 174°C.

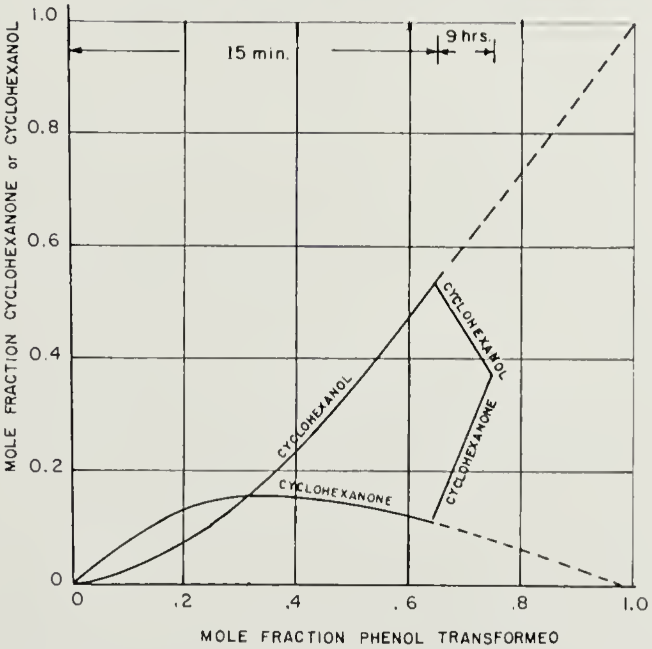


Figure 2. Hydrogenation of phenol[72] (15 min.) followed by hydrogen transfer from cyclohexanol (9 hours). (From an article by Coussemant and Jungers, Ref. 72)

The complete kinetic analysis of this reaction is complicated by the fact that the cyclohexanol formed reacts slowly with the original phenol to form cyclohexanone. This is shown by Figure 2. Here phenol was hydrogenated to 61 per cent completion of reduction after which the reaction mixture was allowed to equilibrate over the catalyst without additional hydrogen. This hydrogen transfer reaction is very slow below 150°C, but increases rapidly with increasing temperature.

Zil'berman[464] studied the free energy changes accompanying the hydrogenation of phenol to cyclohexanone and cyclohexanol, and set up equations relating such free energy changes to reaction temperature. d'Or and

Orzechowski[83] studied the vapor phase hydrogenation of phenol over cerium oxide supported nickel catalysts. From investigations of adsorption of reactants and products on the catalyst at various temperatures, these authors concluded that the reaction must take place between adsorbed hydrogen atoms and gaseous phenol. On the basis of further studies of this same reaction, Orzechowski[271] concluded that the vapor phase hydrogenation of phenol over the nickel-cerium oxide catalyst proceeds through the intermediate cyclohexanone, and that the process is reversible.

Ungnade and McLaren[407] studied the preparation of cyclohexanols by catalytic reduction of phenols. By adding a small amount of aqueous sodium hydroxide to the phenols, these authors were able to reduce substituted phenols and obtain high yields of the corresponding cyclohexanols. These reactions did not occur to an appreciable extent without the addition of the base. The catalyst was Raney nickel, pressures ranged from 100 to 300 atmospheres, and the temperature used varied with the particular compound reduced. In general, alkyl phenols were reduced in the temperature range 100 to 200°C, although higher temperatures were necessary for the phenols with substituents in both *ortho* positions. These were not reduced to cyclohexanols in the absence of alkali. Alkenyl and acylphenols were readily reduced, first to the corresponding alkylphenol and then to the cyclohexanol.

Further work by Ungnade and Nightingale[408] showed that the addition of solid sodium hydroxide to form a small amount of phenoxide caused phenol and alkylphenols to undergo hydrogenation more rapidly and at lower temperatures than was found for the phenols alone. Water hindered the hydrogenation.

These workers also observed that in the absence of sodium phenoxides, the order of ease of hydrogenation for the cresols was similar to that observed for the xylenes[369], i.e., *para* > *meta* > *ortho*. Similarly with the xylenols, the symmetrically substituted 3,5-dimethylphenol was the most readily hydrogenated, while those with *o*-methyl groups were the most difficult to reduce. In the presence of 0.3 mole per cent sodium phenoxide, hydrogenation of each cresol (0.5 moles with 3 grams of Raney nickel and 130 to 150 atmospheres hydrogen pressure) started at 60°C and was complete in one-half hour. In the presence of 0.4 mole per cent of their sodium salts, all of the xylenols tested were completely reduced to cyclohexanols in three-tenths of an hour at 170°C and in all cases the absorption of hydrogen started at 85°C. In general the presence of the sodium salt had little effect on the particular isomer produced by the reduction. For the cresols, these were always the *trans* forms.

Yamamoto[454] also studied the velocity of hydrogenation of the cresols over nickel catalysts. He also obtained the *trans* methylcyclohexanols as products. He found that the ease of hydrogenation as indicated by initial reaction temperatures was *para* > *meta* > *ortho*. However, this same order was not followed when the velocity of hydrogenation was measured. Macbeth and Mills[219] state that *m*-cresol in ethanol when hydrogenated over Raney nickel for 1½ hours at 200°C and 1000 psi pressure forms *trans*-dl-3-methylcyclohexanol, while dl-3-methylcyclohexanone in ethanol when hydrogenated over the same catalyst for 2 hours at 140°C and 1800 psi pressure gives primarily *cis*-dl-3-methylcyclohexanol. Other workers who studied the catalytic hydrogenation of phenol and cresols, usually over some form of nickel catalyst, to give cyclohexanols include Schrauth[329], Brochet[57], Armstrong and Hilditch[28], Tishchenko and Belopolskii[391], Komatsu, Tanaka and Waida[184], Fujita[109], Braun and Irmisch[56], Orloff, Shestakovskii and Shabaroff[270], Belotzerkovsky[50], Bag, Egupoff, and Volokitin[32], Sasa[325a], Slavik and Jansa[354], and Jackman, Macbeth, and Mills[158]. Yuknovskii and Sorokin[456] state that cobalt and copper in the catalyst are beneficial. Komatsu and Hagiwara[181] examined the reduction of phenol at 250°C in the presence of copper and hydrogen at 85 atmospheres pressure. They obtained a product consisting primarily of cyclohexanol, with some cyclohexane and dicyclohexyl ether. D'Or and Orzechowski[84] made a series of mixed nickel and cerium oxide catalysts and studied the reduction of phenol to cyclohexanol. They measured the actual nickel surface of these catalysts by adsorption of hydrogen at 180°C and 1 atmosphere pressure. (Only the nickel adsorbs hydrogen under these conditions.) For the most active catalysts, the activity per unit area is equivalent to that of pure nickel while for inactive catalysts (low nickel content) the fraction of surface occupied by nickel is much too high for this correlation.

Benzene rings containing more than one OH substituent have also been reduced to the corresponding cyclohexanepolyols[154]. Senderens and Aboulenc[334] hydrogenated quinols in alcohol or water over nickel with pressures of 30 kg per square centimeter to produce cyclohexanediols. Resorcinol may be hydrogenated in the presence of alkali over Raney nickel at 50°C and 1000 to 1500 psi pressure to form the diketone, dihydroresorcinol, in high yields[390]. Such diketones may be further hydrogenated to form cyclohexanediols and cyclohexanols[129]. Fujita[110, 111] hydrogenated the isomeric dihydroxyphenols and several trihydroxyphenols as well as the isomeric aminophenols over nickel at 320°C and obtained primarily cyclohexanediols, triols, and aminocyclohexanols. Pyrochatechol and 3,5-dipropylpyrochatechol have been reduced at 140 to 160°C over Raney nickel in the presence of absolute ethanol, sodium hydroxide, and 2000 psi hydrogen pressure to form 1,2-cyclohexanediols[96]. Pyrogallol in ethanol has been reduced over Raney nickel at 165°C and 3000 psi hydrogen pressure to form a mixture of 1,2,3-cyclohexanetriols[70]. The reduction may also be carried out over copper chromite or palladium. The product is mainly *cis, cis, cis*-1,2,3-cyclohexanetriol with minor amounts of the *cis, cis, trans* and *cis, trans, cis* configurations[68]. Hexahydroxybenzene has been reportedly hydrogenated over platinum to give good yields of *meso*-inositol[441], although others have reported failure to achieve such results[20, 377]. The reduction of hexahydroxybenzene has also been carried out in ethanol or ethanol-water over Raney nickel at 175 to 190°C and 1910 psi hydrogen pressure to yield a mixture of isomeric cyclitols from which five crystalline forms have been isolated[20].

As mentioned at the beginning of this section, phenols may also be reduced to form aromatic hydrocarbons, cyclohexanone and aliphatic compounds resulting from ring cleavage. The hydroxybenzene to be reduced has generally been treated with hydrogen at 300 to 500°C and pressures of from 50 to 150 atmospheres. Molybdenum sulfide has been used as the catalyst[244, 245, 247, 248, 397] although molybdenum oxide alone[23] or in the presence of oxides of aluminum, silicon, chromium, and barium[34, 119] as well as ammonium molybdate[65] have been employed. Other catalysts include tungsten oxide and sulfide, cobalt oxide and sulfide and nickel oxide[216, 306, 396, 398]. This process was of some interest in England and Russia around 1930–1935 as a possible method of producing hydrocarbons for gasoline.

Ethers

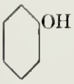
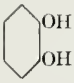
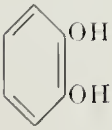
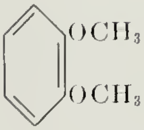
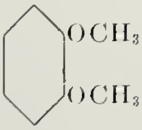
It has been known for many years that ether linkages attached to the benzene ring are not particularly resistant to reducing agents. Under the conditions necessary for catalytic hydrogenation of the benzene nucleus, cleavage of the ether linkage is quite common. Most literature reports simply relate that such a linkage was broken during hydrogenation. This phenomenon has occasionally been an aid in organic synthesis, but many times the loss during catalytic hydrogenation of a group attached to the benzene ring has been an unwanted and unexpected result.

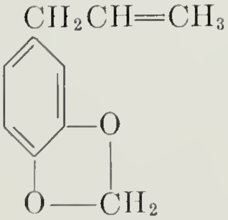
The splitting of a phenyl alkyl ether may or may not be complete depending upon the catalyst, compound, and reaction conditions. In addition, cleavage may occur in the C—O bond adjacent to the benzene ring or that involving the alkyl group. Probably both cleavages occur to some extent in most cases, but cleavage of the C—O bond adjacent to the ring predominates in most work reported and is often the only one mentioned.

Ipatieff and Lugovoy[148, 149] reported that hydrogenation of anisole with nickel (oxide) at 240°C and 50 atmospheres hydrogen pressure gave 50 per cent hexahydroanisole plus some cyclohexane and cyclohexanol. The diethyl ether of catechol and the dimethyl ethers of resorcinol and hydroquinone were also reduced under the same conditions. For all three compounds a certain amount of splitting occurred so that the products were mixtures.

Amatatsu[19] found that hydrogenation of the dimethyl ether of catechol yielded several products, and compared the distribution of these with those obtained by reduction of catechol and the dimethyl ether of 1,2-cyclohexanediol. His reductions were carried out over nickel at pressures of 50 to 60 atmospheres and temperatures of 140 to 200°C. The results are shown in Table 6. He also hydrogenated safrol,

TABLE 6. REDUCTION PRODUCTS OF CATECHOL, CATECHOL DIMETHYL ETHER, AND 1,2-CYCLOHEXANEDIOL DIMETHYL ETHER

Starting Compound	Mole % 	Mole % 	Mole % 
	4	7	82
	7	21	68
	5	19	65



,

to propylcyclohexanol. On the basis of his experiments, he concluded that the velocity of splitting of the oxygen phenyl bond was in the order

$$\mathrm{OH} < \mathrm{OCH_3} < \text{—O—CH}_2\text{—O}.$$

Waser and co-workers[434] studied the hydrogenation of phenyl alkyl ethers over platinum black at room temperature and 1 atmosphere hydrogen pressure to obtain mixtures of compounds of the types $C_6H_{11}OR$, $C_6H_{11}OH$, C_6H_{12}, ROH, and RH. Their results indicated splitting at either the phenyl or alkyl ether linkage. Others who have studied the splitting of phenyl ethers over Raney nickel to form cyclohexanols and cyclohexanes include Van Duzee and Adkins[415], Ruggli, Leupin, and Businger who worked with *p*-methoxyphenol and *p*-methoxyphenylacetic acid[315], and Palfray and Gauthier[114, 277].

Schneider and Keller[326] report that the hydrogenation of trianisylbenzene takes place over Adams platinum catalyst with the absorption of more than 12 moles of hydrogen per mole of the trianisylbenzene to yield 1,3,5-tris(cyclohexyl)cyclohexane in better yields than when triphenylbenzene is hydrogenated under similar conditions. Similar splitting of the phenyl-oxygen bond with saturation of the benzene ring was found for anisole, *p*-methylanisole, anethole and dianisylethylene. Diphenyl ether reduced in the presence of nickel at 170 to 250°C and 60 atmospheres hydrogen pressure is reported to yield a mixture of cyclohexane and cyclohexanol[182].

The kinetics of hydrogenation of methoxybenzenes in acetic acid solution over Adams platinum and alumina supported rhodium catalysts have also been studied[374]. The reduction is first order with respect to hydrogen, zero order with respect to the methoxybenzene, and directly proportional to the catalyst weight under the conditions of agitation employed. Rate constants for the platinum-catalyzed reactions calculated from the equation

$$\log p = \log p_0 + \frac{k}{V} t$$

and referred to 1 gram of standard catalyst give values very close to those obtained for corresponding methylbenzenes. In the above equation, V refers to the total volume of hydrogen gas. Furthermore, the order of velocity of hydrogenation is anisole = 1,4-dimethoxybenzene > 1,3-dimethoxybenzene > 1,2-dimethoxybenzene > 1,2,3-trimethoxybenzene, which indicates the same influence of symmetrical substitution for methoxy- and methylbenzenes. This was true in spite of the fact that from 20 to 50 per cent of the methoxy groups were cleaved as indicated by hydrogen uptake. This splitting increased with increasing temperature (the range from 20 to 50°C was covered) and with the number of methoxy substituents. For the three isomeric dimethoxybenzenes, the fraction of methoxy groups cleaved during the reduction process was the same. Activation energies were in the range of 4500 to 6500 calories, which is to be compared with a figure of 7400 calories for the hydrogenation of benzene under similar conditions[367].

Over rhodium on alumina, the same kinetic laws were followed. The splitting was much less, ranging from about 2 per cent for anisole to 25 per cent for the dimethoxybenzenes. Again, the percentage splitting became greater as the temperature was increased. Activation energies for the reduction over the rhodium catalyst varied from 5000 to 8500 calories per mole.

Acids and Esters

A number of investigators have hydrogenated the benzene ring in the presence of carboxyl substituents. When such a group is attached directly to the ring, there is resonance interaction betseen the two; in the case of reactions involving the carboxyl group this is reflected by significant differences in rates of reaction when compared with those for similar reactions when the acid group is insulated from the benzene ring. For instance, the rate of esterification of benzoic acid in methanol at 25°C is 135 times slower than that for phenylacetic acid. This is reflected in a difference of more than 5000 calories in the activation energies[361]. In catalytic hydrogenation, such resonance interaction does not appear to influence the rate of hydrogenation of the benzene ring. This is illustrated in Table 7 which gives the rate constants for hydrogenation of some phenyl substituted acids over platinum catalysts[357]. Furthermore, the activation energies for hydrogenation of benzoic and phenylacetic acids are found to be the same. This has been interpreted to indicate that the resonance of the benzene ring is destroyed when it is adsorbed on a catalytic surface, and hence resonance between the benzene ring and carboxyl group is also removed. Table 7 also shows that the presence of both alkyl and carboxyl groups close to the benzene ring retards the hydrogenation rate.

Table 7. Rate Constants for Hydrogenation at 30°C of Some Phenyl-Substituted Acids over Platinum

Acid	k_{30} l. min.$^{-1}$ g^{-1}
Benzoic	.112
Phenylacetic	.112
β-Phenylpropionic	.097
γ-Phenylbutyric	.111
δ-Phenylvaleric	.108
α-Phenylpropionic	.039
α-Phenylbutyric	.013

Willstatter and Mayer[447] and also Waser[433] hydrogenated benzoic acid over platinum black in ethanol or water at room temperature to form cyclohexanecarboxylic acid. Over Adams platinum, the reduction proceeds only in acidic solvents such as glacial acetic acid[1] unless the alkaline constituents formed in the preparation of the catalyst are removed[173]. Komatsu and Mitsui[183, 241] hydrogenated ethyl benzoate over nickel at 225°C and 92 atmospheres pressure to form ethyl cyclohexanecarboxylate in quantitative yields. Benzoic acid may also be reduced over rhodium catalysts[35]. Smith and Schmehl[375] reduced the benzene ring in phenylstearic and phenylundecanoic acids in alcohol using pressures of 175 to 200 atmospheres and temperatures of 165 to 230°C. They also reduced phenylundecanoic acid in acetic acid solution over Adams platinum catalyst at 80°C.

The rates of hydrogenation over Adams platinum of methyl-substituted benzoic acids have been determined[372] and are given in Table 8. These rates show that hydrogenation is in general retarded by the accumulation of substituents on the benzene ring, although the influence of symmetrical substitution is clearly indicated; i.e., among benzene rings with the same substituents, those arranged symmetrically are reduced more rapidly than those in which substituents are in adjacent positions. A comparison of these rates with those of the methyl-substituted benzenes (Table 4) shows that the substitution of a carboxyl for a methyl group causes the hydrogenation rate to be decreased by a factor of about two and one-half.

TABLE 8. HYDROGENATION OF METHYL-SUBSTITUTED BENZOIC ACIDS OVER ADAMS PLATINUM CATALYST

Acid	$k_{30} \times 10^{4a}$
Benzoic	1120
2-Methyl-	312
3-Methyl-	813
4-Methyl-	942
2,6-Dimethyl-	200
2,3-Dimethyl-	186
2,5-Dimethyl-	404
2,4-Dimethyl-	289
3,4-Dimethyl-	350
3,5-Dimethyl-	641
2,3,4-Trimethyl-	83.6
2,3,6-Trimethyl-	77.4
2,4,6-Trimethyl-	209
2,4,5-Trimethyl-	211
2,3,4,6-Tetramethyl-	61.3
2,3,5,6-Tetramethyl	35.2
2,3,4,5,6-Pentamethyl-	23.2

[a] The units of k are liters grams^{-1} min.$^{-1}$. All rate constants are referred to a standard catalyst which gives the indicated value (1120) for hydrogenation of benzoic acid.

It has also been shown that certain salts of aromatic acids when mixed with nickel oxide and heated to 270 to 300°C under a hydrogen pressure of 80 atmospheres react to form salts of hexahydrobenzoic acid[148, 156, 157]. Sodium, lithium, calcium, and barium benzoates gave 60 per cent yields of the desired product. Potassium, zinc, nickel and iron salts were unsatisfactory for this purpose. Kahl and Biesalksi[169] bubbled hydrogen through a solution of sodium benzoate containing colloidal platinum, palladium or rhodium and a foam-producing agent, and reduced the benzene ring to yield sodium cyclohexanecarboxylate.

Reduction of the hydroxybenzoic acids has also been reported by several authors. Balas and Srol[40, 42] reduced *ortho-*, *meta-*, and *para*-hydroxybenzoic acids in alcohol with platinum black as catalyst and recovered the *cis* forms of the corresponding hydroxycyclohexanecarboxylic acids. Edson[93] reduced the same acids in water solution with platinum oxide catalyst and obtained mixtures of the hydroxycyclohexanecarboxylic acids with cyclohexanecarboxylic acid. The splitting of the hydroxy group was about 80 per cent for the *para* acid, 50 per cent for the *meta* acid, and 15 per cent for the *ortho* acid.

Lukes, Trojznek and Blaha[216a] also investigated the reduction of the isomeric hydroxybenzoic acids. They used platinum oxide in aqueous suspension at 21 to 25°C with about 740 mm hydrogen pressure. Hydrogenolysis increased in the order *ortho* (20.8 per cent) $<$ *meta* (67.8 per cent) $<$ *para* (84.5 per cent). Aquirreche also reduced salicylic acid over platinum oxide to form hexahydrosalicylic acid[25]. Hardegger and co-workers[125], however, reported that hydrogenolysis was the main reaction. Levin and Pendergrass[192] studied the low pressure hydrogenation of *meta-* and *para*-hydroxybenzoic acids over platinum oxide in 95 per cent ethanol, and reported that acidic reagents increased splitting to form greater percentages of unsubstituted cyclohexanecarboxylic acid, while basic reagents reduced hydrogenolysis, but also slowed down the over-all reaction rate. These authors also report that the low pressure hydrogenation of ethyl-*p*-hydroxybenzoate in ethyl acetate with palladium-on-strontium carbonate as catalyst resulted in a mixture of reduction products containing about 25 per cent of the ethyl cyclohexanecarboxylate and 75 per cent ethyl 4-hydroxycyclohexanecarboxylate. However, high pressure hydrogenation gave a quantitative yield of the hydroxy-ester. These experiments are claimed to indicate that hydrogenation and hydrogenolysis are competing reactions, with increased pressure favoring hydrogenation. Edson[93] had suggested that the *cis* acid formed by the hydrogenation of *para*-hydroxybenzoic acid is easily lactonized, and that hydrogenolysis of the lactone then gives cyclohexanecarboxylic acid. The experiments of Levin and Pendergrass indicate that this lactone mechanism is not entirely tenable, and the behavior of the esters indicates a different mechanism for hydrogenolysis which probably competes with the hydrogenation. *cis*-3-Hydroxycyclohexanecarboxylic acid was unchanged when subjected to hydrogenation over platinum. Levin and Pendergrass hydrogenated the sodium salt of *para*-hydroxybenzoic acid under high pressures over Raney nickel at 200 to 250°C and obtained mainly cyclohexanol. Mitsui[241] hydrogenated ethyl *ortho*-hydroxybenzoate over reduced nickel at 100 atmospheres pressure. He found no reduction below 240°C. At higher temperatures cyclohexane, cyclohexanol, and ethanol were obtained. Hexahydro compounds were also obtained from the *meta*- and *para*-hydroxy acids. On the other hand, Ungnade and Morriss[409] reduced ethyl esters of all three hydroxybenzoic acids in ethanol solution with 0.3 mole per cent (ester basis) of sodium ethoxide over Raney nickel at 160 to 220°C and 240 to 270 atmospheres and obtained 75 to 87 per cent yields of the corresponding ethyl hydroxycyclohexanecarboxylates.

Ipatieff and Razuvaev[148, 156, 157] reduced the sodium salts of *ortho*- and *para*-hydroxybenzoic acids with hydrogen at 80 atmospheres pressures over nickel oxide at temperatures of 275 to 290°C. The carboxyl groups underwent hydrogenolysis to yield cyclohexanol as the reduction product.

Some work has also been done on the hydrogenation of the benzene dicarboxylic acids, anhydrides and esters. Willstatter and Jaquet[448], using platinum catalyst and acetic acid solvent, reduced both phthalic anhydride and phthalic acid to form *cis*-1,2-cyclohexanedicarboxylic acid; they also reduced isophthalic and terephthalic acids to form *cis* and *trans* mixtures of both the 1,3- and 1,4-cyclohexanedicarboxylic acids. Aquirreche also reduced phthalic anhydride[25] and phthalic acid[26] using platinum oxide catalyst and acetic acid as the solvent. Komppa and Rohrmann[185] used hydrogen at 3 atmospheres and colloidal platinum to reduce terephthalic acid and obtain the *cis* form of the hexahydro derivative. Wittig and Pook[453] carried out the same reduction using a nickel-cobalt-copper catalyst and high temperature and pressure of hydrogen to obtain a mixture of the *cis*- and *trans*-1,4-cyclohexanedicarboxylic acid. Similar results were obtained when the ester or potassium salt was used. Both the *cis* and *trans* forms of each of the cyclohexanedicarboxylic acids, monomethyl esters and dimethylesters have been prepared by hydrogenation of the phthalic acids or esters to yield the *cis* forms with simultaneous or subsequent isomerization to obtain the *trans* configurations[143, 365].

Amines

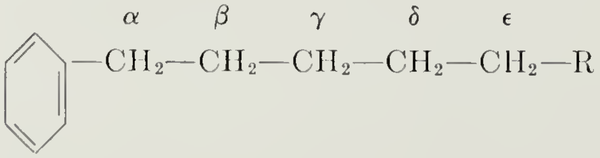
The catalytic hydrogenation of aromatic amines has been investigated over several catalysts. Mugisima[252] found that when aniline was hydrogenated over nickel at 260 to 300°C, not only cyclohexylamine but also dicyclohexylamine, ammonia, benzene, cyclohexane, cyclohexylaniline, and diphenylamine were among the products. Debus and Jungers[80] studied the role of various intermediates in the reduction of aniline over nickel to yield cyclohexyl- and dicyclohexylamines plus other products. They found that the decrease in rate as the reaction proceeds is due to inhibition by ammonia and liquid products. If the catalyst is flushed during the reaction, so as to remove residual gases, the rate is increased, though it does not attain its original value. These authors also noted that dicyclohexylamine is formed through the condensation of cyclohexylamine with aniline to yield phenylcyclohexylamine which is subsequently reduced to dicyclohexylamine.

Winans[452] studied the hydrogenation of aniline with nickel on kieselguhr, Raney nickel, Raney cobalt, pure cobalt oxide and technical cobalt oxide activated by lime, with best results from the latter. Sadikov and Shagalov[324] tested cerium and lanthanum as activating agents for nickel and osmium in the hydrogenation of aniline, and found that they affected the distribution of primary and secondary amines and benzene in the products. The reduction of aniline in acetic acid solution, i.e., of the anilinium ion, has been studied over Adams platinum and found to have an activation energy of 7500 calories[360]. Skita and Berendt[347] used colloidal platinum in acetic acid at room temperature to catalyze the hydrogenation of aniline, the toluidines and methyl, dimethyl, and diethyl anilines to obtain the corresponding cyclohexyl amines. These workers found that they could obtain either primary or secondary cyclohexyl amines by regulating temperature and concentration as well as the amount of hydrochloric acid added to the colloidal platinum catalyst. Sugino and Suzuki[384] hydrogenated *ortho-*, *meta,* and *para*-toluidine over nickel at 190°C and copper at 220°C to obtain cyclohexylamines. They found that the primary amine yield was greatest for *ortho*-toluidine and smallest for the *para*-compound. They further found that *ortho*-compounds form bis(methylcyclohexyl)amine, *meta*-compounds form methylcyclohexyltolylamine, and *para*-compounds form methylcyclohexyltolyl- and ditolylamines. Skita and Rolfes[352], using platinum catalyst and water as solvents, hydrogenated aniline and N-alkylanilines to the corresponding cyclohexyl compounds. Acetylation greatly decreased the rate of reduction of the benzene ring. Methoxy, ethoxy, or phenoxy substituents in aniline were cleaved on hydrogenation to give cyclohexyl amine and dicyclohexylamine. The same result was obtained for *meta-* and *para*-aminophenols. Hiers and Adams[136] hydrogenated triphenylamine over platinum oxide in hydrochloric acid solution to obtain tricyclohexylamine together with some dicyclohexyl and cyclohexylamines. Benzidine (4,4′-diaminodiphenyl) has been reduced in acetic acid at 50°C with a platinum catalyst and hydrogen at 0.1 atmospheres pressure to form the 4,4′-diaminodicyclohexyl[41]. Metayer has published several papers dealing with the hydrogenation of the benzene nucleus in the presence of amine substituents[231, 232, 233, 234, 235]. He used Raney nickel as catalyst, usually ethanol as solvent, temperatures of 150 to 200°, and hydrogen pressures of 60 to 150 kilograms per square centimeter. As a result of the study of a number of compounds, he made the following observations:

(1) When an amino group is attached to the benzene nucleus, hydrogenation takes place readily, but reaction to form secondary amines is pronounced.

(2) When an amino group is in the alpha position of an alkylbenzene, hydrogenation proceeds easily and satisfactory results are obtained.

(3) Raney nickel is unsuitable as a hydrogenation catalyst for arylalkylamines with primary amino groups located in the β, γ, δ, or ϵ positions.



For such compounds, deamination occurs. The primary amino group in the β position hinders reduction of the ring. For substituents in the positions γ, δ, or ϵ to the ring, there is no influence on the reduction of the benzene nucleus, and only the resistance of these groups to hydrogenation or hydrogenolysis has any effect on the reaction.

(4) While hydrogenation of the benzene nucleus is impossible with a primary amino group in the β position, substitution in the amino group aids the reduction so that a tertiary amino substituent in the β position allows easy reduction of the benzene ring.

While reduction of simple aromatic monamines takes place readily, as indicated in (1) above, more complex amines may be difficult to reduce. Barkdoll and co-workers[46] found it impossible to reduce *bis*(4-aminophenyl)-methane over Raney nickel or cobalt on alumina catalysts to the dicyclohexyl derivative. The reaction was attempted by exposure for 6½ hours to hydrogen at 200 atmospheres pressure and 200°C. Dioxane was used as solvent. At 915 atmospheres, some reduction was observed. When ruthenium dioxide or an alkali-promoted cobaltic oxide was employed as a catalyst, good yields of the desired product, *bis*(4-aminodicyclohexyl)-methane, were obtained.

Polyphenyl Compounds

The complete hydrogenation of compounds containing more than one benzene nucleus generally results in the conversion to polycyclohexyl derivatives. The reduction could conceivably pass through intermediate stages during which the individual rings are saturated in some definite sequence, or the polyphenyl compound could remain in contact with the catalyst until all rings are saturated. In the latter case, no partially saturated intermediate could be isolated. Whether one or the other of these possibilities predominates will depend on both the relative catalyst surface coverage of the initial and intermediate compounds and on the relative rates at which the two undergo hydrogenation at equal surface coverages. On most catalysts at ordinary temperatures, these hydrogenations are zero order with respect to the initial polyphenyl compound. If one prepares a pure intermediate with both saturated and unsaturated rings, the reduction of this material is also zero order with respect to the intermediate. This is interpreted as indicating equal (complete) coverage of the active spots of the catalyst with the starting material by itself or by the intermediate when no starting material is present.

TABLE 9. HYDROGENATION RATES OF PHENYL- AND CYCLOHEXYL SUBSTITUTED COMPOUNDS OVER ADAMS PLATINUM CATALYST AT 30°C

Phenyl-substituted	k[a]	Cyclohexyl-substituted	k[a]
Biphenyl	.0541	Phenylcyclohexane	.0614
Diphenylmethane	.0629	Phenylcyclohexylmethane	.0665
1,1-Diphenylethane	.0474	1-Phenyl-1-cyclohexylethane	.0366
Triphenylmethane	.0135	Diphenylcyclohexylmethane	.0129
Diphenylacetic acid	.0182	Phenylcyclohexylacetic acid	.0191
Diphenylglycolic acid	.0146	Phenylcyclohexylglycolic acid	.0163

[a] The units of k are liters grams^{-1} min.$^{-1}$. Initial hydrogen pressures were 64 psia.

TABLE 10. FRACTION OF PHENYLCYCLOHEXYL INTERMEDIATE PRESENT AT HALF-HYDROGENATION OF A DIPHENYL COMPOUND OVER ADAMS PLATINUM AT 30°C

Initial Compound	Per Cent Phenylcyclohexyl Intermediate	Analytical Method
Biphenyl	65	Distillation
Diphenylmethane	95–100	Distillation
1,1-Diphenylethane	95–100	Distillation
Diphenylacetic acid	90–100	Esterification
Diphenylglycolic acid	65	Colorimetry

It has been amply demonstrated that, at least under some conditions, the rate of hydrogenation of a polyphenyl compound is not changed by saturation of one ring.[358]. This is illustrated in Table 9 for platinum-catalyzed low pressure, room temperature hydrogenation in acetic acid solution. The ratio of the rate constants for hydrogenation of the polyphenyl compounds to those for the corresponding phenylcyclohexyl derivatives is 1.0 ± 0.1. If the adsorption of the two were equally strong, i.e., the fraction of surface covered by each were proportional to its mole fraction in the solution in equilibrium with the catalyst, then the percentage of a phenylcyclohexyl derivative which should be present when a diphenyl compound has been reduced with enough hydrogen to saturate one ring only may be calculated to be 36 per cent. Table 10 gives the experimental value of the fraction found.

The equilibrium existing on the catalytic surface during the hydrogenation of a diphenyl compound may be assumed to be

$$\text{adsorbed } A + B \leftrightarrows \text{adsorbed } B + \text{A}$$

where A represents the diphenyl and B the phenylcyclohexyl compound. It is assumed that adsorption of the completely hydrogenated product is negligible. The equilibrium constant for the adsorption is given by

$$K = \sigma_B C_A / \sigma_A C_B$$

where σ_A and σ_B are the fractions of catalyst sites occupied by adsorbed A and B. The rates of consumption of A and of accumulation of B may be expressed as:

$$-dC_A/dt = k\sigma_A p_{\text{H}_2}$$

$$+dC_B/dt = k(\sigma_A - \sigma_B)p_{\text{H}_2}$$

where k is the first order rate constant for hydrogenation of either the initial or intermediate compound. It follows that

$$\frac{dC_{\text{B}}}{dC_A} = \frac{KC_{\text{B}}}{C_A} - 1.$$

This may be integrated[371] to obtain the equation

$$\log \frac{\text{C}_A}{C^\circ_{\text{A}}} = \frac{1}{K - 1} \log \left[1 - (\text{K} - 1) \frac{\text{C}_B}{C_A} \right]$$

where C°_A is the initial concentration of A. Thus, if one can analyze a partly hydrogenated mixture for the unhydrogenated and partly hydrogenated component, this information will be sufficient to calculate K which is actually the ratio of σ_B to σ_A when $C_A = C_B$, or the relative adsorption tendencies of A and B. By this method it has been shown that benzilic acid is 4.6 times more extensively adsorbed than the half-hydrogenated intermediate, phenylcyclohexylglycolic acid.

Such information is useful in preparing partially hydrogenated derivatives. For instance, Adamson, Barrett, and Wilkinson[5] prepared a number of substituted phenylcyclohexyl carbinols by hydrogenation of the corresponding diphenylcarbinols using platinum catalyst and acetic acid solution. They were able to obtain better yields of the desired product when they added 3.3 to 3.4 moles of hydrogen per mole of diphenylcarbinol rather than the 3.0 moles equivalent to half-saturation.

Conditions may sometimes be found where the relative adsorptions of a polyphenyl compound differs so much from that of a partially saturated intermediate that the reaction virtually ceases after hydrogenation of one benzene ring only. Thus Miescher and Hoffmann[237] reported that the hydrogenation of methyl or ethyl diphenylacetate over a supported nickel catalyst in an autoclave proceeds only as far as the phenylcyclohexylacetate. Under the same conditions, methyl benzilate absorbs 4 moles of hydrogen per mole of the benzilate to give methyl phenylcyclohexylacetate. Sandoval[325] reported that when diphenylacetic acid was hydrogenated at 176°C over Raney nickel, only 3 moles of hydrogen were absorbed, with the formation of phenylcyclohexylacetic acid.

Hall and Cawley[123] found that biphenyl could be hydrogenated over molybdenum sulfide at 200 to 300 atmospheres hydrogen pressure and 300°C to give phenylcyclohexane. Under the same conditions, biphenylene oxide gave *ortho*-cyclohexylphenol. Goodman[116] found that biphenyl could be reduced over Raney nickel in alcohol solution at 100°C and 900 psi hydrogen pressure to give 87 per cent yields of phenylcyclohexane, while at 200°C and 1450 psi hydrogen pressure, 93 per cent of dicyclohexyl was obtained. Musser and Adkins[254] studied the hydrogenation of certain hydroxy and alkoxy derivatives of diphenyl over Raney nickel. The possible products are as follows:

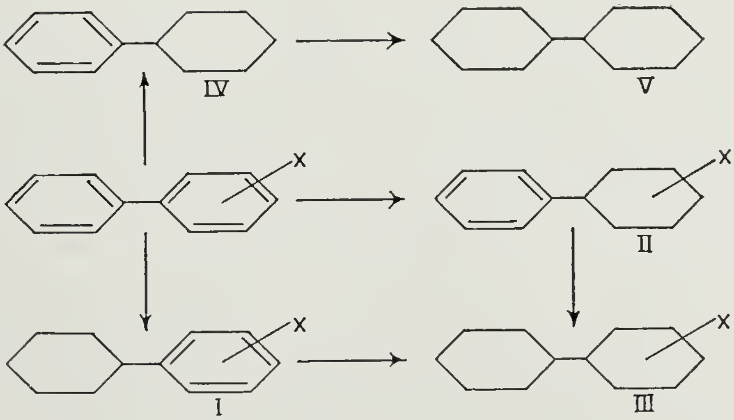
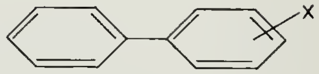


Table 11 gives the distribution of products obtained. The results show that, in general, for the 2- or 3-substituted diphenyls, the substituted ring is more readily reduced, while for the 4-substituted diphenyls, the reverse is found; i.e., the substituted ring is the more resistant to hydrogenation. When copper chromite was used as catalyst, 2-ethoxydiphenyl underwent cleavage to form diphenyl and dicyclohexyl, while the compound 4-hydroxydiphenyl was not so cleaved, but underwent reduction in the substituted rather than the unsubstituted ring. Fieser and co-workers[99] used hydrogenation over Raney nickel and also over platinum to obtain a number of 4′-cyclohexylcyclohexyl substituted naphthoquinones for testing as antimalarials. Adkins and co-workers[13, 458] studied the hydrogenation over nickel of a number of polyphenyl compounds including triphenylmethane, phenyldicyclohexylmethane, 1,3,5-triphenylbenzene, bi-2,4,6-triphenylphenyl, triphenylcarbinol and triphenylamine. They also studied the hydrogenation of all of the polyphenylethenes to form polyphenylethanes and polycyclohexylethanes. They found that an accumulation of phenyl groups increased the resistances of the ethylene group toward reduction. On the other hand, they observed that while there is some decrease in the rate of hydrogenation of the benzene rings as the number of phenyl groups increases, this decrease in rate is small when the great increase in molecular weight, number of unsaturated groups and complexity of the molecule is taken into consideration. This conclusion is in line with their observation that triphenylbenzene was hydrogenated without difficulty to tricyclohexylcyclohexane. The accumulation of phenyl groups also increased the tendency of the ethane linkage to cleave in the process of hydrogenation. For pentaphenylethane, the molecule was readily cleaved even at 125°C to

TABLE 11. HYDROGENATION OF DERIVATIVES OF DIPHENYL 

OVER RANEY NICKEL

X	T°C	Time.[a] (hr)	Per cent yields of product types[c]				
			I	II	III	IV	V
2-Hydroxy[b]	160	9.5		16	50		4
2-Methoxy	150	4.0		23	30		18
2-Ethoxy	150	6.0		24	36		18
2-Cetoxy	150	3.0		19			47
2-Hydroxy-4-ethyl	130	(1.5)		74		6	
3-Hydroxy	160	(0.5)		79			
3-Hydroxy	160	4.0			89		
3-Ethoxy[b]	140	3.5	29	27			13
4-Hydroxy	160	5.0		78			
4-Hydroxy	160	(0.7)	43	13	17		
4-Methoxy[b]	150	3.3	37		41		8
4-Ethoxy	150	6.5	27		24		10
4-Cetoxy	150	1.0	67				10

[a] Reactions carried out until no further hydrogen was absorbed except in cases where times are given in parentheses.

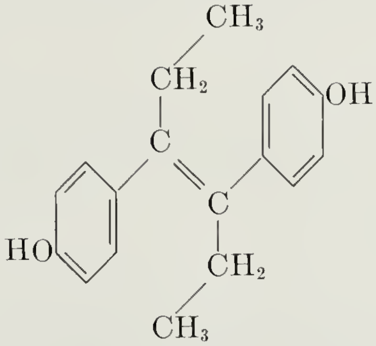
[b] 20 to 30 per cent starting material recovered.

[c] For designation of product types see reaction scheme given above.

give mainly di- and tricyclohexylmethanes. A 20 per cent yield of the pentacyclohexylethane was obtained at 160°C where hydrogenation was more rapid. When such polyphenylethylenes or ethanes were reduced over copper chromite at 200°C and 130 atmospheres pressure, the carbon-carbon linkage was cleaved and polyphenylmethanes were produced. Over either nickel or copper-chromium oxide catalysts, no cleavage of polycyclohexylethanes occurred. Even pentacyclohexylethane was perfectly stable at 200°C over these catalysts.

Tuot and Guyard[404] also studied the hydrogenation of a number of polyphenylethylenes, ethanes or ethanols as well as 1-phenyldecene over Raney nickel at 185°C or platinum in acetic acid solution to form the corresponding cyclohexyl-substituted hydrocarbons.

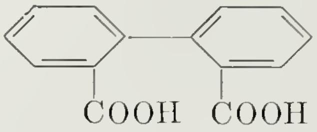
The hydrogenation of diethylstilbesterol,



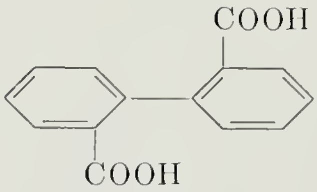
has been of some interest. The reduction has been accomplished in methanol solution over Raney nickel at 210°C and 270 atmospheres hydrogen pressure to form 3,4-*bis*(4-hydroxycyclohexyl)hexane and several isomers of the latter have been identified[121, 405, 406, 410]. The same reduction has also been carried out in acetic acid solution over platinum oxide or palladium oxide catalysts[249]. Reduction of the monomethyl ether over copper chromite at 400°C in dioxane with hydrogen pressures of 4000 psi results in saturation of one ring only, that with the hydroxyl rather than the methoxyl group[443, 444].

Willstatter and Waldschmidt-Leitz[451] hydrogenated diphenylacetic acid over platinum to obtain dicyclohexylacetic acid. Huzise[144] found that *ortho*-phenylbenzoic acid yielded *ortho*-cyclohexylbenzoic acid when reduced with hydrogen in acetic acid solution and with platinum oxide catalyst; however, *ortho*-phenylcyclohexanecarboxylic acid was produced by reduction with sodium and amyl alcohol. Buck and Ide[59] reduced benzoin, *ortho*-chlorobenzanisoin and *ortho*-chlorobenzoveratroin in acidified alcohol solution with hydrogen over platinum oxide at 70°C to obtain α,β-dicyclohexylethane and another compound which was probably α,β-dicyclohexylethylene glycol. They also reduced *p*-dimethylaminobenzoin, *p*-dimethylaminoanisoin, and *ortho*-, *meta*-, and *para*-chlorodimethylaminobenzoin to form 4-dimethylamino-α,β-dicyclohexylethane. Dauben and Tanabe[76] using Raney nickel catalyst, hydrogen at 2500 psi pressure and temperatures of 75 to 125° reduced *para*-(*para*-hydroxyphenyl)benzoic-acid to the intermediate phenylcyclohexyl derivative and also to the dicyclohexyl product; they also studied the configuration of the intermediate products. Similar experiments were carried out with *meta*-(*para*-hydroxyphenyl)benzoic acid.

Linstead and co-workers[204] found that 2,2′-diphenic acid, when hydrogenated over platinum, formed the *cis-syn-cis*-perhydrodiphenic acid. Assuming that the two benzene rings are adsorbed on the catalyst in a flat manner, and that the hydrogen adds from one side only (the catalyst side), Linstead concluded that the diphenic acid must be adsorbed in the coiled rather than the zigzag form. No reason for this preference is apparent.



Coiled form



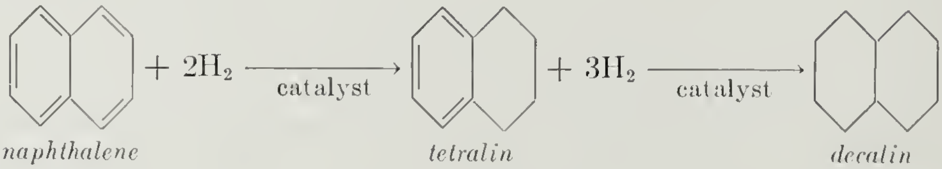
zigzag form

Many other examples of reduction of polyphenyl compounds to corresponding cyclohexyl derivatives may be found in the chemical literature.

Fused Benzene Rings

When two or more benzene rings are fused together, the resulting structure may undergo hydrogenation to form a variety of intermediates and also several isomeric compounds may result from complete saturation of the rings.

The hydrogenation of the naphthalene nucleus has been studied by a number of investigators[263], and, unlike benzene, proceeds through two distinct stages, as follows:

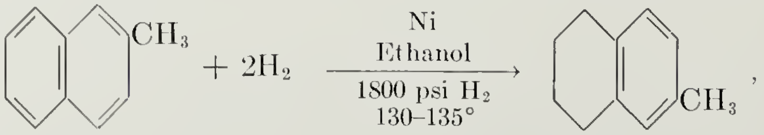


While only one isomer is possible for tetralin, the completely saturated decalin may exist in *cis* or *trans* forms[267]; the *cis* form may conceivably exist in four different conformations and the *trans* form, three[422], depending on whether the cyclohexane rings are in the chair or boat forms and whether the ring fusion involves polar or equatorial bonds[442]. Bastiansen and Hassel[48] have demonstrated conclusively that *cis*-decalin is made up of two chair-form cyclohexane rings joined by equatorial-polar bonds, and the currently accepted structure of the *trans* configuration is also believed to consist of two chair conformations of cyclohexane, fused by equatorial linkages[127]. The energy difference between the *cis* and *trans* forms of decalin is approximately 2.4 kcal[161, 402], so that it is to be expected that isomerization of the primary product of naphthalene hydrogenation will usually occur except under very mild conditions of hydrogenation. Willstatter and Seitz[449] state that hydrogenation of naphthalene or tetralin over platinum at temperatures from 20 to 80°C gives pure *cis*-decalin. However, the physical constants of the products they obtained when compared with those of the pure isomers[335] indicate the presence of some *trans*-decalin. Baker and Schuetz[36] also indicate that *cis*-decalin is produced when tetralin is hydrogenated at 25°C over Adams platinum in the presence of acetic acid with hydrogen pressures of 1700 psi. Under similar conditions, these authors find that naphthalene is reduced to a mixture of 23 per cent *trans*- and 77 per cent *cis*-decalin.

Hydrogenations of naphthalene to form the intermediate tetralin are reported as taking place over a variety of catalysts. Over various types of nickel catalyst, the hydrogenation may proceed only as far as tetralin, or the tetralin may be further hydrogenated to decalin depending on pressure, temperature and activity of the nickel[66, 88, 287, 332, 394a]. Lush claims that under the same conditions of temperature and pressure, vapor phase hydrogenation of naphthalene over nickel yields tetralin, while decalin is produced when liquid phase is present[217]. Waterman and co-workers state that when naphthalene is reduced over nickel supported on kieselguhr at 100 kg/cm² hydrogen pressure and temperatures above 200°C, tetralin is formed, and further hydrogenation with used catalyst is impossible. However, when fresh catalyst is used, the tetralin may be hydrogenated to decalin (mixture of *cis* and *trans* isomers) at temperatures as low as 100°C[435]. Maillard[221] studied the equilibrium between naphthalene, tetralin and hydrogen. He states that tetralin begins to dehydrogenate at 100°C, and that dehydrogenation of decalin yields naphthalene. The same author states that above 180°C, naphthalene forms methane and carbon in the presence of nickel[222]. Musser and Adkins[254] found that, while tetralin could be reduced over Raney nickel to form decalin, over copper chromite at temperatures up to 200°C, naphthalene yielded tetralin as the end reduction product. It is also reported that reduced copper is a preferable catalyst to copper chromite or Raney copper for reduction of naphthalene to tetralin[236]. Naphthalene is reduced to tetralin over molybdenum oxide or sulfide and also tungsten oxide at temperatures around 400 to 450°C and hydrogen pressures around 100 atmospheres[88, 292, 417]. Hall reports that the tetralin thus formed yields various alkylbenzenes[122]. It has been proposed that methylhydrindene and hydrindene are formed as intermediates in the catalytic destructive hydrogenation of tetralin[97].

Baker and Schuetz[36] noted a rather strange kinetic behavior in the rate at which naphthalene undergoes hydrogenation. They studied this reaction over Adams platinum with acetic acid as solvent and initial pressures of 1850 psi hydrogen. The reaction was not observed to follow first order kinetic behavior until about 40 per cent of the hydrogen requirement had been absorbed, after which the usual linear relationship between the logarithm of the pressure and time was followed. In the 40 per cent range, which corresponds to the formation of tetralin, an inflection in the log p *versus* t plot occurred. The authors suggested that the peculiar behavior was due to poisoning of the catalyst by the intermediate tetralin. This is hardly a logical explanation, since the hydrogenation rate for tetralin itself is as great or greater than that for naphthalene under similar conditions.

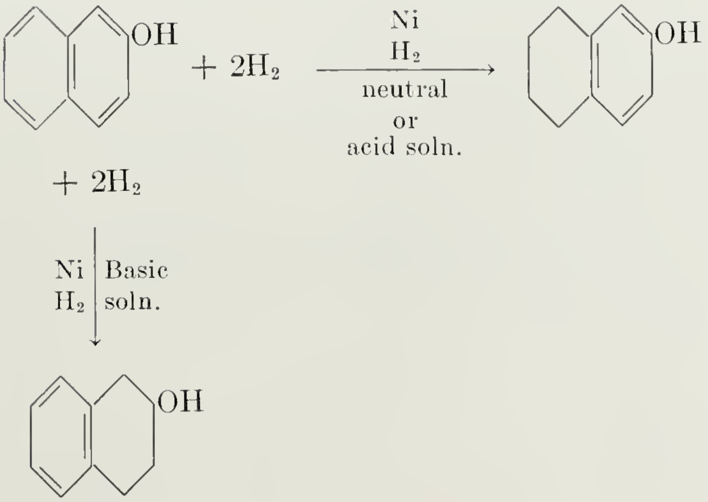
When one hydrogenates a substituted naphthalene to a tetralin, two isomers are possible depending on which ring was saturated. For instance, Fieser[101] found that when 2-methylnaphthalene was hydrogenated, the non-substituted ring was reduced with the formation of 6-methyltetralin:



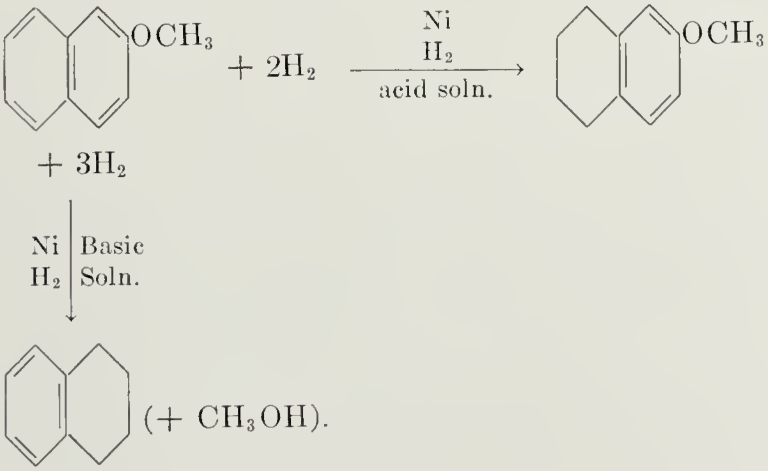
instead of 2-methyltetralin.

Naphthols may be readily hydrogenated to form tetrahydronaphthol (tetralol) and decahydronaphthol (decalol)[254, 276]. In general, the hydroxy-substituted ring is reported to be the more readily reduced[58, 75, 175, 275, 330], with yields of the 1,2,3,4-tetrahydronaphthol around 85 per cent and of the 5,6,7,8-tetrahydronaphthol around 15 per cent. This seems to be true whether the 1-naphthol or 2-naphthol is reduced, and whether the catalyst is nickel or copper chromite.

Stork[378] studied the reduction of 2-naphthol, and found that the reduction was greatly influenced by the acidity of the medium. The hydrogenations were accomplished in absolute ethanol solvent with initial pressures of 3400 psi and temperatures of 85°C. The results may be summarized by the equations:

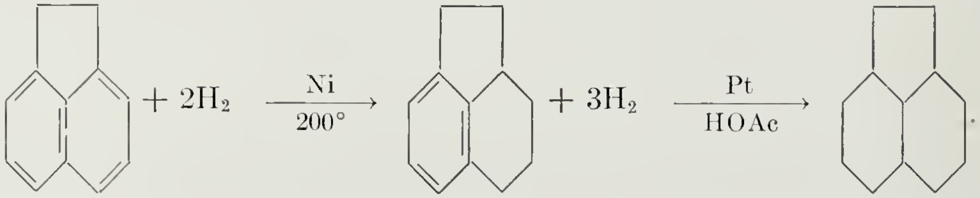


With methoxynaphthalene, Stork found that the non-substituted ring was reduced in the presence of acid and the substituted ring in the presence of base; however, under the latter conditions, the ether linkage was cleaved.



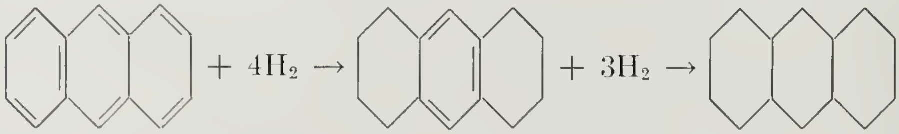
This reduction has also been studied by Arbit[27] and by Adkins and co-workers[254, 415] who were able to prepare 1,2,3,4-tetrahydro-2-methoxynaphthalene using Raney nickel as catalyst.

The naphthoic acids have been reduced in acetic acid using platinum oxide catalyst[191]. Either 1-naphthoic or 2-naphthoic acid may absorb 1, 2, or 5 moles of hydrogen to form the dihydro (2 isomers), tetrahydro, or decahydronaphthoic acids which have been isolated and characterized[299]. Naphthalic (naphthalene-1,8-dicarboxylic) acid has also been reduced to the tetrahydro and decahydro derivatives, the latter being a mixture of *cis* and *trans* isomers[64]. 2-Naphthoic acid has been reduced in basic dioxane solution over Raney nickel at a temperature of 150°C and 3400 psi initial hydrogen pressure. The only product that could be isolated was the 5,6,7,8-tetrahydro-2-naphthoic acid[378]. Ipatieff[146] observed that sodium 2-naphthoate when heated with nickel oxide and hydrogen under pressure was reduced through the tetrahydro to the decahydro acid. Under similar conditions, sodium 1-naphthoate gave tetrahydronaphthalene. Acenaphthene is reported to form tetrahydroacenaphthene when it is reduced by hydrogen at 5 to 15 atmospheres over nickel catalyst[425]. It may also be completely hydrogenated over nickel[145], or in acetic acid over Adams platinum catalyst.

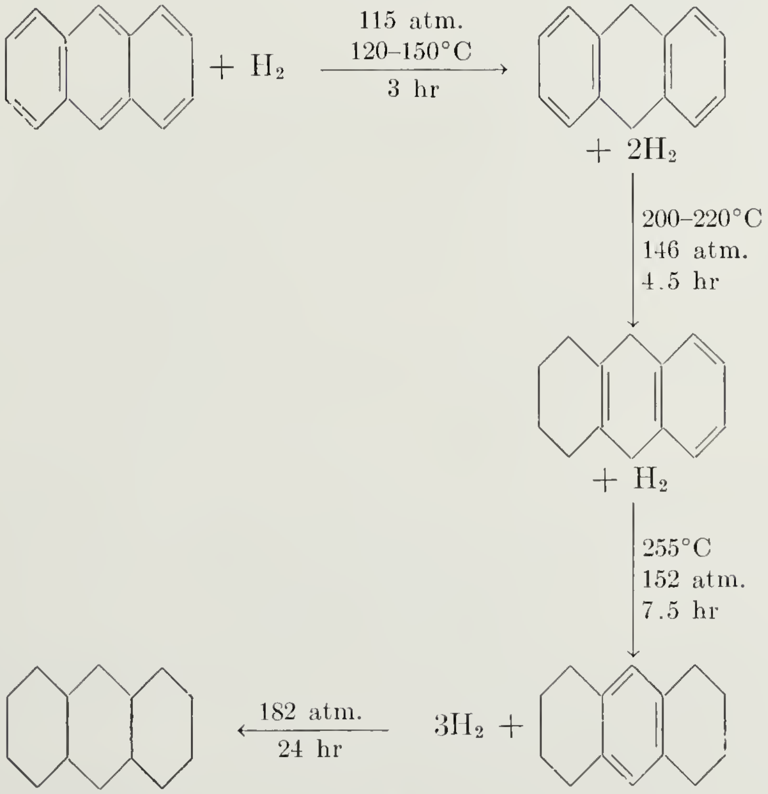


Lozovoy[209] studied the hydrogenation of several condensed ring systems over nickel-alumina catalyst at temperatures between 40 and 140°C and relatively high hydrogen pressures. He concluded that such systems could be classified into two groups with respect to the rates of hydrogenation. One group which included reductions of naphthalene to tetralin, acenaphthene to tetrahydroacenaphthene, and anthracene to octahydroanthracene had rates which were much faster than that for benzene hydrogenation, and can also be carried out under milder conditions. The other group which includes reductions of tetralin to decalin, tetrahydroacenaphthene to decahydroacenaphthene and octahydroanthracene to perhydroanthracene requires more strenuous conditions, and the hydrogenation rates are comparable to those for reduction of substituted benzenes.

As is indicated above, anthracene in the presence of a catalyst accepts four moles of hydrogen rather readily, and three more with some difficulty.

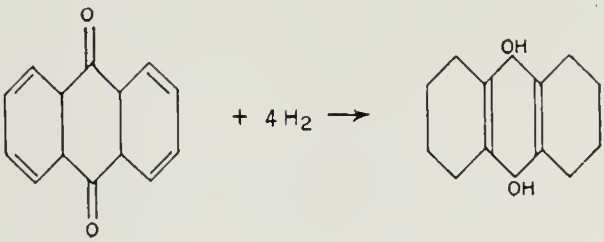


Waterman and co-workers[432] found that anthracene could be hydrogenated over nickel on kieselguhr at 180–280°C and 100 kg cm^{-2} to form octahydroanthracene; hydrogenation to the completely reduced perhydroanthracene could be accomplished only when a fresh catalyst sample was employed. The product was a mixture of two isomers. The course of this hydrogenation is actually more complex. Under certain conditions, one molecule of hydrogen first adds to form 9,10-dihydroanthracene. Subsequent addition may give successively the tetrahydro, hexahydro, octahydro, and dodecahydro derivatives. Sugino and Outi[381] made a rather thorough study of this reduction over a copper catalyst. The course of the reaction and the conditions necessary for each step are as follows (the catalyst was added as cupric oxide):



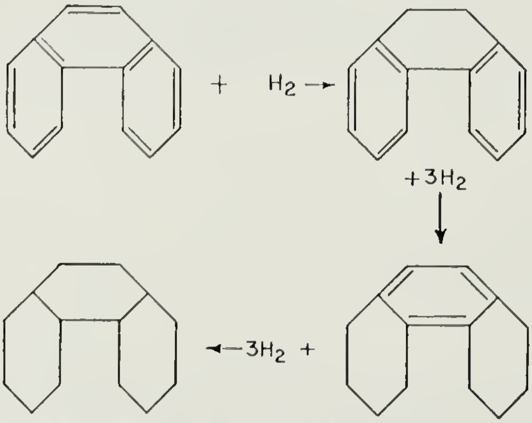
Similar studies have been reported with platinum[419], nickel[108, 223, 226, 331], molybdenum sulfide[290, 291, 293], molybdenum oxide[186] and copper chromite[63, 113] catalysts. Most of these reports do not mention the formation of the hexahydro compound. Orchin[264] found that in the presence of palladium on charcoal, anthracene extracted hydrogen from tetralin to form 1,2,3,4-tetrahydroanthracene.

Anthraquinone may also be readily hydrogenated as follows[346, 350, 351]:



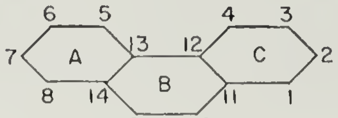
The hydrogenation of anthraphenone has been studied over Raney nickel in ethanol solvent, and is stated by Horeau and Jacques[140] to form after absorption of two moles of hydrogen a mixture of 9,10-dihydroanthrylphenylcarbinol and 2,3-tetramethylene-1-benzoyl-naphthalene.

The hydrogenation of phenanthrene over nickel or copper chromite catalysts may form the 9,10-dihydro, 1,2,3,4,5,6,7,8-octahydro or tetradecahydro derivative[85].

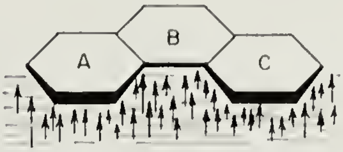


Durland and Adkins[86], starting with phenanthrene and hydrogen at 200 atmospheres pressure, obtained the 9,10 derivative over copper chromite at 150°C, the sym-octahydro derivative over Raney nickel at 100°C, and the tetradecahydro product over Raney nickel at 250°C. Prokopets and co-workers[293] report that with molybdenum sulfide catalyst, hydrogen pressures of 160 to 180 atmospheres and temperatures of 290 to 450°C, no dihydrophenanthrene is formed, but a tetrahydro as well as the sym. octahydro- and perhydroanthracenes are obtained.

A very thorough study of the stereochemistry of the catalytic hydrogenation of phenanthrene and its derivatives was made by Linstead and his co-workers[78, 79, 193, 200, 201, 202, 203, 204, 205, 206, 207]. These workers used Adams platinum catalyst and acetic acid or alcohol as solvent with hydrogen pressures of 60 psi. The compounds hydrogenated to the corresponding perhydro products included diphenic acid, its ester and anhydride, *cis*-hexahydrodiphenic acid, *trans*-hexahydrodiphenic acid, 9-phenanthrol, *cis-cis*-octahydro-9-phenanthrol, *cis*-9-keto-octahydrophenanthrene and 9,10-phenanthrenequinone. The diphenic acids can be obtained from the phenanthrenes by oxidation. When phenanthrene is completely hydrogenated, four asymmetric carbon atoms are possible, and are those given the numbers 11, 12, 13, and 14 in the following formula:

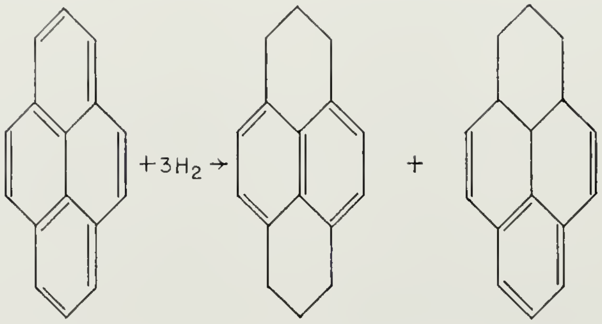


The configuration of the ring fusion AB (or BC) is called *cis* or *trans* depending on whether the pair of hydrogen atoms on C_{13} and C_{14} (or C_{11} and C_{12}) are on the same side of the molecule or on the opposite side. The configuration of the so-called backbone (the $C_{12}-C_{13}$ bond) is designated as *syn* if the hydrogens on C_{12} and C_{13} are on the same side of the molecule and *anti* if on opposite sides. Thus, one has six possible isomeric perhydro derivatives, which may be designated as *cis-syn-cis*, *cis-syn-trans*, *trans-syn-trans*, *cis-anti-cis*, *cis-anti-trans*, and *trans-anti-trans*. Linstead was able to show that in virtually every case the configurations of the products were *cis* and *syn*. Configurations having *trans* or *anti* configurations were present in either undetectable or relatively small amounts. As a result of his studies he proposed that, when one or more aromatic rings are catalytically hydrogenated during a single period of adsorption, the hydrogen atoms add to one side of the molecule. It was further suggested that the stages in the hydrogenation involved the adsorption of the aromatic molecule upon a suitable part of the catalyst followed by the addition of hydrogen from the underside so that all of the added hydrogen atoms appear on the same side of the molecule. This is illustrated as follows:

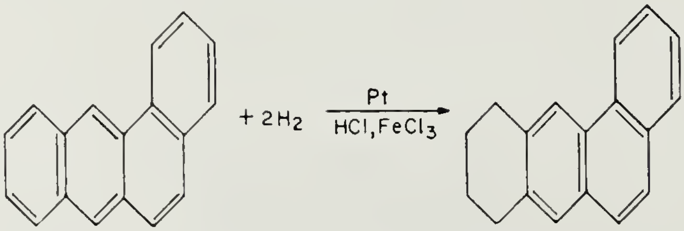


Here the heavy lines on the phenanthrene skeleton represent the front part of the molecule as it lies parallel to and above the catalyst surface, and the arrows represent the approach of hydrogen. Linstead further suggested that the orientation of the adsorption of the aromatic molecule on the catalyst surface is affected by hindrance between the catalyst and the substrate. Thus, if one hydrogenates *cis-cis*-octahydrophenanthrene (rings B and C saturated), the adsorption on the catalyst will be such that ring C in the adsorbed molecule will be oriented away from the catalyst. If the hydrogen approaches from the catalyst side as postulated, the perhydrophenanthrene formed by saturation of ring A will have the *cis-syn-cis*-configuration which is observed experimentally. This same reasoning is applicable to the hydrogenation of diphenic acid, provided it is hydrogenated in the coiled rather than the open phase.

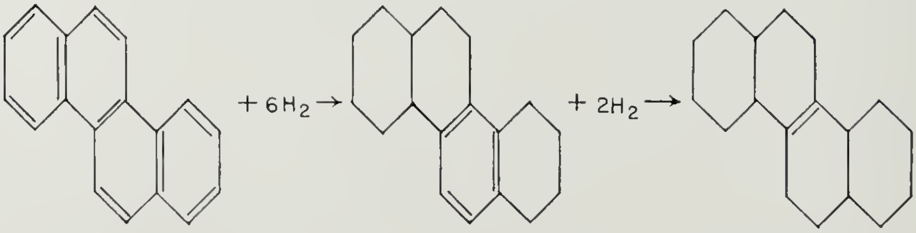
Hydrogenation of still more complicated products has been carried out. For the hydrocarbons themselves, Cameron, Cook, and Graham[63] found that hydrogenation of pyrene over copper chromite in alcohol solution with 130 atmospheres hydrogen pressure and a temperature of 100 to 105°C yielded a mixture of hexahydro derivatives:



Over Raney nickel, some completely hydrogenated hexadecapyrene was obtained. Lock and Walter[208] also obtained the symmetrical hexahydropyrene by catalytic hydrogenation. Fieser and Hershberg[100] reduced benzanthracene over Adams platinum in the presence of hydrochloric acid and ferric chloride to the 5,6,7,8-tetrahydro derivative. Similar results were obtained with the 10-methyl compound.

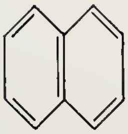
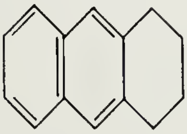
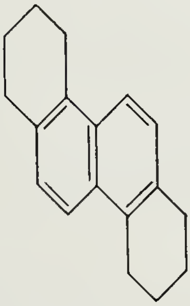
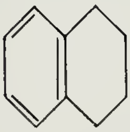
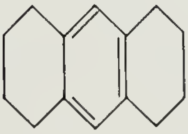


von Braun and Irmisch[424] investigated the hydrogenation of chrysene over nickel to form dodecahydro- and hexadecahydrochrysene. They were unable to obtain any octadecahydrochrysene.



Spilker[376] reports the complete hydrogenation of chrysene over nickel in decalin solution.

Lozovoy and Senyavin[215] studied the relative rates of hydrogenation of naphthalene, anthracene, and chrysene over a tungsten sulfide catalyst at 400°C and 150 atmospheres hydrogen pressure. The results, as well as those obtained over molybdenum sulfide[214] and nickel-alumina[209], are given in Table 12. For all three catalysts, the rate of hydrogenation of benzene is used as standard, and arbitrarily set equal to 100. These authors point out the interesting comparison of the relative rates of hydrogenation of two series of compounds over tungsten sulfide, as follows:

COMPOUND		RELATIVE RATE
Naphthalene		2300
Tetrahydroanthracene		449
Octahydrochrysene		96
Benzene		100
Tetralin		250
Octahydroanthracene		291

This comparison shows that the rate of reduction of naphthalene is decreased as cyclohexane rings are fused to it, while the rate of reduction of the benzene ring itself is increased under similar circumstances.

Zinke and Beundorf[465] studied the hydrogenation of perylene over palladium catalyst and formed the octahydro- and tetradecahydroperylenes. The reaction is presumably as follows:

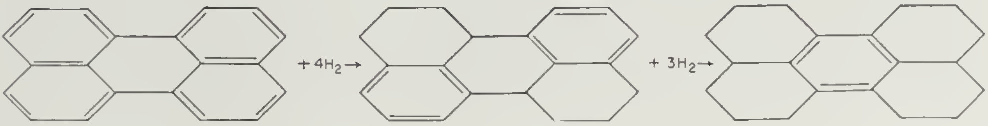
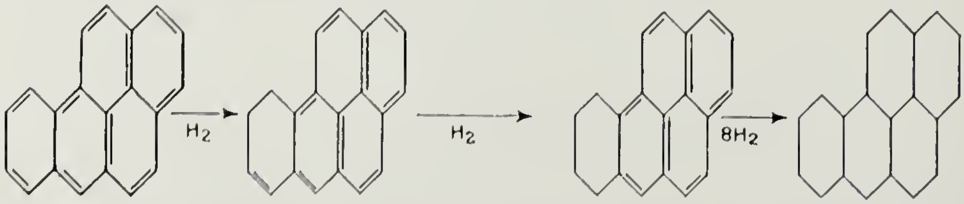


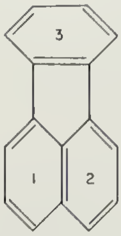
Table 12. Rate of Hydrogenation of Naphthalene, Anthracene, Chrysene, and Partially Hydrogenated Intermediates over Various Catalysts

Reaction	Rate ($C_6H_6 + H_2 \rightarrow C_6H_{12}$, rate = 100)		
	WS_2 400°C, 150 atm.	MoS_2 420°C, 200 atm.	$Ni\text{-}Al_2O_3$ 120–202°C, 30–50 atm.
Benzene → Cyclohexane	100	100	100
Naphthalene → Tetralin	2300	1409	314
Tetralin → Decalin	250	287	24
Anthracene → 9,10 Dihydroanthracene	6187		326
9,10-Dihydroanthracene → Tetrahydroanthracene	1295		308
Tetrahydroanthracene → Octahydroanthracene	449		147
Octahydroanthracene → Perhydroanthracene	291		4
Chrysene → Tetrahydrochrysene	80		
Tetrahydrochrysene → Octahydrochrysene	76		
Octahydrochrysene → Dodecahydrochrysene	96		

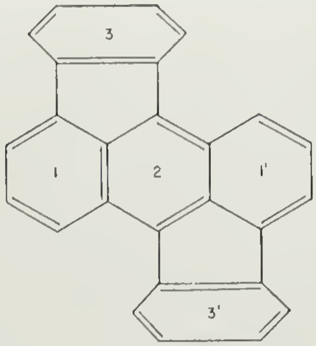
Lijinsky and Zechmeister[198a] investigated the course of the hydrogenation of benzpyrene over Adams platinum catalyst at room temperature. They obtained the completely hydrogenated product. They were also able to isolate a dihydrobenzpyrene and a tetrahydrobenzpyrene. The structure of the tetrahydro compound as well as the probable structure of the dihydro derivative are as follows:



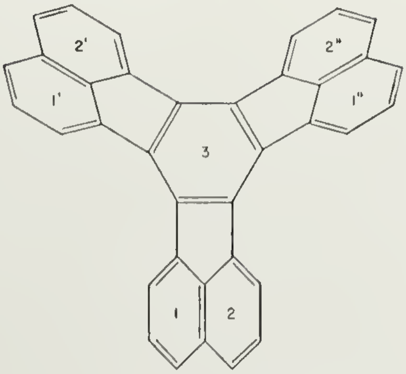
von Braun and co-workers[426, 427] studied the hydrogenations over nickel catalyst at high temperature and pressure, of fluoranthene, rubicene, and decacyclene. They also did some studies of the reduction of fluoranthene using platinum and palladium catalysts. They found a definite order of ring saturation. For fluoranthene the order was 1,3,2. For rubicene rings 1,1′, 3 and 3′, all hydrogenated at once with the absorption of 10 moles of hydrogen per mole of rubicene. Ring 2 was hydrogenated with difficulty. For decacyclene, the order of saturation was rings 1,1′,1″ in a group to form dodecahydrodecacyclene, then rings 2,2′, and 2″ to add an additional 9 moles of hydrogen. The authors were unable to reduce ring number 3.



Fluoranthene



Rubicene

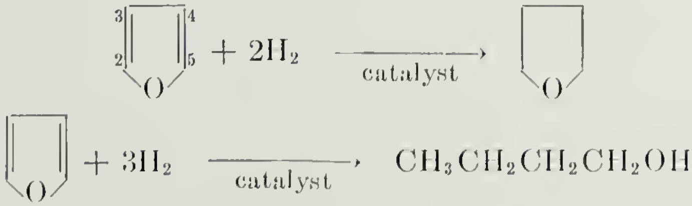


Decacyclene

In general, it appears that condensed ring systems are hydrogenated in such a manner as to maintain a maximum of resonance in any intermediate products, even if this involves a shift in unsaturation from one ring to another. It also appears that a central benzene ring surrounded by other rings is resistant to hydrogenation. The reduction of such systems has become of much importance in connection with studies of physiologically active compounds and natural products.

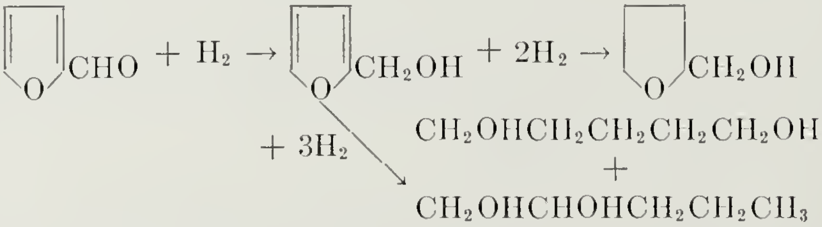
The Hydrogenation of the Furan Nucleus

The hydrogenation of the furan nucleus takes place over a wide variety of conditions and in the presence of a number of catalysts. The molecule of furan may absorb two molecules of hydrogen to form tetrahydrofuran or three molecules of hydrogen to form *n*-butanol.



The two reactions are competitive rather than consecutive, for under the same conditions necessary to produce the butanol from furan, tetrahydrofuran is quite stable[162, 366, 383]. In fact, the side chain of tetrahydrofurfuryl alcohol may be effectively split off to give tetrahydrofuran, hydrogen, and carbon monoxide[33, 389]. An intermediate dihydrofuran has never been isolated; nevertheless, there is some evidence through the formation of diols when the hydrogenation of furan takes place in the presence of water that addition to one double bond precedes the other, and that this addition is 2:3 rather than 2:5[317, 327, 385, 393]. Hydrogenation of the double bonds to form tetrahydrofuran takes place readily over nickel at 20 to 30 atmospheres hydrogen and 100°C[162, 336], while the formation of butanol is accomplished over a platinum catalyst at room temperature[55, 172, 366] or copper, either as copper on kieselguhr or copper chromite, at 275°C and 250 atmospheres pressure[162], although it is reported that tetrahydrofuran may be produced over reduced copper oxide[380]. Alkylfurans may be similarly hydrogenated to tetrahydrofurans or alcohols[60, 279, 336]. Catalysts tested include palladium[342] and osmium[461] both of which are reported to give the tetrahydrofuran derivative without cleavage.

Considerable interest has been shown in the hydrogenation of 2-furaldehyde (furfural) which is readily available in commercial quantities. A variety of products may be formed, depending on how much hydrogen is absorbed and whether ring splitting occurs[8, 380]. The first step is the hydrogenation of the aldehyde to furfuryl alcohol followed by reduction of the ring



Copper, copper chromite, and platinum catalysts are effective. The reduction to the alcohol is very rapid as compared to subsequent steps. With nickel, cobalt and iron catalysts[256] or with copper or copper chromite at temperatures around 200°C[61, 416], the aldehyde group is usually reduced to methyl, so that 2-methylfuran, 2-methyltetrahydrofuran, and amyl alcohols may be products. With molybdenum sulfide catalyst and temperatures of 230 to 320°C, saturated hydrocarbons are obtained[268]. Fufurylidene ketones and 2-furanacrylic acids may be hydrogenated over nickel (60 to 100°C, 90 to 150 atm.) to give mainly tetrahydrofuran derivatives[189, 285].

2-Furancarboxylic (furoic) acid and its esters have been subjected to catalytic hydrogenation. According to Kaufmann and Adams[172], the platinum catalyzed reduction in alcohol solvent gives the tetrahydro derivative, while Smith and Fuzek[366] found that under similar conditions except for the use of acetic acid solvent, the principal product was 5-hydroxyvaleric acid. Paul and Hilly[280] reduced 2-furoic acid and its ethyl ester over Raney nickel at 110°C and 50 kg cm^{-2} hydrogen pressure, and obtained the tetrahydro derivatives in high yields. Smith, Conley, and King[364] reduced both the 2- and 3-furoic and 2- and 3-furanacetic acids in acetic acid solution over Adams platinum catalyst. Their results, shown in Table 13, indicate relatively small differences in reaction rates or energies of activation for the various reductions, even though the furoic acids should exhibit resonance between the carboxyl and furan groups, while the furanacetic acids should not. Since it is known that other reactions such as esterification show the influence of resonance, it is probable that the conjugation between the carboxyl and furan groups is destroyed in the adsorption complex on the catalyst surface. A number of other articles have been published in which the distribution of products from substituted furans hydrogenated over various catalysts has been determined[87, 139, 178, 218, 278, 286, 337, 338, 356].

Kariyone[171] investigated the hydrogenation of a number of furan derivatives over platinum black, colloidal platinum, colloidal palladium, and palladium supported on barium sulfate. He divided them into four groups, depending on their ease of hydrogenation; his classification is as follows (1 is most readily reduced):

(1) Derivatives containing CH_2 or CH— in the 2 position.

(2) Derivatives containing CO in the 2 position.

Table 13. Hydrogenation of Furoic and Furanacetic Acids on Platinum

Acid	$k_{30°} \times 10$ (l.g.$^{-1}$ min.$^{-1}$)	ΔH_a cal. mole^{-1}
2-Furoic	1.67	8100
2-Furanacetic	3.39	9100
3-Furoic	2.53	7600
3-Furanacetic	3.80	8000

(3) Furfural and its derivatives.

(4) 2-Furancarboxylic acid and its derivatives.

Smith and Fuzek[366] measured the first order rate constants for hydrogenation of furan derivatives over Adams platinum catalyst in acetic acid solvent, and compared them with similar values for reduction of benzene derivatives. The results (see Table 14) show that the furan nucleus is reduced more readily than that of benzene. The activation energies for reduction of the furan nucleus were found to be slightly greater than for the phenyl group.

In general, it is apparent that the furan nucleus is readily reduced under a variety of conditions, but that temperature, pressure, solvent, and nature of the catalyst employed influence both the speed of hydrogenation and the nature of the products formed.

The Hydrogenation of the Pyrrole Nucleus

The pyrrole nucleus is very similar to the furan nucleus and hence one might expect similar behavior. Thus, one would predict reduction to tetrahydropyrrole (pyrrolidine) or butylamine. Pyrrole and simple substituted pyrrols are not particularly stable in air, and hence not too much work has been done on these materials. Padoa[273] and Putokhin[296] passed pyrrole and hydrogen over nickel at temperatures of 180–200°C, and obtained some pyrrolidine. The latter also identified ammonia, dimethylamine, methylpropylamine, butylamine, amylamine, ethylpropylamine and in addition obtained an unidentified base of formula $C_6H_{13}N$. Adkins and Cramer[10] report a 37 per cent yield of pyrrolidine from the hydrogenation of pyrrole at 200°C. More recently Adkins and co-workers[298, 343] found that 2,3,4, or 5 alkylpyrroles are reduced by hydrogen over nickel or copper chromite at 200 to 250°C, but the introduction of a carbethoxy group on one of the ring carbons made it impossible to reduce the ring without causing hydrogenolysis of the carbethoxy group. If, on the other hand, the carbethoxy group

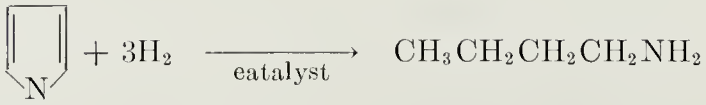


TABLE 14. COMPARISON IN RATE OF HYDROGENATION OF FURAN AND BENZENE DERIVATIVES

Derivative	k_{300} (l.g.$^{-1}$ min.$^{-1}$)		Ratio Furan/Benzene
	Furan Cpd.	Benzene Cpd.	
Parent Compound	0.554	.288	1.9
2-CH_3	.490	.178[b]	2.8
2,5-$(CH_3)_2$	.700	.186[c]	3.8
2-COOH	.167[a]	.112[d]	1.5
2-CH_2COOH	.339[a]	.112[d]	3.0
3-COOH	.253[a]	.112[d]	2.3
3-CH_2COOH	.380[a]	.112[d]	3.4
2-CH_2OH	.384	.133	2.9
2-CHO	.269		
Dibenzofuran	.386		
Average			2.7

[a] From Smith, Conley and King[364].
[b] From Smith and Pennekamp[368].
[c] From Smith and Pennekramp[369], data for *p*-xylene.
[d] From Smith, Alderman, and Nadig[357].

were on the nitrogen, the pyrrole nucleus could be selectively hydrogenated. An alkyl group on the nitrogen was relatively ineffective in promoting reduction of the ring. Phenylpyrroles were readily hydrogenated over nickel with yields of pyrrolidines around 80 per cent[9].

Early attempts to reduce the pyrrole nucleus over platinum or palladium were not very satisfactory[133, 134, 135, 445, 446]. In 1929, Andrews and McElvain[24] reported the successful reduction of N-methylpyrrole over Adams platinum in acetic acid solution, but only when the reactant had been carefully purified by distillation over sodium in a hydrogen atmosphere. These authors were unable to reduce methyl and carbethoxy-substituted pyrroles and this was corroborated by others[74, 227]. However, Putokhin[297] reported successful reduction of pyrrole to pyrrolidine over a palladium (oxide) catalyst; he also reported the reduction of 2-pyrrolealdoxime, 2-pyrrolecarboxylic acid, and 2-pyrrolemethylamine over Adams platinum using a mixed solvent consisting of glacial acetic acid, absolute ethanol, and a small amount of ferric chloride. Other successful reductions of pyrroles over palladium on asbestos have been reported by Zelinskii, Yurieff, and Shenyan[457, 463].

de Jong and Wibaut[82] successfully reduced a number of pyrroles to pyrrolidines with hydrogen over Adams platinum catalyst. Acetic acid was the most suitable solvent, although the hydrogenation would proceed in methanol, ethanol, or dilute hydrochloric acid. In no instance could a partially hydrogenated intermediate of the pyrroline (2,5-dihydropyrrole) type be isolated. Furthermore, comparative experiments with pyrrole and pyrroline demonstrated the greater ease of reduction of the pyrroline. The importance of high purity of the compounds to be reduced was emphasized by these workers. Jong and Wibaut found that, in general, substitution had little effect on the rate of reduction. However, it was demonstrated that alkyl- and arylpyrroles hydrogenate more rapidly than pyrrole itself, that 2-substituted pyrroles show a greater speed of reduction than the corresponding 1-substituted compounds, and that di-substituted pyrroles were more readily reduced than those with only one substituent.

Smith and Conley[363] made a thorough study of the kinetics of hydrogenation of pyrrole and methyl-substituted pyrroles. They used Adams platinum catalyst, acetic acid as solvent, and hydrogen pressures from 14 to 64 psi. The pyrroles were carefully purified before each experiment. The reductions were, in general, first order with respect to hydrogen pressure and zero order with respect to the pyrrole except for the 2,5- and 3,4-dimethylpyrroles which followed first order kinetics only in the lower pressure ranges studied. The values of the rate constants at 30°C, all referred to 1 gram of catalyst, are given in Table 15. From these results it appears that methyl substitution increases the rate of reduction of the pyrrole nucleus, and that this increase is greatest when substitution is on or close to the nitrogen atom. In general, the dimethylpyrroles have lower activation energies than the monomethyl derivatives.

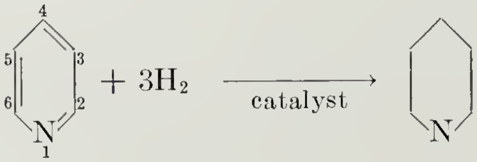
The conflicting data of various authors concerning the ease of and influence of substituents on the rate of hydrogenation of pyrroles can probably be ascribed to the instability of pyrroles in air together with their lack of careful purification prior to hydrogenation as well as to the differences in experimental conditions of hydrogenation.

THE HYDROGENATION OF THE PYRIDINE NUCLEUS

The catalytic hydrogenation of pyridine and its derivatives has been investigated by several authors. With most catalysts and temperatures below 250 to 300°C, the pyridine nucleus adds 3 molecules of hydrogen to form the piperidine nucleus.

TABLE 15. CATALYTIC HYDROGENATION OF THE PYRROLE NUCLEUS

Compound	$k_{30°}$ l.min.$^{-1}$g.$^{-1}$	ΔH_a cal. mole^{-1}
Pyrrole	.027	6200
N-Methylpyrrole	.052	8800
2-Methylpyrrole	.032	6900
3-Methylpyrrole	.029	6000
2,3-Dimethylpyrrole	.063	4500
2,4-Dimethylpyrrole	.077	7100
2,5-Dimethylpyrrole	.233	4700
3,4-Dimethylpyrrole	.053	4100



As early as 1912 Skita successfully reduced pyridine, 2-methylpyridine (α-picoline) and 4-methylpyridine (γ-picoline) at temperatures of 25 to 45°C over colloidal platinum as catalyst[348, 349]. The reductions were rather slow. Zelinskii and Boriskoff[459] also formed piperidine by catalytic hydrogenation of pyridine employing palladinized asbestos as catalyst. Sadikoff and Mikhailoff[323] used a platinum catalyst and hydrogen under pressure to reduce pyridine while Hamilton and Adams[124] employed platinum oxide catalyst and ethanol or acetic acid as solvent. Adkins and co-workers investigated the hydrogenation of pyridine and substituted pyridines at elevated temperatures and pressures[8, 12]. Nickel on kieselguhr, Raney nickel and copper chromite were employed as catalysts. These authors found that a higher temperature is necessary for conversion of pyridine to piperidine than that required to produce cyclohexane from benzene. They also noted that derivatives of pyridine with substituents in the 2 or 2,6 positions sometimes underwent hydrogenation at a temperature lower than that required for reduction of pyridine itself. However, variations in initial hydrogen pressure, amount of catalyst and type of solvent undoubtedly affected the times necessary for the reductions to take place.

Ushakoff, Broneffsky and Ivanova[411, 412, 413] studied the hydrogenation of pyridine and the picolines (monomethylpyridines) in the liquid phase at a temperature of 150°C and pressures of 50 to 100 atmospheres. The catalyst used was a 50 per cent nickel-silica gel mixture. All hydrogenations were complete to the hexahydro derivatives. By reducing mixtures of these pyridines and determining which were reduced first, these authors ascertained that the velocity of hydrogenation of the pyridine nucleus was decreased by introduction of a methyl group, and that this decrease became greater as the methyl group was introduced into the 2, 3 or 4 position. They further noted that addition of cobalt to the catalyst caused no difficulty, but that the presence of iron was detrimental.

Sugino and Mizuguchi[382] quantitatively reduced pyridine over nickel at hydrogen pressures of 160 atmospheres and temperatures of 220 to 230°C with quantitative yields of piperidine. When copper catalyst was employed, only 50 per cent piperidine was obtained, with the remainder present as a high molecular weight compound. Borisoff[52] studied the formation of 2-methylpiperidine (*alpha*-pipecoline) by hydrogenation of 2-methylpyridine over palladinized asbestos at 160°C, and the same reaction has also been studied over osmium and nickel catalysts[163, 322]. McElvain and Carney[228] reduced a number of alkyl pyridines over Raney nickel to form the corresponding piperidines.

Smith and Stanfield[373] studied the hydrogenation of pyridine and methyl pyridines over Adams platinum catalyst with glacial acetic acid as solvent, hydrogen pressures of 16 to 64 psi and temperatures of 15 to 45°C. The products were piperidine and methylpiperidines. The kinetic behavior of these reductions differed from that for benzene hydrogenation in that the reactions deviated slightly from the usual first order dependence on the hydrogen pressure and zero order dependence on the concentration of organic compound undergoing reduction. A five-fold increase in the pyridine concentration caused a decrease in the first order rate constant of 20 to 50 per cent depending on the particular compound involved, and a decrease in pressure from 64 to 16 psi caused an increase of first order rate constants of 50 to 100 per cent. When logarithms of rate constants are plotted against the reciprocal of absolute temperature, two straight-line portions are found which intersect at a point equivalent to a temperature of 23 to 26°C. This is another indication of a changing reaction order, with the heats of adsorption entering into the apparent heat of activation. Typical plots are shown in Figure 3. Table 16 shows calculated first order rate constants for concentrations of pyridines of .01 moles in 50 ml of acetic acid at initial hydrogen pressures of 64 and 16 psi, and also gives activation energies for the ranges 15 to 23°C and 23 to 45°C. The rate constants are all referred to one gram of standard catalyst. An examination of Table 16 shows that, as in the case of the five-membered pyrrole ring, the rate of reduction of the picolines depends on the position of the methyl group. The rate is decreased as the substituent is further removed from the nitrogen atom. However, all methyl-substituted pyridines are reduced at a slower rate than pyridine itself, as was also noted by Overhoff and Wibaut[272]. One also finds some similarity to the influence of the position of methyl substituents on the rate of hydrogenation of the benzene nucleus. Thus, 2,5-dimethylpyridine is reduced more rapidly than the 2,3-dimethyl compound, just as *para*-xylene was reduced more readily than *ortho*-xylene.

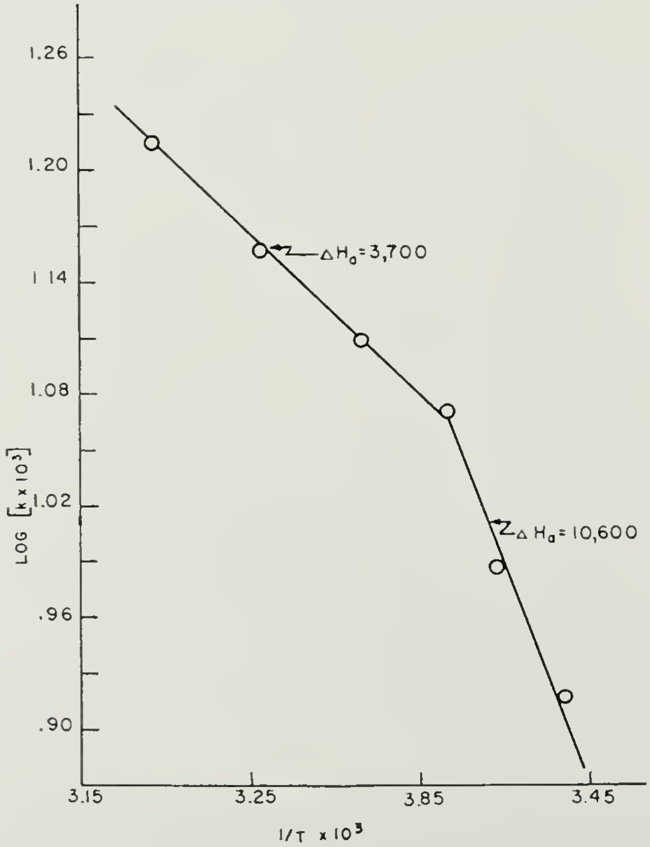


Figure 3. Temperature coefficient plot for hydrogenation of 2-methylpyridine over platinum in acetic acid solution (.01 *M*) at 16 psi pressure.

A number of other derivatives of pyridine have also been subjected to catalytic hydrogenation. Binz and Rath[51] used hydrogen at 40 atmospheres over nickel containing 1 per cent copper and temperatures of 200 to 235°C to reduce 2-pyridone (C_5NH_4OH) and nitrogen methyl, ethyl, propyl, butyl, isopropyl, octyl and benzyl derivatives to the corresponding piperidones. Wibaut[439] used platinum, hydrogen at ordinary temperature and pressure and acetic acid solvent to hydrogenate isonicotinic acid (pyridine-4-carboxylic acid) to the hexahydro product, Graves[117] reduced 2-aminopyridine over platinum to the tetrahydroaminopyridine, and Nienberg[258] hydrogenated the 3-aminopyridine over Adams platinum in the presence of hydrochloric acid to the di-hydrochloride of 3-aminopiperidine. It is also reported that 2-aminopyridine in a mixture of acetic acid and acetic anhydride may be hydrogenated in the presence of platinum oxide at room temperature and 500 mm hydrogen pressure to give N,N-diacetyl-2-aminopiperidine. 2-Benzylpyridine has been converted to the piperidine derivative in dioxane solution under hydrogen pressures of 95 atmospheres over Raney nickel at 150°C[30], and the 2- and 4-benzylpyridines have been similarly reduced over platinum in acetic acid solution[272].

TABLE 16. HYDROGENATION OF PYRIDINES

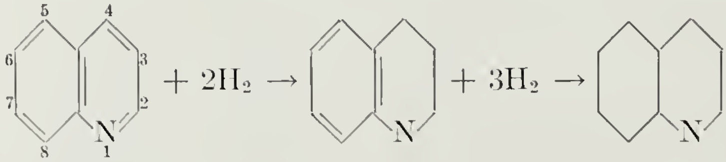
Methylpyridine	$k_{30°}$ l.g.$^{-1}$min.$^{-1}$		ΔH_a (cal. mole^{-1})	
	64 psi	16 psi	15–23°	23–45°
Parent compound	.142	.178	8300	3800
2-Methyl	.041	.073	10,600	3700
3-Methyl	.034	.061	9500	5700
4-Methyl	.022	.040	8000	6300
2,3-Dimethyl	.013	.022	11,300	5100
2,4-Dimethyl	.011	.022	9900	5000
2,5-Dimethyl	.030	.052	8400	4200
2,6-Dimethyl	.030	.054	11,100	5900
2,3,6-Trimethyl	.015	.019	10,400	7100
2,4,6-Trimethyl	.016	.024	13,000	4900

Dipyridils may be reduced over Adams platinum to obtain dipiperidyls[265, 266, 355]. A number of pyridylpyrroles have also been hydrogenated over Adams platinum[262]. It is reported that in all cases, the pyridine nucleus is the first to be reduced. It was reported that methyl substituents on the pyrrole nucleus exerted no marked influence on the production of piperidylpyrrolidines, but that when carboxyl groups were present on the pyrrol nucleus, it was impossible to carry hydrogenation beyond the piperidylpyrrole stage.

The catalytic reduction of phenylpyridines over Adams platinum in acid solvents has been studied[176, 272]. It is stated that 2-phenylpyridine gives 2-phenylpiperidine, but that 4-phenylpyridine is not hydrogenated. N,N-diphenyl-2-aminopyridine gives the N,N-diphenyl-2-aminopiperidine, but 2,6-diphenylpyridine and 2,4,6-triphenylpyridines give dicyclohexyl- and tricyclohexylpyridines. It is further stated that with 2,3,5,6-tetraphenylpyridine reduction of three of the five rings takes place, while with pentaphenylpyridine, one phenyl group is split off and the other four phenyl groups are reduced.

THE HYDROGENATION OF THE QUINOLINE NUCLEUS

Early experiments on the hydrogenation of quinoline over nickel with hydrogen at atmospheric pressure resulted in isomerization to methylindole instead of reduction of the fused benzene and pyridine rings[274]. However with 110 atmospheres of hydrogen, the reduction over nickel at 240°C proceeded through tetrahydroquinoline to decahydroquinoline. The pyridine nucleus was saturated in the tetrahydro compound[10, 150]. Similar results were obtained when quinoline was reduced at temperatures of 25 to 50°C with acetic acid, or ethanol with added hydrogen chloride as solvents[124, 272]. Rapaport[303] showed that reduction of quinoline over molybdenum sulfide at 220°C gave *ortho*-substituted anilines, probably by the mechanism of hydrogenation of the pyridine nucleus followed by splitting and degradation.



Von Braun and co-workers[422, 423, 428] studied the influence of methyl substitution on the formation of tetrahydroquinolines. They used a nickel catalyst, temperatures around 200°C, and hydrogen pressures of 20 atmospheres. For each substituted quinoline studied, the percentage of reduction of the benzene ring as compared to that for the pyridine ring was determined. The findings, listed in Table 17, show that increased methyl substitution on either ring makes its reduction more difficult so that one may successfully reduce either ring by loading the other with substituents. This result is in line with the observation discussed in previous sections that increased methyl substitution on either benzene or pyridine decreases the rate at which the hexahydro derivative is produced by catalytic hydrogenation.

Kinetic studies have also been carried out on the hydrogenation of quinolines in acetic acid solution over Adams platinum catalyst at 20 to 70°C with hydrogen pressures of 1000 to 2000 psi[73]. The reaction was found to be zero order with respect to the quinoline and first order with respect to hydrogen pressure. The hydrogenations proceeded through the tetrahydroquinoline to the decahydro derivatives, although some of the latter was formed before all of the quinoline was converted to the tetrahydro form. The distributions of 1,2,3,4- and 5,6,7,8-tetrahydro forms in a reaction mixture which had absorbed 2 moles of hydrogen per mole of quinoline were generally in line with those determined by von Braun and co-workers (Table 17). The relative rates of hydrogenation to the 1,2,3,4-tetrahydro- and to the decahydroquinolines are given in Table 18. The energies of activation for reduction of the pyridine nucleus ranged from 3,700 to 6,400 calories per mole, while for the benzene nucleus the cor-

TABLE 17. HYDROGENATION OF SUBSTITUTED QUINOLINES TO TETRAHYDROQUINOLINES

Compound	% Benzene Reduction	% Pyridine Reduction
8-Methyl-	0	100
7-Methyl-	0	100
6-Methyl-	0	100
4-Methyl-	33	66
2-Methyl-	4	96
2,3-Dimethyl-	44	56
2,4-Dimethyl-	80	20
2,3,4-Trimethyl-	100	0
2-Propyl-	35	65
2-Methyl-4-Phenyl-	84	16
2,6-Dimethyl-	1.5	98.5
2,4,5,8-Tetramethyl-	4	96
2,4-Dimethyl-7,8-tetramethylene-	0	100

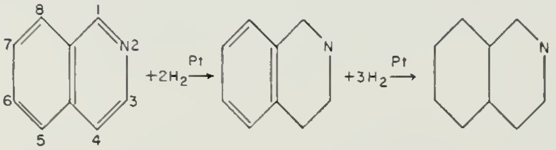
TABLE 18. RELATIVE RATES OF HYDROGENATION OF QUINOLINES AND 1,2,3,4-TETRAHYDROQUINOLINES OVER PLATINUM

Compound	Relative Rate for		
	Quinoline		Tetrahydroquinoline
	High Pressure	Low Pressure	High Pressure
Quinoline	1.00	1.00	1.00
2-Methyl-	0.94	0.46	1.31
3-Methyl-	1.40		1.70
4-Methyl-	0.05	0.04	0.08
6-Methyl-	0.87	0.66	0.90
7-Methyl-	0.93	0.60	0.63
8-Methyl-	1.21	1.90	0.20

responding range was 7,200 to 12,600. Similar studies were carried out at lower pressures (50–60 psi). The relative rates of reduction for these conditions are also included in Table 18[128].

6-Hydroxyquinoline has been hydrogenated at pressures of 60 to 100 atmospheres over nickel at a temperature of 140°C to the 1,2,3,4-tetrahydro derivative. At 180°C, decahydroquinoline is formed[242, 243]. 8-Amino-6-methoxyquinoline has been reduced over Raney nickel at 110°C and 40 atmospheres hydrogen pressure[45] or over copper chromite at 200°C and 2000 psi pressure[288] to give 8-amino-6-methoxy-1,2,3,4-tetrahydroquinoline. 4-Nitro-, 4-hydroxy-, and 4-methoxyquinoline-1-oxides have been hydrogenated over Raney nickel at 117 kg cm^{-2} pressure. In general, 5,6,7,8-tetrahydroquinoline derivatives were formed, although some 1,2,3,4-tetrahydroquinolines and decahydroquinolines were obtained[255].

Isoquinoline has also been subjected to catalytic hydrogenation. Like quinoline, the first reduction product is 1,2,3,4-tetrahydroisoquinoline.



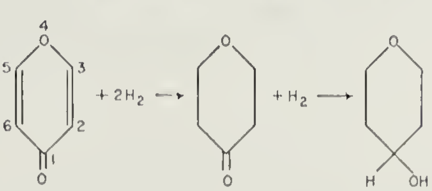
Most of the work has been done over platinum catalysts. Under conditions leading to the complete reduction of quinoline, the hydrogenation of isoquinoline stops at the tetrahydro stage[43, 300]. However, under more drastic conditions, the completely hydrogenated decahydroisoquinoline may be obtained.

THE HYDROGENATION OF OTHER AROMATIC COMPOUNDS

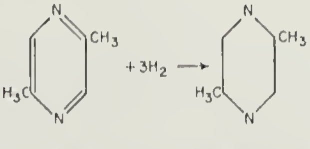
In addition to those aromatic nuclei the hydrogenation of which has already been discussed, reduction of a number of others has been investigated. In most cases, the work has been carried out from the standpoint of preparative organic chemistry or of determining the course of a reduction when more than one ring system is involved.

Thiophene has been studied in connection with catalytic hydrogenation but primarily from the standpoint of its poisoning action on many catalysts. Orloff and Brown[269] investigated the hydrogenation of thiophene in gasoline at high temperatures (around 400°C) over metal catalysts formed from oxides of cobalt, molybdenum and a mixed catalyst which was primarily nickel. Much of the sulfur was removed by the catalyst, but mercaptans, sulfides and disulfides were also formed. Moldavsky and Kumari[246] investigated the hydrogenation and decomposition of thiophene over several metal sulfides. Molybdenum and cobalt sulfides were the best catalysts, while copper was unsatisfactory. Nickel, manganese, and cadmium sulfides were included. The reaction order was between zero and one and activation energies between 17,000 and 30,000 calories per mole. Tetrahydrothiophene was one of the products. It would be expected that the course of the reaction would be similar to that found for hydrogenation of furan. 3,4-Dyphenylthiophene sulfone has been hydrogenated over platinum oxide to give a mixture of 2,3-diphenylbutadiene sulfone, 3,4-diphenyltetrahydrothiophene sulfone, and 3,4-dicyclohexyltetrahydrothiophene sulfone[31].

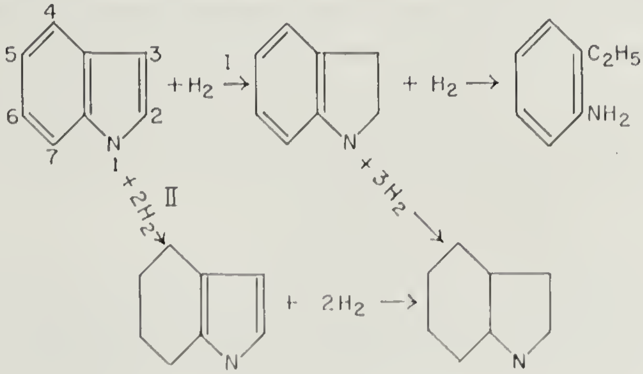
The hydrogenation of pyrones has been investigated by Mozingo and Adkins[251]. These authors used copper chromite or Raney nickel as catalyst at temperatures of 120 to 125°C and obtained tetrahydropyrone and γ-hydroxytetrahydropyran. The reaction is as follows:



2,6-Dimethyl- and 2,6-dicarbethoxypyrone have been reduced in acetic acid over platinum catalyst to the tetrahydro derivatives[77]. The pyrazine nucleus (as 2,5-dimethylpyrazine) has been hydrogenated over nickel or platinum in acetic acid to give *trans*-2,5-dimethylpiperazine[115].



A rather interesting study of the hydrogenation of indoles in decalin solution at 220 to 250°C over nickel was performed by von Braun, Bayer, and Blessing[421]. This system is readily hydrogenated to form dihydroindole. Further reduction either saturates the benzene ring or ruptures the pyrroline ring to form substituted aniline. This is shown by mechanism (I).



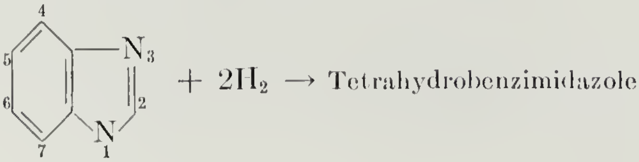
When, however, there are methyl groups substituted in the pyrrole ring, this reduction is hindered, and a portion of the methyl-substituted indole is reduced by route (II). These workers first studied the reduction of methyl-substituted dihydroindoles, and determined the fraction of substituted aniline and perhydroindole obtained from each compound. They then reduced corresponding methyl-substituted indoles, and analyzed the product for substituted anilines, tetramethylenepyrroles and perhydroindoles. By combining data on the reduction of the dihydroindoles and indoles, it was possible to calculate the percentage reduction of the pyrrole and benzene rings for each indole. The results are summarized in Table 19.

Table 19. Hydrogenation of Indoles over Nickel

Compound	% Aniline	% Tetrahydroindole	% Perhydroindole	% Reduction	
				Benzene ring	Pyrrole ring
Dihydroindoles					
Unsubstituted	79		21		
2-Methyl-	20		50		
3-Methyl-	57		43		
1,2-Dimethyl	55		45		
Indoles					
Unsubstituted	76		24	0	100
2-Methyl-	24	35	38	50	50
3-Methyl-	5	55	36	90	10
1,2-Dimethyl-	0	25	75	100	0

It is interesting that methyl substituents on the pyrrole ring decrease its percentage hydrogenation, for it has been previously noted (Table 15) that methyl substituents may increase the rate of reduction of the pyrrole nucleus by itself.

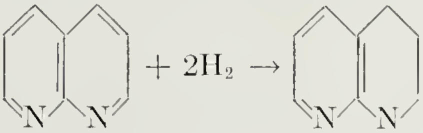
The catalytic hydrogenation of benzimidazole over nickel was attempted by Weidenhagen and Wegner[440], who reported that reduction could not be accomplished even at high temperatures and pressures. However, Hartman and Panizzon[126] were able to reduce successfully some benzimidazole derivatives to the tetrahydro forms by employing platinum (as platinum oxide) and acetic acid solvent at 80 to 90°C.



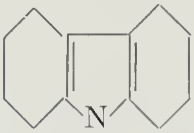
The 2-methyl and 2-ethyl compounds were reduced as well as the 2-phenyl derivative. In the latter case, the 2-cyclohexyltetrahydrobenzimidazole was formed. The reduction of 2-methyl-5-ethoxybenzimidazole was accompanied by splitting of the ether linkage. Presumably the tetrahydrobenzimidazoles are tetramethylenepyrroles.

Coumarone (benzofuran) has been reduced by passing it with hydrogen over palladium on asbestos at 175°C. The product is a mixture of the completely reduced ring system together with 2-ethylcyclohexanol and β-cyclohexylethanol, which result from splitting the furan ring. Hydrogenation over nickel results in more extensive ring splitting[388]. Liquid phase hydrogenation at atmospheric pressure in ethanol at 20 to 50°C over platinum black or platinum on charcoal proceeds analogously, but the intermediate dihydrobenzofuran may be obtained. The dihydrointermediate has also been obtained from 3-methyl-6-hydroxycoum-arone[289]. Several benzopyrones (chromones) have been catalytically reduced to chromans (benzopyrans)[251, 289].

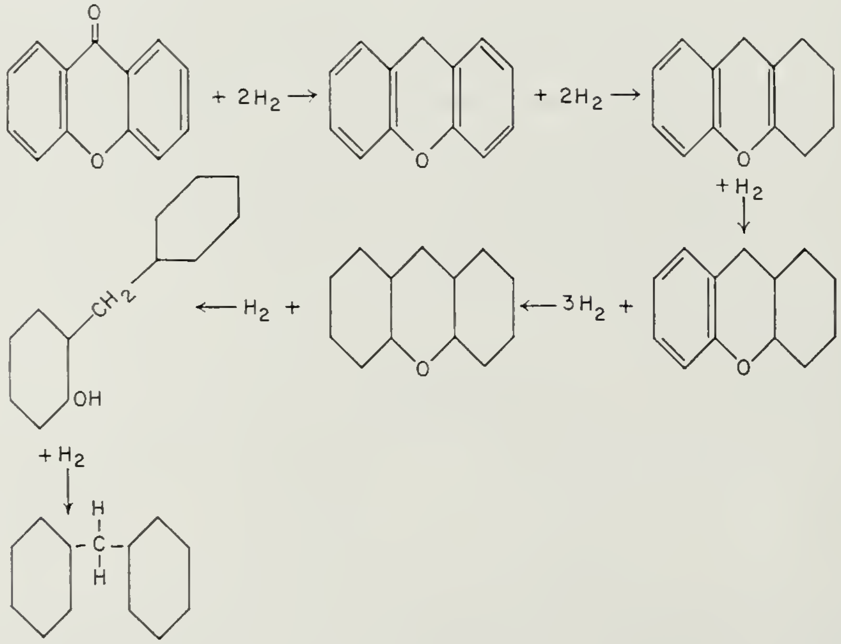
The reduction of 1,8-naphthyridine, which proceeds readily to the tetrahydro form, has been investigated[261]. For the 4-methyl and 2,4-dimethyl derivatives, the substituted ring is not hydrogenated. The reduction of quinolines and naphthyridines has also been compared[221].



The reductions of both dibenzofuran and dibenzopyrrole (carbazole) have been investigated. The pyrrole and furan rings appear to be quite stable, thus requiring 6 moles of hydrogen for complete reduction[55]. It has been suggested that, for dibenzofuran on platinum, both benzene rings are completely hydrogenated before the molecule is desorbed from the catalyst, since no intermediate could be isolated in a partially hydrogenated mixture, but only the starting material and the final product, dicyclohexylene oxide, were obtained[366]. For carbazole, with nickel catalyst, von Braun and coworkers[429, 430] obtained intermediates containing 4 and 5 moles of hydrogen. For the former, the structure proved to be:



The reduction of xanthene (dibenzopyran) and 3-methylxanthene was not achieved by Johnson and Ambelang[160] in the presence of Adams platinum catalyst, acetic acid solvent and 1.5 to 2 atmospheres of hydrogen. Use of high pressures and temperatures plus Raney nickel or copper chromite catalysts resulted in decomposition. However, von Braun and Bayer[120] employing nickel and hydrogen, reduced xanthone through xanthene and various further intermediates including dodecahydroxanthene to dicyclohexylmethane. The steps are as follows:



Many other examples of catalytic reduction of complex aromatic compounds, particularly from the standpoint of preparation of physiologically active materials, may be found in the chemical literature.

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CHAPTER 5

HYDROGEN ISOTOPES IN THE STUDY OF HYDROGENATION AND EXCHANGE

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INTRODUCTION

The isotopes of hydrogen have been used rather extensively since their discovery in attempts to elucidate the mechanism of hydrogenation reactions. With the aid of modern analytical instruments, particularly mass spectrometers, it has been possible to learn even more about the intimate details of what happens during catalytic reactions of hydrogen. It is not certain, however, that the mechanisms of the reactions have been entirely clarified. Instead, the use of isotopes and modern instruments have demonstrated how complicated the reactions really are.

When deuterium and an olefin such as 1-butene are brought together in the presence of a nickel catalyst, it would seem at first thought that simple addition of deuterium to the double bond should occur. Instead of obtaining $C_4H_8D_2$ as expected, one finds that light butane containing no deuterium may be one of the most abundant products in the initial stages of the reactions. Under certain conditions the di-deutero-butane may predominate in the final products, but all of the more highly deuterated butanes are also obtained.

The system is even more complicated than indicated above because such reactions as the following can also occur on the catalyst surface under hydrogenation conditions:

Chemisorption on the catalyst surface
Addition to the double bond
Redistribution of hydrogen and deuterium in the molecules
Exchange between olefin and deuterium
Exchange between olefin molecules
Double bond migration
Cis-trans isomerization
Self-hydrogenation and decomposition
Dehydrogenation and polymerization

Investigation of some of these reactions along with the addition reaction can add much to our understanding of what occurs on the catalyst surface. With all of the above complications, it is not surprising that there has been no general agreement with respect to the details of the mechanism of hydrogenation. In this review, the applications that have been made of deuterium (and tritium) to the study of hydrogenation will be summarized. Other reactions will also be included where they add to an understanding of the surface processes or to information on the behavior of the catalysts. The discussion will not follow a strictly chronological development, but rather it will be organized with respect to the research of groups supporting the various proposed mechanisms.

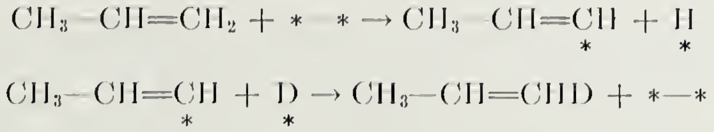
The researches to be summarized will be limited to those that have used the hydrogen isotopes or have investigated systems closely related to such researches. More complete references to the literature on this and other aspects of hydrogenation reactions can be obtained from the several excellent reviews already available[32, 49, 57, 69, 84, 119, 196, 217, 228].

In one of the earliest papers on the reaction of deuterium with olefins on nickel catalysts, Farkas, Farkas and Rideal[97] found that deuterium not only added to the double bond, but that it also exchanged with hydrogen of the ethylene. At temperatures below about 60°C the rates of both reactions were independent of the ethylene pressure and proportional to the deuterium pressure. There was also a marked inhibition of the para-hydrogen conversion during hydrogenation. The kinetics of the hydrogenation and exchange as well as the inhibition of the conversion showed that ethylene was strongly adsorbed as compared to hydrogen or deuterium. Their study of the simultaneous occurrence of the exchange and addition reactions as a function of temperature and pressure demonstrated that the use of deuterium could give valuable information about the catalytic reactions of hydrogen. Some of this information is not obtainable by kinetic measurements alone.

Shortly after the above work, Horiuti, Ogden and Polanyi[122], and Horiuti and Polanyi[125] found that exchange between deuterium and benzene on platinum and on nickel catalysts occurred much more rapidly than did the addition of deuterium to benzene. The rate of this exchange between deuterium and benzene was about 10^5 times greater than the exchange between D_2O and benzene. Ethylene and D_2O exchanged even slower. The rate of exchange between ethylene and heavy benzene (C_6D_6) was about one-fiftieth the rate of exchange of D_2O and benzene. Their analysis of these results led them to conclude that a dissociative mechanism could not explain these great differences. Instead, they proposed a mechanism which has since become known as the "associative" or "half-hydrogenated state" mechanism as opposed to a "dissociative" mechanism supported by Farkas and Farkas.

Since the time of the above publications, much of the literature on the use of deuterium in the study of hydrogenation and exchange reactions has been concerned with the support that the research gives for or against the "dissociative" or the "associative" mechanism, or some modification of them. The dissociative mechanisms include a step in which hydrogen is transferred from carbon to the catalyst:

(1)

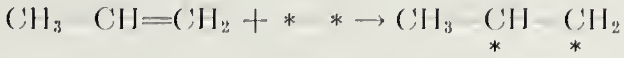


$$CH_3-CH=CH_2 + *\ \ * \rightarrow CH_3-CH=\underset{*}{CH} + \underset{*}{H}$$

$$CH_3-CH=\underset{*}{CH} + \underset{*}{D} \rightarrow CH_3-CH=CHD + *-*$$

where the stars represent the catalyst. The associative mechanisms involve a step in which the olefin is adsorbed to the catalyst by opening of the double bond:

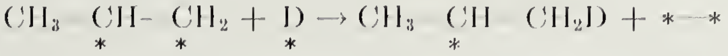
(2)



$$CH_3-CH=CH_2 + *\ \ * \rightarrow CH_3-\underset{*}{CH}-\underset{*}{CH_2}$$

followed by addition of a chemisorbed hydrogen or deuterium atom to give a half-hydrogenated state:

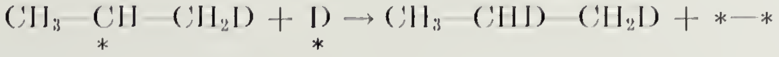
(3)



$$CH_3-\underset{*}{CH}-\underset{*}{CH_2} + \underset{*}{D} \rightarrow CH_3-\underset{*}{CH}-CH_2D + *-*$$

This half-hydrogenated intermediate (chemisorbed alkyl radical) can then react with another adsorbed hydrogen or deuterium resulting in hydrogenation:

(4)



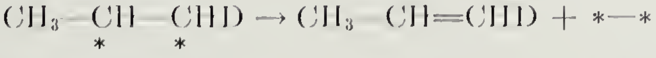
$$CH_3-\underset{*}{CH}-CH_2D + \underset{*}{D} \rightarrow CH_3-CHD-CH_2D + *-*$$

Exchange results when reactions (2) and (3) are reversed:

(5)

$$CH_3-\underset{*}{CH}-CH_2D + *\ \ * \rightarrow CH_3-\underset{*}{CH}-\underset{*}{CHD} + \underset{*}{H}$$

(6)



$$CH_3-\underset{*}{CH}-\underset{*}{CHD} \rightarrow CH_3-CH=CHD + *-*$$

The arguments in favor and against each of these mechanisms and associated processes are presented in the following sections.

DISSOCIATIVE MECHANISM

In a series of papers by Farkas and Farkas and their associates[1, 79-100] the dissociative mechanism has been proposed as one of the basic steps in the formulation of the interaction of deuterium with a number of compounds. Their researches and views on the mechanisms of the various reactions are summarized in a paper by Farkas[82] and their later work has extended these ideas to other systems[1, 90, 92-96].

Much of the experimental work on which they based their mechanisms has involved determinations of the effects of changes in pressure, temperature, catalyst and reactants on the rates of the reactions or nature of the products. The following general methods were used:

(1) Rates of addition to the double bond were determined by observing pressure changes manometrically:

$$C_2H_4 + D_2 \rightarrow C_2H_4D_2 \tag{7}$$

(2) Exchange of deuterium for hydrogen was determined from the increase in hydrogen content of the deuterium plus hydrogen gas after freezing out other components. A microthermal conductivity method was used for this analysis:

$$C_2H_4 + D_2 \rightarrow C_2H_3D + HD \tag{8}$$

(3) The rates of conversion of para- to ortho-hydrogen in the absence of olefin and during the reactions were followed by thermal conductivity measurements:

$$p\text{-}H_2 \rightleftharpoons o\text{-}H_2 \tag{9}$$

(4) Rates of equilibration of mixtures of H_2 and D_2 in the absence of olefin and during the reactions were also followed by thermal conductivity measurements:

$$H_2 + D_2 \rightleftharpoons HD \tag{10}$$

Activation of Hydrogen and Deuterium

Measurements (3) and (4) listed above were used by Farkas and Farkas as an indication of the rate of dissociation of hydrogen or deuterium on surfaces. In the presence of a second adsorbed molecule, the decrease in the rates of these reactions gave a measure of the surface available for the activation of hydrogen or deuterium prior to addition or exchange. Their arguments for these conclusions are given in the following paragraphs.

From earlier work[79] as summarized by Farkas[82], it was concluded that the rate of catalytic conversion of para-hydrogen or ortho-deuterium was controlled by dissociative chemisorption of hydrogen on the surface followed by recombination of the hydrogen atoms[41, 42, 43, 108, 219]:

$$p\text{-}H_2 \rightleftharpoons \underset{*}{H} + \underset{*}{H} \rightleftharpoons o\text{-}H_2 \tag{11}$$

$$o\text{-}D_2 \rightleftharpoons \underset{*}{D} + \underset{*}{D} \rightleftharpoons p\text{-}D_2 \tag{12}$$

Similarly

$$H_2 + D_2 \rightleftharpoons \underset{*\ *}{HH} + \underset{*\ *}{DD} \rightleftharpoons 2HD \tag{13}$$

When they observed[80, 86, 90] that all three of these reactions proceeded at similar rates, they took this as additional evidence that all three reactions occurred according to the same mechanism. Dissociation was considered to be the rate controlling step rather than migration of atoms in the surface layer. This follows because reaction (13) can occur only if the hydrogen atoms formed by the dissociation migrate and reunite as HD, whereas migration would not be necessary for the para-conversion. On the basis of the above information and arguments, the rate of para-hydrogen conversions, or the rate at which H_2 and D_2 molecules equilibrated was taken as a direct measure of the rate at which hydrogen molecules dissociated and recombined on the surface of the catalyst.

When another molecule such as ethylene is present, displacement of some of the hydrogen will be evident from a lowering of the rate of the para-hydrogen conversion or the H_2-D_2 equilibration since less surface is available for the dissociation of hydrogen. Farkas and Farkas[90] found, for example, that on a platinum catalyst, the activation energy of reaction (8), (9), and (10) was about 10 to 11 kcal/mole and that the reactions proceeded with relative rates of 1:0.51:0.67. In the presence of ethylene the rate of para- conversion was appreciably slower owing to replacement of hydrogen from the surface and loss of hydrogen atoms by the addition reaction. This result showed that ethylene was much more strongly adsorbed than hydrogen. The rate of para- conversion in the presence of excess ethylene was assumed to be proportional to the number of sites not available for adsorption of ethylene. During the reaction of ethylene with an excess of deuterium on nickel[97], it was found that very little para- conversion or return of HD to the gas phase occurred. However, when most of the ethylene was used up, a fast conversion took place. This indicated to them that all hydrogen atoms formed by dissociation of para-hydrogen, for example, added to ethylene immediately before they had a chance to recombine as normal hydrogen. On the basis of this result, it was assumed that once H_2 or D_2 is dissociated, the same two atoms add rapidly and simultaneously to the ethylene. They suggested that independent and consecutive addition of hydrogen atoms might occur to an appreciable extent at higher temperatures.

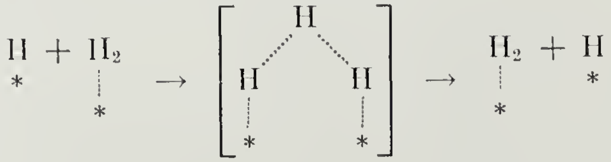
Similar considerations were used in studies of the reaction of deuterium with benzene vapor and with benzene liquid[84, 88]. In the gas phase reaction with benzene on platinized platinum it was found that there was no appreciable inhibition of the para-hydrogen conversion even though the rate of addition was independent of the benzene pressure and proportional to the deuterium pressure indicating surface saturation with respect to benzene. They concluded that only a small amount of benzene is adsorbed on platinized platinum in the presence of hydrogen or deuterium and then only on certain sites not used by deuterium. On those sites suitable for its adsorption, benzene is held rather strongly. The adsorbed deuterium effective in producing addition was assumed to be adsorbed adjacent to the benzene and then only weakly owing to a displacement effect, hence the first order dependence on deuterium pressure. Liquid benzene appreciably decreased the rate of the para-hydrogen conversion indicating more extensive coverage of the surface than for the gas phase reaction.

In the presence of acetylene[92] the rate of para-hydrogen conversion on platinized platinum was reduced by a factor of 15 whereas the same pressure of ethylene reduced it by a factor of 3. These results indicated to them that acetylene displaces hydrogen or deuterium rather extensively from the surface layer and that acetylene is much more strongly adsorbed than ethylene. Saturated hydrocarbons have very little effect on the rate of the conversion, and therefore do not appreciably displace hydrogen or deuterium.

There seems to be little doubt that the use of reactions (8), (9) and (10) yields some useful information relative to the reaction of unsaturated compounds with hydrogen and deuterium. However, for a time, serious questions were raised as to whether or not the chemical mechanism of the para-hydrogen conversion or of the H_2-D_2 reaction was in all cases given by Equations (11), (12) and (13).

Rideal[185, 186] had suggested, on the basis of studies by Roberts[192], that these reactions might take place by a valency switch mechanism between chemisorbed hydrogen atoms and hydrogen molecules adsorbed by Van der Waals' forces on unfilled gaps on the surface:

(14)



Eley[67, 72] had found that evaporated tungsten films adsorb a layer of deuterium atoms that is not readily removed by pumping at room temperature and that these chemisorbed deuterium atoms undergo rapid surface exchange with hydrogen at a rate comparable with the para-hydrogen conversion. Eley suggests the following general formulation:

$$\underset{*}{D} + H_2 \rightleftharpoons HD + \underset{*}{H} \tag{15}$$

$$\underset{*}{H} + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + \underset{*}{H} \tag{16}$$

Farkas and Farkas[96] have found a similar result for evaporated nickel films, but for palladium the conversion rate was fifteen times the exchange rate and for platinum five times the exchange rate. At higher temperatures for most metals, and for weak chemisorption at lower temperatures, mechanisms (11), (12) and (13) undoubtedly contribute appreciably or principally to the conversion or exchange. If the mechanism were given by (14), (15) and (16), one could conclude that the rate of the para-hydrogen conversion or H_2-D_2 exchange is not necessarily a measure of the rate of dissociation of hydrogen or deuterium into chemisorbed atoms on the surface of a catalyst as suggested by Farkas and Farkas[82].

Recently, however, after the work of Frankenburg[102], Rideal and Trapnell[187, 188, 189, 226] from surface coverage determinations as a function of temperature and pressure, and from the fact that the isothermal heats of adsorption fall from 14 kcal to 3 kcal with increased coverage, concluded that the chemisorbed layer is mobile, continuously evaporating and condensing when the surface coverage is high. They now support the original Bonhoeffer-Farkas mechanisms (11), (12) and (13).

Similar support for the Bonhoeffer-Farkas mechanism comes from the work of Kummer and Emmett[152, 153] on a singly promoted iron catalyst as distinguished from the doubly promoted iron catalysts which catalyzed conversion but not exchange. Both catalysts adsorbed hydrogen at −195°C, but only that adsorbed by the singly promoted one was reversible by pumping at this temperature and catalyzed both conversion and H_2-D_2 exchange. This reversible hydrogen chemisorption seems to be required for the Bonhoeffer-Farkas mechanism on metals as well as oxide catalysts as found by Taylor and his co-workers[217, 218] and Beebe and Dowden[17]. There is not general agreement yet since both the Rideal mechanism[56, 113] and the solution theory[20, 23, 27, 106] receive some support. Thus it appears that the mechanism of these simple reactions is not known with certainty and further experiments are needed particularly with respect to surface coverage by the hydrogen and other adsorbed molecules.

In spite of the uncertainties, the utility of these reactions of hydrogen and deuterium has been demonstrated. However, considerable caution must be used in inferring the extent of surface coverage from changes in the rates of exchange and conversion. This is illustrated by studies on the poisoning[26, 73, 128, 227] of these reactions by ethylene, oxygen, nitrogen and carbon monoxide. Nitrogen reduced the conversion rate on tungsten filament by 340, oxygen by 750, and ethylene by 1000; yet for the case of nitrogen only about 50 per cent of the surface was covered[227, 229]. Thus, the conclusion that the change in rate of conversion or exchange represents an equivalent change in the surface available for adsorption of hydrogen may not be justified. It is not profitable to review this field further here since Eley[55, 56, 68-72], Trapnell[226, 227, 229] and others[5, 20, 21, 24, 34, 113, 120, 155, 156, 180, 187, 217, 223, 245] have published a number of reviews and articles on the catalytic activation and adsorption of hydrogen. Reference to these will give further details on the problems referred to here as well as more complete references to the literature.

Experimental Results of Farkas and Farkas

The following is a summary of the experimental results of Farkas, Farkas, and their co-workers using the general methods discussed previously (p. 260).

Acetylene. Investigation of the reaction of hydrogen and deuterium with acetylene on platinized platinum[92] at pressures from 70 to 150 mm and temperatures from 20 to 140°C showed that the reaction was considerably slower than with ethylene. The rate increased with the hydrogen pressure and was appreciably reduced with increased acetylene pressure. The activation energy was 12 to 17 kcal compared to 7 to 10 kcal for ethylene on the same catalyst and in the same temperature range. This can be compared to 10.9 for the activation energy for the hydrogenation of acetylene on nickel[205-209]. Acetylene was first hydrogenated to ethylene and, as the acetylene was used up, a rapid increase in rate occurred as the ethylene that had formed was hydrogenated to ethane. With deuterium, the rate of addition was 67 per cent of the rate of addition of hydrogen. The rate of exchange was slow. For example, only a 1 per cent decrease in D-content of the deuterium gas occurred during the reaction of 88 mm of deuterium with 38 mm of acetylene at 90°C. This was much slower than the exchange with ethylene under similar conditions. Thus there was a 34 per cent decrease in the deuterium content during the reaction of 62 mm of deuterium with 47 mm of ethylene.

As stated previously, the rate of para-conversion of hydrogen was reduced to $\frac{1}{15}$ its original value by acetylene whereas it was reduced to only $\frac{1}{3}$ its value by ethylene. The results indicate that acetylene is much more strongly adsorbed than hydrogen or ethylene. This accounts for the selective hydrogenation of acetylene with respect to ethylene. They proposed a mechanism of the hydrogenation in terms of simultaneous addition of two hydrogen atoms and a mechanism of deuterium exchange by the dissociation of acetylene on the surface into $\underset{*}{C_2H}$ and $\underset{*}{H}$ followed by recombination of the radical with deuterium atoms in the surface layer.

Actually, the reactions of hydrogen and deuterium with acetylene are not always as simple as the formation of ethylene followed by further hydrogenation to ethane. The work of other authors will be considered later (pp. 316, 361).

Ethylene. The results of experiments by Farkas, Farkas and Rideal[97] on the exchange and addition reactions of ethylene and deuterium on a nickel catalyst were summarized previously (p. 258). Farkas and Farkas[90] have made a more complete investigation of these reactions of ethylene on a platinized platinum catalyst at pressures from 10 to 100 mm in the temperature 0 to 236°C. Up to 150°C the temperature coefficient of the addition reaction is greater than unity with an energy of activation of 10 kcal. Above 150°C the reaction becomes slower corresponding to a negative temperature coefficient in agreement with other investigators[53, 109, 146, 164, 174, 178, 179, 184, 194, 200, 201, 202, 204, 230, 256]. At the lower temperatures, the progress of the reaction could be approximately represented by $p = p_0e^{-kt}$ where p and p_0 represent the pressure of the reactant not in excess at time t and $t = 0$, respectively. Increasing the pressure of ethylene decreased the rate of reaction, while increasing the pressure of hydrogen increased the rate.

The rate of addition was about 1.2 times faster with hydrogen than with deuterium, although larger factors have been reported by others[146, 153, 179, 230, 249] for different catalysts. Concurrently with the addition of deuterium, as measured by the pressure decrease, the exchange reaction was determined by measuring the change in D-content of the deuterium plus hydrogen and of the ethylene. The exchange reaction was observable only at the higher temperatures and had an activation energy of 22 kcal, which is considerably higher than that for the addition reaction. The ratio of the rate of exchange to addition was 0.02 at 25°C; 0.5 at 100°C; 2.3 at 146°C; and 13.3 at 23.5°C. The rate of exchange did not decrease at the higher temperatures as was observed for the addition reaction. As with the addition reaction, the exchange rate decreases with increased ethylene pressure and increases with increase in deuterium pressure. Under the conditions of the reactions, they had established that no polymerization, formation of methane, or exchange with ethane occurred.

On the same platinized platinum catalyst, the para-hydrogen conversion, ortho-deuterium conversion, and the H_2-D_2 equilibration were all found to proceed at comparable rates with activation energies of 10 to 11 kcal, which is the same as for the addition reaction. During the reactions of p-H_2 and o-D_2 with ethylene, the rates of the addition reactions were about the same as the rates of conversion. This indicated to them that the rate controlling step in the addition reaction was the dissociation of hydrogen. The fact that the conversion was particularly slow during addition on nickel[97] led them to the conclusion that once activated, two hydrogen atoms added to the double bond simultaneously before they had time to recombine and desorb as normal hydrogen (see p. 261). The differences in the temperature coefficients and activation energies of the exchange and addition reaction as a function of temperature indicated to them that the two reactions proceeded by entirely different mechanisms. Dissociation of adsorbed ethylene was assumed by Farkas and Farkas to be the rate controlling step for the exchange reaction. This dissociation,

$$C_2H_4 \rightarrow \underset{*}{C_2H_3} + \underset{*}{H} \tag{17}$$

they assumed, increased at higher temperatures to such an extent that it decreased the concentration of adsorbed ethylene available for hydrogenation. This effect, rather than the setting in of desorption of hydrogen or of ethylene, as frequently proposed, they felt, was the cause of the decrease in the rate of hydrogenation at higher temperatures.

The results and conclusions of a few of the large number of other investigations[11, 18, 21, 28, 52, 62, 74, 111, 114, 128, 130, 145, 166, 171, 195, 231, 232, 236, 239, 240, 241, 249] relative to the reactions of ethylene with deuterium will be discussed in later sections of the review.

Benzene. Following the initial work of Horiuti, Ogden and Polanyi[122, 125] on the reaction of benzene with deuterium on platinum and nickel catalysts referred to previously (p. 258), and to be discussed more fully later, Farkas and Farkas[87, 88] studied this and other reactions in both the liquid and the gas phase on a platinized platinum catalyst. A comparison was made also of the rates of exchange of deuterium with a number of other substances in the liquid and vapor phase[87]. With water and alcohol, the exchange rates were much faster in the gas than in the liquid phase, while for benzene and ethyl ether, the reactions were faster in gas phase but not greatly so. The rates of exchange were in the order alcohols (H in OH) > acetone > benzene > ethyl ether. Rates of para-hydrogen conversion as compared to the rates of exchange showed that conversion was considerably more rapid than exchange for ether, benzene, and acetone in the vapor phase. In the liquid phase, the two reactions were about the same rate. This lack of inhibition in the gas phase indicated only slight adsorption of the vapor compared to hydrogen. For water and alcohols, the rates of the conversion and exchange reactions were about the same, both in the vapor and liquid phase. However, strong inhibition of the conversion indicated rather complete coverage of the surface. From these results and from experiments on the effect of increased pressure, they concluded, as others have also done, that both deuterium and the other reactant must be in the adsorbed layer and that the rates of the reaction are affected by replacement of one of the reactants from the surface by the other. On this basis, the authors doubted that the conclusions of Horiuti and Polanyi[125], which were based on a comparison of the rates of exchange of D_2 and D_2O with benzene, could be regarded as disproving the dissociative mechanism or proving the associative mechanism. The answer to this by Horiuti and Polanyi is discussed later (p. 275).

In the more detailed study of the interaction of deuterium with benzene in the vapor phase on a platinized platinum catalyst, Farkas and Farkas[88] found that the absolute rate (number reacting per unit time) of the hydrogenation reaction was proportional to the deuterium pressure and practically independent of the benzene pressure. The absolute rate of the exchange reaction, as measured by the decrease in D-content of the deuterium gas, was independent of the deuterium pressure and varied as the 0.4 power of the benzene pressure. Thus, their results for the two rates were

$$\text{Hydrogenation} \sim p_{D_2} p_{C_6H_6}^{0} \tag{1}$$

$$\text{Exchange} \sim p_{D_2}^{0} p_{C_6H_6}^{0.4} \tag{2}$$

The apparent activation energies were 7 kcal for hydrogenation and 9 kcal for the exchange. The half-life time for exchange with 26 mm of benzene and 27 mm of deuterium at 18°C in one experiment, for example, was 50 min. compared to 63 min. for hydrogenation, or a ratio of 1.26. In general, the ratio of the rate of exchange to hydrogenation increased the lower the hydrogen pressure and the higher the benzene pressure.

Para-conversion (as discussed previously, p. 266) proceeded about 100 times faster than exchange or hydrogenation, in contrast to the situation with ethylene, acetylene, alcohol or water. In liquid benzene, the rate of hydrogenation was appreciably slower than hydrogenation in the gas phase, the half-life times being 37.5 compared to 155 minutes. The exchange and para-conversion proceeded in the liquid phase at about the same rate, but both were somewhat faster than hydrogenation. The rate of exchange of liquid benzene was proportional to the deuterium pressure rather than independent of it as in the gas phase. Hydrogenation also varied as the hydrogen or deuterium pressure. That is, for the benzene liquid:

$$\text{Hydrogenation} \sim p_{D_2} \tag{3}$$

$$\text{Exchange} \sim p_{D_2} \tag{4}$$

The rapid para-conversion in the vapor phase reactions indicated slight coverage of the surface with benzene, but the pressure dependencies ($P_{C_6H_6}^{0.4}$ for exchange and $P_{C_6H_6}^{0}$ for hydrogenation) indicated rather complete coverage. This contradictory behavior was reconciled by assuming that benzene occupies only a certain few places which adsorb the molecules very strongly leaving many other sites for the para-conversion. From the variations in the rates of hydrogenation and exchange with pressure and temperature, they concluded that the reactions proceeded by two distinctly different mechanisms that could not be explained in terms of the common half-hydrogenated intermediate assumed in the associative mechanism of Horiuti and Polanyi. Instead, they prefer mechanisms in which hydrogenation involves simultaneous addition of two hydrogen atoms, whereas exchange consists of the dissociation of benzene into phenyl radicals followed by reunion of a phenyl radical with a deuterium atom present in the adsorption layer. The rate determining step of exchange in the gaseous phase was assumed to be the dissociation of benzene into a phenyl radical and one hydrogen, since in the neighborhood of the point of adsorption, relatively large amounts of hydrogen will be adsorbed. In the liquid phase, however, the concentration of deuterium on the surface is small and the rate determining step is no longer the rupture of C—H bonds but is the supply of deuterium atoms to the C_6H_5 radicals. Hence, the exchange in the liquid should be dependent on the deuterium pressure, and independent of it in the gaseous phase. They recognized that diffusion of deuterium to the surface in liquid benzene might be controlling rather than the dissociation of deuterium, but they did not evaluate the relative magnitude of these rates. Both, however, under these conditions would be dependent on the deuterium pressure. Recent studies of benzene-deuterium reactions on metal films will be discussed later (p. 366).

Exchange with Saturated Hydrocarbons. Some of the arguments used by Farkas and Farkas for the dissociative mechanism of exchange come from the results of experiments on the exchange of deuterium with saturated hydrocarbons. That saturated hydrocarbons do exchange with deuterium and exchange hydrogen atoms between themselves was first shown by Morikawa, Benedict and Taylor[168, 169, 170] and Morikawa, Trenner and Taylor[171]. Their results will be discussed later (p. 322). Later, Farkas and Farkas[94, 95] studied the exchange of ethane, propane, butane, *n*-hexane and cyclohexane on active platinum catalysts. The first three substances were investigated at pressures of about 20 mm for each reactant at temperatures from 26 to 126°C. All hydrogen atoms of butane, for example, were exchangeable. The half-time for the exchange of butane at 97°C was 14.5 minutes. Exchange with propane was $\frac{1}{4}$ to $\frac{1}{5}$ the exchange rate with butane. With ethane, the exchange rate was $\frac{1}{36}$ that with propane giving the following order for hydrocarbons: $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10} < C_6H_{14}$.

The energy of activation for butane was 26 kcal in the temperature range 26 to 41°C and about 11 kcal at 77 to 95°C. For propane it was 12 to 9 kcal. In another series of experiments they found the half-time for the exchange of *n*-hexane with deuterium on a similar platinum catalyst was 11 min. at 82°C, and for cyclohexane it was 9 min. at 98°C. These half-times were independent of total pressure. The latter reaction was complicated by dehydrogenation to benzene, but it was shown that exchange was about 47 times faster than dehydrogenation at 97° and 8.5 times faster at 127°C. Energies of activation of *n*-hexane were 9 kcal at 55 to 126°C and 17 kcal at the lower temperatures. Unfortunately, they did not measure the half-times for exchange of unsaturated hydrocarbons on these same catalyst preparations, so it is not possible to make quantitative comparisons from their work.

Qualitatively, in the series acetylene, ethylene, ethane, the rate of exchange of ethylene is much greater than that for acetylene or ethane so they point out that there is not necessarily a relation between unsaturation and ease of exchange. The rates are probably influenced more by relative adsorbabilities of the compounds and of deuterium as well as by the loosening of the C—H bond. The fact that some of the saturated compounds did exchange at appreciable rates in the same temperature range as the unsaturated compounds is cited as further evidence for the dissociative mechanisms because exchange with saturated compounds undoubtedly occurs via dissociation of hydrogen from the hydrocarbon on the catalyst surface. Farkas and Farkas could see no reason why unsaturated compounds should exchange by a different mechanism than saturated ones do. Arguments against this point of view cite the results of Taylor and his co-workers[171] in which exchange with ethylene was detectable at −80°C, while it was detectable with ethane only above 100°C.

Mechanisms Proposed by Farkas and Farkas

Formulations of mechanisms proposed in the papers of Farkas and Farkas[82, 94] for a variety of reactions are summarized here. The experimental work that led them to these ideas was described in the previous sections and will not be discussed further again. Comments of others about these mechanisms will come later.

Hydrogenation. A detailed formulation for hydrogenation is not given but their mechanism does specify that it occurs in the adsorption layer between the unsaturated compound and two chemisorbed hydrogen atoms, both of which are from the same molecule, and both of which add simultaneously rather than consecutively. They maintained that exchange occurs by a different mechanism involving the dissociation of an adsorbed olefin. Apparently they do not consider the olefin dissociated on the surface for the hydrogenation reaction. Thus, it would appear that their mechanism of hydrogenation would be formulated as follows:

(18) $$\mathrm{R{-}CH{=}CH_2 \rightleftharpoons (R{-}CH{=}CH_2)_{ads.}}$$

(19) $$\mathrm{D_2 \rightleftharpoons \underset{*-*}{DD}}$$

(20) $$\mathrm{(R{-}CH{=}CH_2)_{ads.} + \underset{*-*}{DD} \rightarrow R{-}CHD{-}CH_2D}$$

It was assumed that the rate of dissociation of hydrogen on the catalyst and hence the maximum rate of hydrogenation could be measured by the para-conversion of hydrogen, the ortho-conversion of deuterium, or by the reaction $H_2 + D_2 \rightleftharpoons 2\ HD$. With these as indicators, information about the composition of the adsorption layer on the catalyst could be inferred. It was emphasized that the concentration of the reacting partners in the adsorption layer are of primary importance in determining the rate of hydrogenation.

With respect to the addition of two deuterium atoms at once, it should be pointed out here that there is now considerable evidence from mass spectrometric and infrared studies of the products that this is not the principal mechanism of addition, though it may contribute in certain cases at lower temperatures. These researches will be described later (pp. 298, 342, 344, 362, 374).

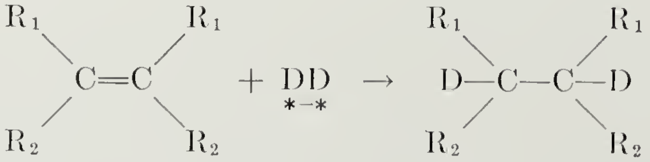
Stereochemical Isomers in Hydrogenation. Starting with the theory that catalytic hydrogenation occurred by the simultaneous addition of two atoms of the same hydrogen molecule, Farkas and Farkas[82, 89] pointed out, as experimentally observed by many previous investigators, that the addition to a double or triple bond would be in the *cis*-position. The following rules were given:

1. Acetylene compounds yield *cis*-ethylene derivatives.

(21)

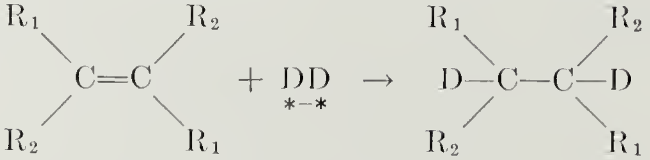
2. *Cis*-ethylene compounds yield meso compounds.

(22)



3. *Trans*-ethylene compounds yield a racemic mixture of optically active compounds.

(23)



Rapid *cis-trans* isomerization during hydrogenation (p. 372) may affect the yield.

With nascent hydrogen or at higher temperatures, the thermodynamically stable isomers would be expected since hydrogenation would then involve consecutive addition of two independent hydrogen atoms. This would usually mean *trans* compounds from acetylene derivatives and *meso* compounds from ethylene derivatives. They reviewed the literature and found that the above rules held in most of the cases known at that time. Greenhalgh and Polanyi[111], however, have pointed out that *cis* addition to acetylene derivatives was not proof of the simultaneous addition of a pair of hydrogen atoms (p. 288). The results of more recent work on stereochemical additions will be discussed later (p. 318).

Exchange Reactions with Deuterium. Farkas and Farkas assume that at sufficiently high temperatures a C—H bond of an adsorbed hydrocarbon is dissociated on the catalyst surface. The hydrogen atom has some mobility but the hydrocarbon radical is firmly held. Deuterium atoms can combine with the radicals which then desorb as exchanged hydrocarbons:

$$(\text{R—CH}{=}\text{CH}_2)_{\text{ads.}} \rightarrow \text{R—CH}{=}\underset{*}{\text{CH}} + \underset{*}{\text{H}} \tag{24}$$

$$\text{D}_2 \rightarrow \underset{*}{\text{D}} + \underset{*}{\text{D}} \tag{25}$$

$$\text{R—CH}{=}\underset{*}{\text{CH}} + \underset{*}{\text{D}} \rightarrow \text{R—CH}{=}\text{CHD} \tag{26}$$

$$\underset{*}{\text{H}} + \underset{*}{\text{D}} \rightarrow \text{HD} \tag{27}$$

The rate determining step is usually the dissociation of the hydrocarbon, although in cases where the surface is nearly completely covered by the hydrocarbon, it may be dissociation of deuterium. The loosening of the C—H bond by the catalyst and the adsorbability of the hydrocarbon will have a marked influence on the rate. Although they do not formulate the detailed mechanism of adsorption they suggest that it may be a chemisorption arising from interaction between the catalyst and the hydrogen atoms of the hydrocarbon.

The authors emphasize that the mechanism of exchange is different from that of hydrogenation. Differences in the rates of these reactions and their dependence on temperature is attributed to the occurrence of the two reactions on different catalyst sites.

Exchange Between Hydrocarbons. Their formulation of the exchange between two hydrocarbons such as CH_4 and CD_4 follows that suggested by Morikawa, Benedict and Taylor[168]:

$$\text{CH}_4 \rightarrow \underset{*}{\text{CH}_3} + \underset{*}{\text{H}} \tag{28}$$

$$\text{CD}_4 \rightarrow \underset{*}{\text{CD}_3} + \underset{*}{\text{D}} \tag{29}$$

$$\underset{*}{\text{CH}_3} + \underset{*}{\text{D}} \rightarrow \text{CH}_3\text{D} \tag{30}$$

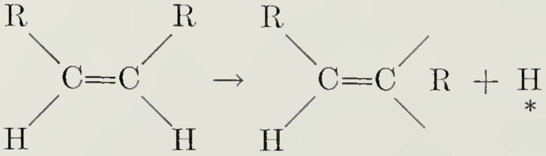
$$\underset{*}{\text{CD}_3} + \underset{*}{\text{H}} \rightarrow \text{CD}_3\text{H} \tag{31}$$

Farkas considered the occurrence of such exchange reactions as direct proof for their proposed dissociative mechanism of exchange reactions in general, that is, for unsaturated as well as for saturated compounds.

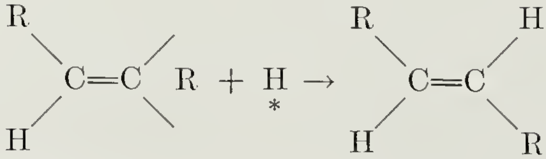
The exchange between CH_4 and CD_4 referred to above was faster than the exchange between CH_4 and D_2, owing to displacement of CH_4 from the surface by D_2. Farkas calls attention to another effect which he feels might influence exchange reactions in the opposite sense. At low concentrations of the hydrocarbon, the rate determining step in the exchange is probably the dissociation of RH into $\underset{*}{R}$ and $\underset{*}{H}$ (Equations 28 or 29), whereas at low concentrations of deuterium the union of $\underset{*}{D}$ with $\underset{*}{R}$ (Equations 30 or 31) might govern the rate. On this basis he states that the absence of an interchange reaction between two hydrocarbons, each of which exchanges readily with deuterium, does not disprove the dissociative mechanism of exchange reactions. (See arguments of Conn and Twigg, p. 290).

Cis-trans Isomerization. This process was formulated as follows:

(32)



(33)



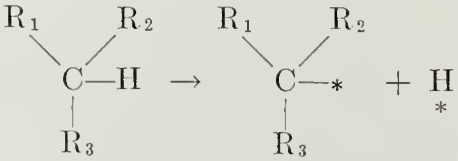
Double-bond Migration. Reactions of this type were assumed to follow the mechanism

$$CH_2{=}CH{-}CH_2{-}CH_3 \rightarrow CH_2{=}CH{-}\underset{*}{C}H{-}CH_3 + \underset{*}{H} \tag{34}$$

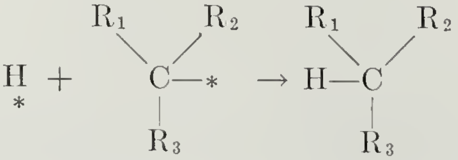
$$CH_2{=}CH{-}\underset{*}{C}H{-}CH_3 + \underset{*}{H} \rightarrow CH_3{-}CH{=}CH{-}CH_3 \tag{35}$$

Racemization of Optically Active Hydrocarbons. The formulation for this process by the dissociative mechanism is

(36)



(37)



Polymerization. Ethylene, for example, may polymerize by the following mechanism:

$$CH_2{=}CH_2 \rightarrow CH_2{=}\underset{*}{CH} + \underset{*}{H} \tag{38}$$

$$\underset{*}{H} + CH_2{=}CH_2 \rightarrow \underset{*}{CH_2}{-}CH_3 \tag{39}$$

$$CH_2{=}\underset{*}{CH} + \underset{*}{CH_2}{-}CH_3 \rightarrow CH_2{=}CH{-}CH_2{-}CH_3 \tag{40}$$

In addition to the above, Farkas[82] also wrote mechanisms for disproportionation and decomposition-dehydrogenation.

Comments of other authors on a number of the above formulations will be discussed when their work is described rather than at this time.

ASSOCIATIVE MECHANISMS

Experimental Work of Horiuti, Greenhalgh, Polanyi and Associates

Exchanges Involving D_2, D_2O and Benzene. Following the discovery of catalytic exchange between deuterium and water by Horiuti and Polanyi[123, 124] and the exchange between deuterium and ethylene by Farkas, Farkas and Rideal[97], the exchange between deuterium and liquid benzene on platinum and nickel was reported in a note by Horiuti, Ogden and Polanyi[122]. With 10 g of benzene, 100 cc of hydrogen containing 1.14 per cent deuterium, the deuterium content was reduced to 0.93 per cent in 15 minutes at about 19°C in the presence of 20 mg of platinum black. The exchange was considerably more rapid than addition, with first order rate constants of 13×10^{-3} min.$^{-1}$ for exchange and less than 1×10^{-3} min.$^{-1}$ for addition. Using 2 g of reduced nickel with 20.9 per cent deuterium in the gas in a similar set of experiments, the deuterium content was reduced to 4.7 per cent in 15 minutes. First order rate constants were 99×10^{-3} min.$^{-1}$ for exchange and less than 1×10^{-3} min.$^{-1}$ for addition. Recent results on the benzene-deuterium reaction on metal films will be discussed in a later section (p. 366).

They wrote equations for three alternative mechanisms for the exchange which may be summarized as follows:

(I) Benzene dissociates to phenyl and adsorbed hydrogen followed by the reaction of phenyl with adsorbed deuterium

$$D_2 \rightarrow \underset{*}{D} + \underset{*}{D} \tag{41}$$

$$C_6H_6 \rightarrow \underset{*}{C_6H_5} + \underset{*}{H} \tag{42}$$

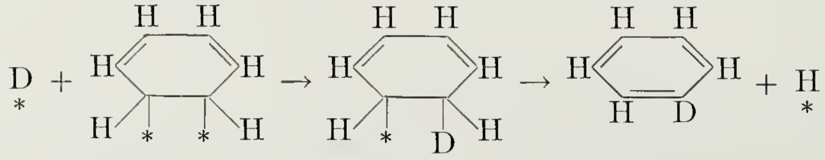
$$\underset{*}{C_6H_5} + \underset{*}{D} \rightarrow C_6H_5D \tag{43}$$

(II) Hydrogen atom departs simultaneously with addition of adsorbed deuterium atom.

$$(44) \qquad \underset{*}{D} + C_6H_6 \rightarrow C_6H_5D + \underset{*}{H}$$

(III) Hydrogen departs at a time after benzene associates with the catalyst and adsorbed deuterium atom.

(45)



In this first paper they did not choose one of these alternatives as the most likely mechanism. However, Horiuti and Polanyi[125] in a later paper decided in favor of reaction (III) and wrote it out in more detail with respect to adsorption of the unsaturated compound on the catalyst and with respect to the relationship between exchange and hydrogenation.

The experiments which led them to select (II) or (III) in preference to (I) were based on the following considerations: If D_2 or D_2O exchange with C_6H_6 by mechanism (I) in which dissociation of C_6H_6 into $\underset{*}{C_6H_5}$ and $\underset{*}{H}$ is the slow step, then the velocity of the exchange should be about the same provided both D_2 and D_2O produce adsorbed deuterium atoms faster than benzene can take them up, and provided the effect is not due to a shift in the adsorption equilibrium or a change in dissociation rate of the adsorbed hydrocarbon molecules. That D_2O furnishes D atoms to the surface of the catalyst at a rather rapid rate is supported by the rapid exchange between deuterium gas and water on platinum or nickel catalyst[123, 124]. No information was available to them at that time to indicate that water would appreciably affect the adsorption equilibrium or the dissociation of benzene on the catalyst.

Ethylene and Benzene Exchange Reactions. Similarly, a comparison of the exchange reactions of the following pairs: C_2H_4-C_6D_6, C_2H_4-D_2O and C_6H_6-D_2O should give evidence for a choice of the mechanism. If mechanism (I) is operative, the authors[125] state that the rate of exchange of C_2H_4 and C_6D_6 will be governed by the dissociation of C_2H_4 or of C_6D_6, whichever is smaller. Consequently, if the exchanges occur through dissociation of the hydrocarbon as the slow step, then one of the pairs C_2H_4-D_2O or C_6H_6-D_2O should not exchange at a rate faster than C_2H_4-C_6D_6. The same provisions with respect to adsorption equilibria apply as in the previous case.

The results of experiments[125] designed to test these ideas were as follows:

At room temperature there was no measurable exchange between liquid benzene and D_2O in 240 hours on platinum black or on nickel in 34 hours. Also, no exchange at room temperature was observable between C_2H_4 and D_2O nor between C_2H_4 and C_6D_6. When the temperature was increased to 80°C, the reaction between C_2H_4 and D_2O on nickel was incomplete in 7 hours and complete in 27 hours. With C_6H_6 and D_2O at 80°C, the reaction was slower than the ethylene exchange, and at 200°C the system reached half completion in about one hour. The exchange between C_2H_4 and C_6D_6 was much slower than any of the other exchange reactions since it reached only about 15 per cent of the way to equilibrium after 24 hours.

Comparison of the above results and those of the exchange between liquid benzene with D_2, and C_2H_4 with D_2, leads to the following general conclusions. The rate of exchange between C_6H_6 and D_2O was lower by a factor of 10^5 than the exchange between C_6H_6 with D_2. The ratio of the rate of exchange between C_2H_4 with D_2O to that between C_2H_4 and D_2 was estimated to be about the same as for the benzene exchanges. The exchange between C_2H_4 and C_6D_6 was about $1/50$ that between benzene and D_2O.

According to their[125] arguments given above, the greatly reduced rate of exchange when D_2O is substituted for D_2 gas showed that mechanism (I) cannot be the correct one for the exchange between C_6H_6 and D_2 or between C_2H_4 and D_2. Also, the fact that the exchange between C_2H_4 and C_6D_6 was much slower than either the exchange between C_2H_4 and D_2O or that between C_6H_6 and D_2O shows that one of the last two reactions cannot be controlled by dissociation of the hydrocarbon. The rate of the exchange between C_2H_4 and C_6D_6 should proceed about as fast as one of these reactions if mechanism (I) were operative. They emphasize that these conclusions are valid only in case the provisions mentioned earlier with respect to adsorption equilibrium are satisfied. Farkas and Farkas[1, 87] (p. 266) doubted that these provisions were satisfied, and suggested that the great differences in rates were due to extensive displacement of one of the reactants from the surface.

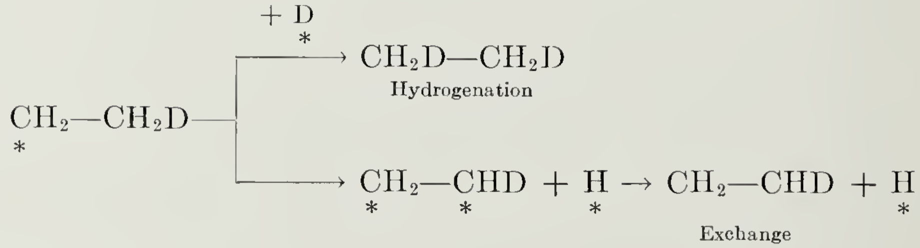
Mechanism of Exchange and Hydrogenation. From the results quoted above, Horiuti and Polanyi[125] concluded that the mechanism must be either (II) or (III). On the qualitative theoretical grounds that (II) involves a five-atom problem and (III) a four-atom problem they favored mechanism (III). It could also account for a number of other processes better. Thus mechanism (III) involves the unsaturated nature of the molecule and can, therefore, account for the more rapid exchange of unsaturated as compared to saturated compounds. It can account for the correlation between cathodic reduction and the catalytic hydrogenating power of the metal used as an electrode because such metals can chemisorb the double bonded compound. Mechanism (III) can account for observed *cis-trans* isomerizations, whereas mechanism (II) does not imply this as a consequence. Double bond shifts as observed in many compounds imply opening of the double bond and mechanism (III) is more applicable in those cases that do and those that do not require the presence of hydrogen.

Their more detailed formulation of the associative mechanism of exchange and hydrogenation may be written as follows, using ethylene as an example:

$$D_2 \rightarrow \underset{*}{D} + \underset{*}{D} \tag{46}$$

$$CH_2{=}CH_2 \rightarrow \underset{*}{CH_2}{-}\underset{*}{CH_2} \tag{47}$$

$$\underset{*}{CH_2}{-}\underset{*}{CH_2} + \underset{*}{D} \rightarrow \underbrace{\underset{*}{CH_2}{-}CH_2D}_{\text{Half-hydrogenated state}} \tag{48}$$



$$\underset{*}{CH_2}{-}CH_2D \xrightarrow{+\underset{*}{D}} \underbrace{CH_2D{-}CH_2D}_{\text{Hydrogenation}} \tag{49}$$

$$\underset{*}{CH_2}{-}CH_2D \rightarrow \underset{*}{CH_2}{-}\underset{*}{CHD} + \underset{*}{H} \rightarrow \underbrace{CH_2{-}CHD + \underset{*}{H}}_{\text{Exchange}} \tag{50}$$

Deuterium is dissociated into chemisorbed deuterium atoms according to Equation (46) and ethylene is chemisorbed by opening of the double bond according to Equation (47). Chemisorbed deuterium atoms adjacent to the chemisorbed ethylene adds to a carbon atom, one at a time, to give first the half-hydrogenated (48) state and then ethane (49). If the half-hydrogenated state reverts to chemisorbed ethylene by loss of hydrogen (50), then on re-evaporation the ethylene molecule contains deuterium and exchange has occurred. On the basis of this mechanism in which hydrogenation results from the statistically independent approach of the two deuterium atoms, the reaction should be second order with respect to hydrogen atoms, whereas exchange should be first order with respect to hydrogen atoms. Consequently, at low pressures the exchange should predominate. The predictions as to the orders of the reactions do not turn out to be correct generally as will be discussed in a review of later papers (pp. 284, 291, 381).

In the above formulation, reaction (46) accounts for ortho-para conversion, reaction (48) for *cis-trans* isomerization, reaction (49) for hydrogenation, and reaction (50) accounts for exchange. Reactions (46) and (47) were considered to be faster than (49) or (50) and the relative rates of (49) and (50) should depend on the pressure of hydrogen and on temperature.

Reciprocal Displacement of Reactants. In order to evaluate further the qualifying provisions of the previous work with respect to reciprocal displacement of reactants from the surface, Horrex, Greenhalgh and Polanyi[126] carried out additional experiments with groups of three exchanging substances. Thus, in general, with the group A, B, C, the exchange rates of the pairs A—B, B—C, and A—C were measured and compared with the exchange in the mixture ABC. If the exchange rate in the mixture corresponded to the rates of exchange of the pairs, they considered this as evidence that these rates were not influenced by the third substance.

The following typical results were obtained for the vapor phase reactions of the group: D_2, D_2O, saturated hydrocarbons (cyclohexane or isopentane). The catalysts were 0.6 g of platinum deposited on glass wool, some reduced at 80°, some at 100°C, and others at 290°C. During the reactions the mixtures were circulated by thermal convection through the catalyst in a 250 cc vessel. The half-period of the exchange between D_2 and cyclohexane extrapolated from measurements at 50, 70, and 90°C to 32°C was 4800 min. with an activation energy of 13.7 kcal on a catalyst reduced at 80°C. This can be compared to a half-period of 10 min. for the D_2—H_2O exchange on the same catalyst at 32°C. The rate of the D_2-cyclohexane exchange decreased slightly with increase in D_2 pressure and did not change with change in partial pressure of cyclohexane. Para-hydrogen conversion with excess cyclohexane present was considerably more rapid than exchange. The pairs D_2O-cyclohexane and D_2O-isopentane, in general, exchanged slightly faster than the pairs D_2-cyclohexane, and D_2-isopentane.

No apparent differences were observed between the hydrocarbons. Cyclohexane only slightly reduced the exchange rate of D_2 with H_2O. In the mixture D_2—D_2O-cyclohexane, the rate of exchange for the cyclohexane was about the same whether D_2 was present or absent. The experiment showed, too, that the D_2-cyclohexane exchange rate was not greater than the D_2O-cyclohexane rate even if water was present. The order of rates for the various pairs can be summarized as follows: $(D_2—H_2O) \gg (D_2O\text{-saturated hydrocarbon}) \simeq (D_2\text{-saturated hydrocarbon})$. The presence of a third member of the group did not greatly affect the rates.

For the group D_2O, benzene, and cyclohexane, the exchange rates of the pairs D_2O-benzene and D_2O-cyclohexane were about the same in the temperature range 66 to 93°C on a platinum catalyst reduced at 100°C. Rates in the mixture of the three were not measured because of the difficulty of separating benzene and cyclohexane for deuterium analysis. In another group (D_2O, cyclohexane (D), isopentane) they found that the exchange rates between cyclohexane containing deuterium and isopentane was slower than the exchange between D_2O and cyclohexane or isopentane. This checks the previous comparison of the pairs D_2O—C_2H_4, D_2O—C_6H_6, and C_6D_6—C_2H_4 (p. 274).

With the group (D_2, HCl or DCl, cyclohexane) the exchange rate for the pair D_2—HCl is very rapid compared to that for the other pairs at 70°C on a platinum catalyst reduced at 100°C. The exchange rate for the pair DCl-cyclohexane was slower than that for D_2-cyclohexane. In a mixture of all three, the D_2—HCl exchange was much more rapid than the other exchanges, although the extent of exchange of the cyclohexane was less than when it is alone with D_2, apparently owing to a poisoning effect of the HCl.

To compare the behavior of saturated and unsaturated compounds, they[126] determined exchange rates for pairs in the group (D_2, H_2O or D_2O, benzene). The exchange rate for D_2O-benzene and D_2O-cyclohexane on the platinum catalyst were the same. In contrast to this, the exchange rate for D_2-benzene is much more rapid than that for D_2O-benzene, the half-periods at 70°C being 2.5 min. and 300 min., respectively. Hydrogenation and exchange rates for the benzene were about the same and this made it difficult to make a comparison with a mixture of the three. However, they showed that the rate of hydrogenation in the presence of water was far more rapid than the exchange between D_2O and benzene.

The half-period of the exchange between D_2 and cyclohexane extrapolated to 29° was 5600 min. compared to 60 min. for the exchange between D_2 and benzene under comparable conditions. No measurements on exchange rates for a mixture of the three substances were made, but the fact that cyclohexane did not affect the hydrogenation rate was taken as an indication that the action of hydrogen was not impaired by the third substance of this group.

They summarize the above experiments as follows: The conversion of para-hydrogen as well as the exchanges D_2—H_2O and D_2—HCl proceed rapidly even though hydrocarbons are present, these exchanges being much faster than D_2O-hydrocarbons or DCl-hydrocarbons. Saturated hydrocarbons and benzene exchange with D_2O at about the same rate, but benzene exchanges more rapidly with D_2 than does the saturated hydrocarbons. Exchange of saturated hydrocarbons with D_2 is slower than exchange with D_2O and the rate of exchange between two hydrocarbons is still slower. Also, cyclohexane exchanges more slowly with DCl than with D_2O or D_2.

The similarity between the exchange rates of saturated hydrocarbons and benzene with D_2O suggests a similar process for the two exchanges, whereas the difference in rates for exchange with D_2 suggests a different mechanism, undoubtedly connected with the unsaturation of benzene.

Summary of Results on Platinum, Nickel and Copper Catalysts. The implication of the above experiments[126] together with that of some additional ones were discussed at length in a succeeding paper by Greenhalgh and Polanyi[111]. In the series of experiments reported in this paper[111], "first order constants" were measured for hydrogenation (k_H), exchange (k_E), para-hydrogen conversion (k_P) and hydrogen-deuterium equilibration (k_{HD}). These constants are defined by the equation $d\ln x/dt = k$, where x is the appropriate variable for each of the processes, i.e., pressure for hydrogenation, per cent D in the hydrogens for exchange, deviation of para-hydrogen content from equilibrium, and deviation of H_2—D_2 concentration from equilibrium. From the relative reaction rates expressed by these k values, the absolute or true reaction rates are obtained by multiplication by the corresponding value of p. The dependence of rate of exchange on the pressure of deuterium, for example, is given by $p_{D_2}k_E = p_{D_2}^{m}$. Pressures are in mm of Hg, time in min., and first order constants in min.$^{-1}$. From a plot of log k_E v.s. log p_{D_2} the dependence n of k_E on pressure could be determined ($k_E = p_{D_2}^{n}$). The power of p_{D_2} to which the rate ($p_{D_2}k_E$) is proportional is then $m = n + 1$. Not all of their data with the several modifications of catalyst used, under a variety of conditions, can be recorded here, but a number of typical results are summarized in Table 1.

Comparison with the Results of Farkas and Farkas. Comparison of the above results with those of Farkas and Farkas[88] (p. 266) show the following differences. Farkas and Farkas found that on platinum catalysts hydrogenation, exchange, and para-hydrogen conversion with liquid benzene all depended linearly on the pressure of hydrogen or deuterium. Also, the H_2—D_2 exchange and para-conversion proceeded at the same rate. Greenhalgh and Polanyi suggest that diffusion processes may have been rate controlling as in their experiments. Farkas and Farkas found the rate of exchange to vary as the 0.4 power of the benzene pressure, that is, the rate of exchange decreased with decrease in benzene pressure, while the rate of hydrogenation remained constant. Greenhalgh and Polanyi found no definite dependence on benzene pressure, but observed both exchange and hydrogenation to decrease to about the same extent with decrease in benzene pressure.

Aman, Farkas and Farkas[1] have made some further measurements on the exchange of several pairs of compounds similar to some of the measurements recorded above. They obtained results for the following on palladium and nickel catalysts: ethylene-D_2O; butene-D_2O; n-butane-D_2O; n-butene-(D)-ethylene; n-butane-D-ethylene. Very little exchange between ethylene and D_2O occurred in 45 hours at 110°C with 17.5 mm of D_2O and 600 mm of ethylene, although polymerization to butene-2 and formation of a little ethyl alcohol and acetic acid occurred. However, when the D_2O pressure was 350 mm and the ethylene pressure was 260 mm, the exchange was much more rapid and no polymerization took place. Exchange between butene (23 mm, 0.0057 moles) and D_2O (230 mm, 0.058 moles) at 120°C on 0.5 g palladium reached about one-half its maximum exchange in about 25

TABLE 1. REACTION ON PLATINUM, NICKEL AND COPPER CATALYSTS[111]

PLATINUM CATALYSTS

LIQUID BENZENE + D_2

Rate of hydrogenation: $\sim p_{D_2}^{0.85 \text{ to } 1.0}$

Rate of exchange: $\sim p_{D_2}^{0.4 \text{ to } 0.66}$

k_E/k_H at same pressure $= 0.5$ to 3.0

k_E/k_H decreases to ⅓ its original value for 10 fold increase in pressure.

Para-hydrogen conversion: 30 times faster than exchange of benzene with deuterium. Rate reduced by presence of benzene to ⅒ the value for the dry catalyst.

H_2—D_2 reaction: Same rate as para-conversion. Indicates to them that diffusion was controlling factor since para conversion is usually faster than the H_2—D_2 equilibration.

LIQUID CYCLOHEXANE + D_2

Rate of exchange: 1/50 that for benzene.

Rate of exchange: $\sim p_{D_2}^{-0.3}$

Presence of cyclohexane does not affect rate of benzene exchange.

BENZENE GAS + D_2

Rate of hydrogenation: $\sim p_{D_2}^{0.4}$ at 42.5°; $\sim p_{D_2}^{0.7}$ at 66°; $\sim p_{D_2}^{1.0}$ at 87°; activation energy 6.8 kcal.

Rate of exchange: $\sim p_{D_2}^{-0.05}$ at 51°C; $\sim p_{D_2}^{0.25}$ at 80°; activation energy 7.3 kcal.

Effect of benzene pressure: Hydrogenation and exchange fall with decrease in benzene pressure. No definite relation could be derived.

H_2—D_2 reaction: About 50 times faster than exchange (or hydrogenation)

CYCLOHEXANE GAS + D_2

Rate of exchange: $\sim p_{D_2}^{-0.1}$

Relative rates: Exchange 1/40 that of benzene exchange; activation energy 13.7 kcal.

NICKEL CATALYSTS

LIQUID BENZENE + D_2

Rate of hydrogenation (20°C): $\sim p_{D_2}^{1.0}$

Rate of exchange (20°C): $\sim p_{D_2}^{0.1 \text{ to } 0.4}$ depending on the catalyst preparation; $k_E \cong 2.5 \times 10^{-4} \text{min.}^{-1}$

Relative rates: Exchange 20 to 40 times the rate of hydrogenation

Para-hydrogen conversion (20°C): At least 1000 times faster than exchange ($k_P \simeq 2.3 \times 10^{-1}$ min.$^{-1}$)

LIQUID CYCLOHEXANE + D_2

Rate of exchange (20°C): $k_E = 8.1 \times 10^{-4}$ min.$^{-1}$

Relative rates on same catalyst: k_E (benzene): k_H (benzene): k_E (cyclohexane) = 800:40:1

BENZENE GAS + D_2

Rate of hydrogenation: $\sim p_{D_2}^{0.25}$ at 48°C and $p_{D_2}^{1.0}$ at higher temperatures; $k_H = 4.7 \times 10^{-3}$ min.$^{-1}$ (204–177 mm, 51°C); activation energy = 10.6 kcal.

Rate of exchange: Pressure dependence similar to that for platinum catalysts. $k_E = 5.0 \times 10^{-2}$ min.$^{-1}$ (207–177 mm, 51°C); activation energy = 15 kcal

Relative rates: Exchange 6 to 16 times hydrogenation rate.

H_2—D_2 equilibration: Approximately 30 times faster than exchange.

CYCLOHEXANE GAS + D_2

Rate of exchange: $\sim p_{D_2}^{-0.3}$. About 1/180 that of the benzene exchange rate.

TABLE 1.—*Continued*

COPPER CATALYSTS

LIQUID BENZENE + D_2

Hydrogenation: None

Rate of exchange (room temperature): Very slow, k_E of the order of 10^{-4} min.$^{-1}$

Para-hydrogen conversion: $\sim p_{D_2}{}^{0.7}$. Conversion rate in presence of liquid benzene was 1/5 that on the dry catalyst.

BENZENE GAS

Hydrogenation: None at 210°C in 1½ hours.

Exchange (100°C): $\sim p_{D_2}{}^{0}$; $k_E = 9 \times 10^{-4}$ min.$^{-1}$ (100 mm D_2, 75 mm benzene, 100°C); activation energy 14 kcal.

Para-hydrogen conversion (100°C): 50 to 300 times the rate of exchange depending on catalyst preparation

CYCLOHEXANE GAS

Rate of exchange: 1/10 to 1/30 the rate of exchange with benzene

ETHYLENE

Hydrogenation (22°C): Half period about 30 min.

Exchange: Negligible at room temperature. Starts at higher temperatures.

Para-hydrogen conversion: None when no exchange occurs. Conversion starts when ethylene is all hydrogenated.

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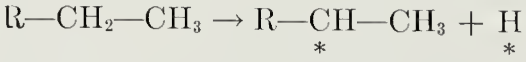
hours. No exchange under the same experimental conditions was observed between n-butane and D_2O nor between butane-D and ethylene. Butene-D and ethylene exchanges with a half-period of about 40 hours at 120°C. The same sample of catalyst that was used for some of these exchange experiments was tested for its activity for the exchange between D_2 (99.6 per cent, 0.0028 moles) and butane (0.0043 moles) at 120°C. After 13.5 hours the deuterium content of the butane was 6 per cent and after 35.5 hours it was 9 per cent.

The results of Horrex, Greenhalgh and Polanyi[126], as summarized above, found that D_2O exchanged with the unsaturated compound, benzene, at about the same rate as with the saturated hydrocarbons cyclohexane and isopentane. Aman, Farkas and Farkas, however, found considerable differences between the exchange rates of D_2O with unsaturated hydrocarbons (ethylene and butene) and saturated ones (butane). The marked effect of ratio of partial pressures of ethylene and D_2O indicates a strong influence of mutual displacement on the rates of exchange. Water probably displaces butane from the surface to such an extent that no significant exchange with D_2O can occur. They conclude that comparison of exchange rates of pairs and mixtures of compounds cannot be generalized because the results depend on the particular experimental conditions of temperature, partial pressures, and relative adsorbabilities on the catalyst preparation.

The result of Aman, Farkas and Farkas, in which it was found that the exchange of the pair D_2-butane was much faster than the exchange of the pair D_2O-butane, is not in agreement with the results of Horrex, Greenhalgh and Polanyi in which they found the D_2-isopentane exchange to be about the same or slightly slower than that for the D_2O-isopentane.

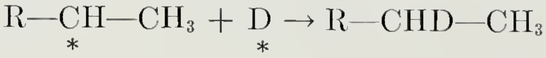
Greenhalgh and Polanyi suggested that the dissociative mechanism can explain their results only if the rate controlling step is the first one in the scheme:

(51)



$$\mathrm{R{-}CH_2{-}CH_3 \rightarrow R{-}\underset{*}{CH}{-}CH_3 + \underset{*}{H}}$$

(52)



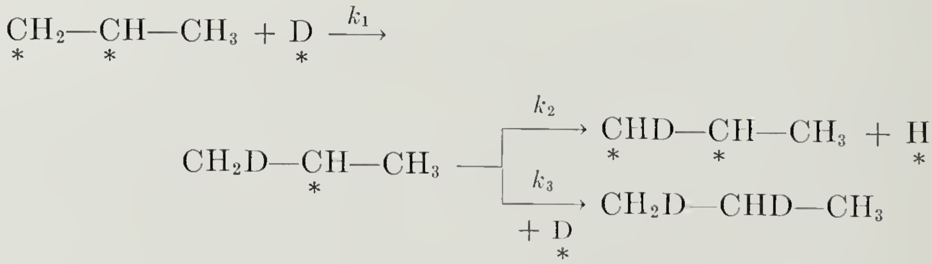
$$\mathrm{R{-}\underset{*}{CH}{-}CH_3 + \underset{*}{D} \rightarrow R{-}CHD{-}CH_3}$$

But they rejected this on other arguments to be summarized presently. If the second step were controlling then, since D_2 furnishes more chemisorbed deuterium atoms to the surface than D_2O, the second step should be faster for the exchange of D_2 with saturated hydrocarbons than for the exchange of D_2O with saturated hydrocarbons. They did not find such a difference and rejected the mechanism in this form also. Aman, Farkas and Farkas[1] do find differences in the rates which they cite as support for the dissociative mechanism. Apparently, further experiments with a number of different compounds, catalysts and experimental conditions are needed before the above approach is convincing for one or the other of the mechanisms.

Associative Mechanism of Hydrogenation and Exchange

Kinetic Equations for Associative Mechanism. The mechanisms proposed for hydrogenation and exchange by Horiuti and Polanyi[125] have already been given (p. 276), but they are repeated again here to facilitate discussion:

(53)



$$\mathrm{\underset{*}{CH_2}{-}\underset{*}{CH}{-}CH_3 + \underset{*}{D}} \xrightarrow{k_1} \mathrm{CH_2D{-}\underset{*}{CH}{-}CH_3} \begin{cases} \xrightarrow{k_2} \mathrm{\underset{*}{CHD}{-}\underset{*}{CH}{-}CH_3 + \underset{*}{H}} \\ \xrightarrow[+\underset{*}{\mathrm{D}}]{k_3} \mathrm{CH_2D{-}CHD{-}CH_3} \end{cases}$$

In deriving a kinetic expression they assumed "ideal adsorption" in which the surface concentration of the unsaturated hydrocarbon C' is proportional to its pressure P', or $C' \sim P'$. The surface concentration of deuterium atoms C_D on this same basis would be proportional to the square root of the deuterium pressure P_{D_2}, or $C_D \sim P_{D_2}^{0.5}$. Setting the surface concentration C^* of the half-hydrogenated state at which branching occurs as invariable with time,

$$k_1C'C_{\mathrm{D}} - k_2C^* - k_3C^*C_{\mathrm{D}} = 0 \tag{5}$$

The dependence of the rate of exchange r_E and of hydrogenation r_H upon pressure then becomes

$$r_E = \frac{k_1'k_2'P'P_{\mathrm{D}_2}^{0.5}}{k_2' + k_3'P_{\mathrm{D}_2}^{0.5}} \tag{6}$$

$$r_H = \frac{k_1'k_3'P'P_{\mathrm{D}_2}}{k_2' + k_3'P_{\mathrm{D}_2}^{0.5}} \tag{7}$$

where k_1', k_2', k_3' are the appropriately defined rate constants. The ratio of the rate of exchange to hydrogenation then becomes

$$\frac{r_E}{r_H} = \frac{k_2'}{k_3'P_{\mathrm{D}_2}^{0.5}} \tag{8}$$

If hydrogenation is very fast relative to exchange, i.e., if $k_3'P_{\mathrm{D}_2}^{0.5} \gg k_2'$,

$$r_H = k_1'P'P_{\mathrm{D}_2}^{0.5} \tag{9}$$

$$r_E = \frac{k_1'k_2'}{k_3'}P' \tag{10}$$

However, if exchange is more rapid then hydrogenation, i.e., $k_2' \gg k_3'P_{\mathrm{D}_2}^{0.5}$

$$r_H = \frac{k_1'k_3'}{k_2'}P'P_{\mathrm{D}_2} \tag{11}$$

$$r_E = k_1'P'P_{\mathrm{D}_2}^{0.5} \tag{12}$$

In both these extreme cases the dependence of r_E and r_H on the pressure of deuterium should differ by 0.5. For intermediate conditions, the pressure dependence can be only roughly approximated by $P_{\mathrm{D}_2}^{m}$, but m should differ again by about 0.5 for the two reactions. Ideal adsorptions, for which these equations apply, are probably not the usual case, at least for one of a pair of reactants. The expressions become rather complicated when non-ideal cases are considered. The authors do not work these out in detail but do arrive at the result that the difference (Δm) between the orders of pressure dependence on deuterium for rates of exchange and hydrogenation may be smaller but should not be greater than 0.5.

For liquid benzene on platinum catalysts, the rate of exchange depended on $P_{\mathrm{D}_2}^{0.4\text{ to }0.5}$, while hydrogenation varied as $P_{\mathrm{D}_2}^{0.9\text{ to }1.0}$ so that Δm was 0.5 in agreement with the above derivations. The values for m of 0.5 for exchange and 1.0 for hydrogenation should be reached only when $r_E \gg r_H$, and this condition was shown to exist for benzene. When nickel catalysts were used with liquid benzene, the experimental values of m for exchange were (0.3 0.1, 0.4, 0.3, 0.4) for a series of separate experiments and the value of m for hydrogenation in each case was 1.0. The value Δm here is greater than allowed for by the theory, but they suggest it may be due to more complete saturation of certain centers that are active for exchange and not for hydrogenation. In the gas phase reaction between deuterium and benzene on platinum, the values of Δm varied from 0.3 to 0.9 with most of them in excess of the 0.5 allowed by the theory. Two similar experiments with nickel gave values of 0.4 and 0.45 for Δm.

Apparently, the kinetic arguments for the associative mechanism are not decisive, but other considerations to be outlined below convinced them that it was essentially correct and the dissociative mechanism was not.

The fact that the rate of hydrogenation decreases at high temperatures where exchange becomes predominant is in agreement with the assumption that the activation energy E_3 for the reaction corresponding to k_3 is small or negative. In this case, if the activation energies corresponding to k_1 and k_2 are such that $E_1 - E_2 < E_3$, the temperature coefficient of r_H will become negative.

Kinetic Equations for the Dissociative Mechanism. Greenhalgh and Polanyi[111] discuss in detail the dissociative mechanism and present the following kinetic and other arguments against it. Formulations of the dissociative mechanisms of Farkas and Farkas may be written:

Exchange:

$$\mathrm{CH_2{=}CH{-}CH_3} \xrightarrow{k_a} \underset{*}{\mathrm{CH}}\mathrm{{=}CH{-}CH_3} + \underset{*}{\mathrm{H}} \tag{54}$$

$$\underset{*}{\mathrm{CH}}\mathrm{{=}CH{-}CH_3} + \underset{*}{\mathrm{D}} \xrightarrow{k_b} \mathrm{CHD{=}CH{-}CH_3} \tag{55}$$

Hydrogenation:

$$(\mathrm{CH_2{=}CH{-}CH_3})_{\mathrm{ads}} + \underset{*-*}{\mathrm{D\ D}} \xrightarrow{k_c} \mathrm{CH_2D{-}CHD{-}CH_3} \tag{56}$$

The rate of the exchange may be controlled (a) by the first step (54), that is, by the dissociation of the hydrocarbon or (b) by the second step (55) which is the recombination of adsorbed deuterium or hydrogen atom with the adsorbed radical. Pressure dependencies for these cases were derived as follows:

(a) For the case of "ideal adsorption," the concentration C' of adsorbed hydrocarbon is proportional to this pressure P', in the gas phase. The rate of exchange, r_E, will be determined by the rate of dissociation of adsorbed hydrocarbon,

$$r_E = k_a P' \tag{13}$$

They infer from this that the rate should not be dependent upon the deuterium pressure if (54) is rate controlling.

(b) Step (55) will be rate controlling if the surface dissociation of the hydrocarbon is not appreciably reversible, except in the presence of a high surface concentration of deuterium or hydrogen. All active centers capable of forming hydrocarbon radical will be fully covered and the surface concentration should be independent of the pressure of the hydrocarbon. Since the surface concentration of D atoms is proportional to $p_{D_2}^{0.5}$ the rate of exchange is

$$r_E = k_b P_{D_2}^{0.5} \tag{14}$$

(c) The rate of hydrogenation by mechanism (56) is a function of the concentration C_{D_2} of molecular deuterium (or hydrogen) adsorbed at the surface and of the concentration C' of adsorbed hydrocarbon. Hence,

$$r_H = k_c P' P_{D_2} \tag{15}$$

For non-ideal adsorption the dependence on pressures will be lower. This situation, of course, weakens any kinetic arguments against the dissociative mechanism, which use the equations in the above form.

Arguments for and against the Dissociative Mechanism. Greenhalgh and Polanyi cite the following arguments against the dissociative mechanism in form (a).

(1) They use their result that the rate of exchange of liquid benzene on nickel catalysts increases with deuterium pressure as a kinetic argument against a dissociative mechanism that is controlled by dissociation of the hydrocarbon. According to Equation (54) the rate for this case should be independent of the deuterium pressure, and they state that "non-ideal" adsorption would not remove the contradiction. Farkas and Farkas[88] also found the rate of exchange to be dependent on the deuterium pressure in the liquid phase on platinum catalysts, but in the gas phase they found the exchange to be independent of deuterium pressure. These differences were explained on the basis of displacement of deuterium from the surface in liquid benzene. The above kinetic argument against the dissociative mechanism does not seem to be conclusive.

(2) Greenhalgh and Polanyi's results showed mutual exchange between two hydrocarbons to be much slower than the exchange of either of them with deuterium. They conclude that the rate of exchange of at least one of the two hydrocarbons is faster than its dissociation. Therefore, dissociation cannot be the rate controlling step of the exchange with deuterium. Farkas

and Farkas would question this conclusion (p. 272) on the grounds that, in the mutual exchange experiments, the concentration of D atoms on the surface would be very small compared to the exchange experiments with deuterium gas.

(3) Unsaturated hydrocarbons exchange much more slowly with D_2O than with D_2 showing at least that with D_2O, surface dissociation of the hydrocarbon cannot be rate controlling. Farkas and Farkas suggest that displacement of the hydrocarbon from the surface would explain these differences, but Greenhalgh and Polanyi cite their experiments on mixtures to discount this suggestion. For example, hydrogenation of benzene in the presence of water was far more rapid than exchange between D_2O and benzene. This indicates to them that the more rapid exchange between D_2 and benzene as compared with D_2O and benzene does not arise from displacement of benzene by water.

Exchange rates of saturated (cyclohexane) and unsaturated (benzene) hydrocarbons with D_2O were found to be the same. Since they found that the saturated hydrocarbon exchanged more rapidly with D_2O than with D_2, saturated hydrocarbons show no sign of being displaced by water. Consequently, they conclude, that water has no displacement effect on the exchange reactions of either saturated or unsaturated hydrocarbons. Aman, Farkas and Farkas[1] did not find the same results with ethylene and butene as compared to butane (see p. 279) and doubt the general validity of the above arguments.

(4) The exchange between DCl and cyclohexane was much slower than the exchange between D_2 and cyclohexane, while the exchange between D_2 and HCl proceeds relatively rapidly. Therefore, dissociation of the hydrocarbon could not be rate controlling, otherwise the exchange rates of DCl and D_2 wtih the hydrocarbon should be more nearly equal. Farkas and Farkas would probably explain this on the basis of relative surface concentrations in the two cases.

(5) On the basis of the above arguments, a dissociative mechanism (a) in which the dissociation of hydrocarbon (54) was rate controlling, was ruled out by Greenhalgh and Polanyi. However, they explained that this did not necessarily rule out a dissociative mechanism in which the combination of phenyl radicals with deuterium atoms was rate controlling. A comparison of Equations (12) with (14) for the condition that exchange is more rapid than hydrogenation (as it is with benzene) shows that both the associative and the dissociative mechanism have the same dependence on deuterium pressure. They cannot, therefore, be differentiated on kinetic measurements.

(6) Form (b) of the dissociative mechanism (55) in which the hydrocarbon radical is firmly attached to the surface cannot, in their opinion, explain the following observation. In contrast to ethylene, neither benzene

nor cyclohexane seems to form a compact covering on the surface of the catalyst becuase the pairs D_2—H_2O, D_2—HCl, D_2—H_2 as well as parahydrogen equilibrate rapidly in the presence of these hydrocarbons. Farkas and Farkas explain these observations on the geometrical grounds that benzene is adsorbed only on relatively few sites as indicated by the $p^0_{C_6H_6}$ dependence of exchange on benzene pressure. The remainder of the surface is available for the other equilibration reactions. Ethylene, on the other hand, can be adsorbed on all sites and leave little surface for the equilibrations. Saturated hydrocarbons are only slightly dissociated and therefore do not monopolize the surface.

(7) In the dissociative mechanism, exchange and hydrogenation are not connected because they are assumed to proceed by different mechanisms. They could, on this basis, proceed on two different sets of catalytic centers, one set of which might be taken to be more saturated with respect to adsorption than the other. No relationship is, therefore, required between pressure dependencies for hydrogenation and exchange. However, a parallelism should exist for exchange of saturated and unsaturated hydrocarbons because they are both assumed to exchange by dissociation of the hydrocarbons.

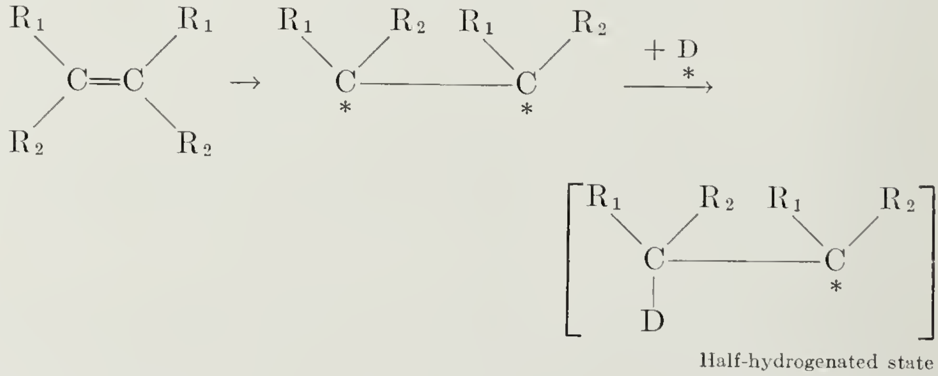
The associative mechanism, on the other hand, does require a parallelism between exchange and hydrogenation, even for "non-ideal" adsorptions, as shown in the kinetic derivations above. No parallelism would be expected for saturated as compared to unsaturated compounds. The expected parallelism for hydrogenation and exchange, namely that Δm for the pressure dependence on deuterium should not be greater than 0.5 was satisfied in their experiments on liquid benzene. Deviations from this rule were observed for some of their other experiments as discussed previously (p. 284), and it has been found not to hold in other cases since then. This kinetic argument in favor of the associative mechanism, therefore, loses much of its force.

(8) Probably one of the most effective arguments presented in favor of the associative mechanism is that deuterium exchanges much more rapidly with unsaturated than with saturated hydrocarbons. They quote their observation that unsaturated (benzene) and saturated hydrocarbons (cyclohexane or *n*-hexane) exchange at about the same rate with D_2O. (However, see the results of Aman, Farkas and Farkas[1] mentioned previously.) Apparently, from these observations, the exchange behavior of the two types of compounds differs only when they are acted upon by a hydrogenating agent and thus indicates that exchange is linked with hydrogenation, presumably through the common half-hydrogenated intermediate. Saturated hydrocarbons exchange slowly with deuterium by a dissociative mechanism and presumably this represents the approximate

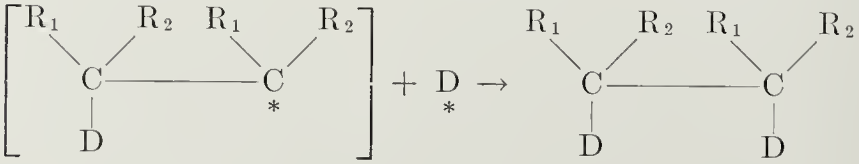
rate at which unsaturated hydrocarbons exchange by such a mechanism. Since this is very small compared to the observed exchange rate for unsaturated hydrocarbons, Greenhalgh and Polanyi conclude that a dissociative mechanism can play only a minor role in their exchange process.

Cis-Addition. Farkas and Farkas[89] have summarized the evidence (see p. 270) that at ordinary temperatures catalytic addition of hydrogen to a double bond occurs in the *cis*-position and have taken this as evidence for simultaneous addition of two hydrogen atoms. Greenhalgh and Polanyi[111] show that *cis*-addition is also consistent with the associative mechanism of consecutive addition of two hydrogen atoms. They represent the scheme as follows:

(57)

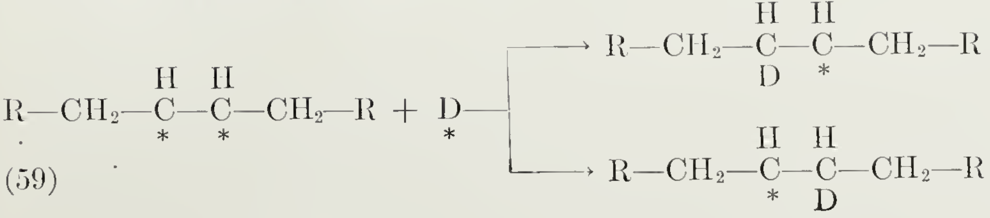


(58)



The optical configuration of the half-hydrogenated state is not destroyed by rotation around the C—C axis. Also, if breaking of the catalyst bond by substitution of hydrogen occurs by the same steric mechanism, as is likely, the final product must be the *meso*-compound. At higher temperatures both *cis* and *trans* addition occur, probably because of migration of the half-hydrogenated state which can lead to randomness of configuration on the C-atom linked to the catalyst. They note that at lower temperatures where *cis* addition takes place, very little exchange occurs. At higher temperatures where *trans* addition sets in, exchange is appreciable.

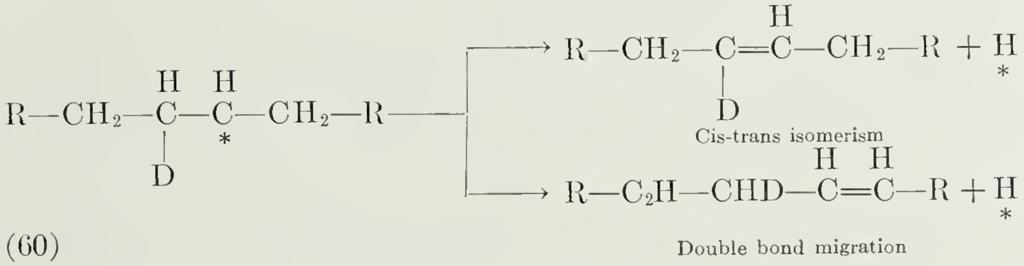
Migration of Double Bonds and Cis-Trans Isomerism. The occurrence of these two reactions in olefinic compounds has been shown to occur on metallic catalysts at temperatures below 100 to 150°C only in the presence of hydrogen, that is only during hydrogenation. Greenhalgh and Polanyi[111] take this as evidence in support of their associative mechanism because it can be predicted to be a consequence of the formation of the half-hydrogenated state. Thus,



(59)

$$R{-}CH_2{-}\underset{*}{\overset{H}{C}}{-}\underset{*}{\overset{H}{C}}{-}CH_2{-}R + \underset{*}{D} \rightarrow R{-}CH_2{-}\underset{D}{\overset{H}{C}}{-}\underset{*}{\overset{H}{C}}{-}CH_2{-}R$$

$$R{-}CH_2{-}\underset{*}{\overset{H}{C}}{-}\underset{*}{\overset{H}{C}}{-}CH_2{-}R + \underset{*}{D} \rightarrow R{-}CH_2{-}\underset{*}{\overset{H}{C}}{-}\underset{D}{\overset{H}{C}}{-}CH_2{-}R$$



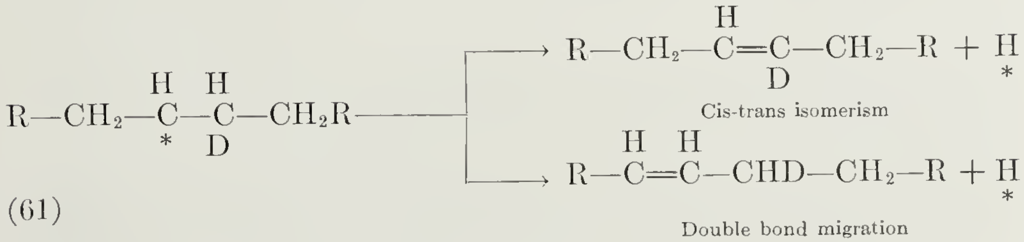
(60)

$$R{-}CH_2{-}\underset{D}{\overset{H}{C}}{-}\underset{*}{\overset{H}{C}}{-}CH_2{-}R \rightarrow R{-}CH_2{-}\underset{D}{C}{=}\overset{H}{C}{-}CH_2{-}R + \underset{*}{H}$$

Cis-trans isomerism

$$R{-}CH_2{-}\underset{D}{\overset{H}{C}}{-}\underset{*}{\overset{H}{C}}{-}CH_2{-}R \rightarrow R{-}C_2H{-}CHD{-}\overset{H}{C}{=}\overset{H}{C}{-}R + \underset{*}{H}$$

Double bond migration



(61)

$$R{-}CH_2{-}\underset{*}{\overset{H}{C}}{-}\underset{D}{\overset{H}{C}}{-}CH_2R \rightarrow R{-}CH_2{-}\overset{H}{C}{=}\underset{D}{C}{-}CH_2{-}R + \underset{*}{H}$$

Cis-trans isomerism

$$R{-}CH_2{-}\underset{*}{\overset{H}{C}}{-}\underset{D}{\overset{H}{C}}{-}CH_2R \rightarrow R{-}\overset{H}{C}{=}\overset{H}{C}{-}CHD{-}CH_2{-}R + \underset{*}{H}$$

Double bond migration

That such reactions occur has been known for a long time. Moore[167] and Hilditch and Vidyarthi[117] showed that *iso*-oleic acids were formed in appreciable yields during hydrogenation of esters of oleic acid. Besides elaidic acid esters, esters with double bonds shifted from the original 9:10 position to the neighboring 8:9 and 10:11 position, were present. Baxendale and Warhurst[16] studied these reactions further using methyl oleate and deuterium on a platinum catalyst. The relative quantities of products were not completely in accord with what they predicted from the associative mechanism. They did not regard their results as positive evidence for the associative mechanism, particularly because of the relatively large amount of *trans*-isomer containing little deuterium. On the other hand, they concluded that the results were definitive evidence against the dissociative mechanism. Experiments of Taylor and Dibeler[220] to be discussed later showed that *cis-trans* isomerization occurs rather rapidly with butene-2 without much deuterium exchange, so it is not surprising that the light elaidic acid ester was the principal product of their reaction.

Twigg and Rideal Associative Type Mechanisms

Ethylene and Deuterium. Twigg and Rideal[240] reinvestigated the nickel catalyzed interactions of ethylene and deuterium that were originally studied by Farkas, Farkas and Rideal.[97] A nickel filament 80 cm long, 0.1 mm in diameter in a 150 cc reaction vessel was activated by repeated oxidations in air at 600°C and reductions in hydrogen at 330°C. Addition was followed by the fall in pressure and exchange was followed by determination of the change in deuterium content of the hydrogen after removal of ethylene and ethane. A micro-thermal conductivity analyzer was used for the deuterium analysis and also for determination of nonequilibration during the reaction. The results of their experiments are summarized in Table 2.

Exchange between Light and Heavy Ethylene. Conn and Twigg[52] in an accompanying paper studied the exchange between C_2H_4 and C_2D_4, using infrared analysis. In the first experiment a nickel wire catalyst was used as in the above experiments. It catalyzed the D_2—C_2H_4 exchange with a half-life of 29 minutes presumably at room temperature. The same wire was used with a mixture of C_2H_4 and C_2D_4. After 70 minutes no exchange was observed, but on testing the catalyst after this reaction, it was poisoned to such an extent that the half-life of the D_2—C_2H_4 exchange was 25 to 50 hours. At 76°C no exchange between C_2H_4 and C_2D_4 was observed in 15.5 hours and the catalyst activity for the D_2—C_2H_4 exchange was reduced to 1/12 its initial value (half-life was increased from 40 min. to 8 hrs). No exchange between C_2H_4 and C_2D_4 was observed after 3¾ hours at 330°C or after an additional half-hour at 360°, although about 0.1 per cent H_2 and D_2 had apparently formed. The half-life for addition at 304° on the wire after use at 360°C was 5 hours and presumably the D_2—C_2H_4 exchange was faster than addition. Since no exchange between C_2H_4 and C_2D_4 was observed under any of these conditions, they concluded that C_2H_4 did not dissociate on the surface as assumed for the dissociation mechanism.

Table 2. Summary of Results of Twigg and Rideal[240] on Nickel Wire

HYDROGENATION

Addition of hydrogen: 1.25 times faster than addition of deuterium at 156°C
Pressure dependencies: Rate $\sim p_{C_2H_4}{}^0\, p_{D_2}$ at 156°C
Activation energy: 13–14 kcal between 60–100°C. Decreases above 207°C

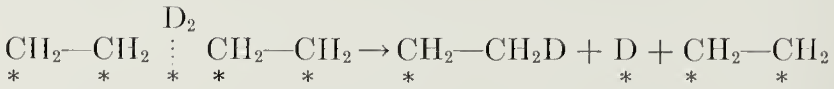
EXCHANGE

Pressure dependencies: rate $\sim p_{C_2H_4}{}^0\, p_{D_2}$ at 156°C
Activation energy: 18.4 kcal 60–100°C. Decreased above 100°C to 4 kcal at 207°C. Activation energies were 4–5 kcal greater than hydrogenation at all temperatures.
Ratio of exchange to hydrogenation: Varied from 2.7 to 4.2 at 156°C. Nearly constant for a given catalyst preparation at constant temperature.
Products: Initial hydrogen returned to gas phase contains only 20 per cent deuterium below 160°C, or about 80 per cent nonequilibrium.
H_2—D_2 equilibration: Inhibited below 160°C. Occurs only through exchange.

Twigg and Rideal used the non-exchange between C_2H_4 and C_2D_4 to decide against the dissociative mechanism in favor of an associative type mechanism. Their arguments were as follows: Ethylene exchanges with deuterium at $-80°C$[171] while methane and ethane, which does exchange by the dissociative mechanism, requires a much higher temperature (100°C)[169, 170]. A dissociative mechanism would yield hydrogen atoms and deuterium atoms in a mixture of C_2H_4 and C_2D_4. On re-evaporation, exchange should occur. On the other hand, no exchange should take place if the associative mechanism holds because hydrogen or deuterium atoms, essential for forming the half-hydrogenated complex, are absent. In the dissociative mechanism one of the two steps might be slowed up by the absence of hydrogen: (1) $C_2H_4 \rightarrow \underset{*}{C_2H_3} + \underset{*}{H}$ or (2) $\underset{*}{C_2H_3} + \underset{*}{D} \rightarrow C_2H_3D$. Reaction (1) should go at the same rate as it does in the exchange with deuterium. Since the slow step in the exchange with deuterium is the activation of deuterium, the dissociation and re-combination of ethylene should be fast and the stationary D atom concentration should be kept down to the dissociation concentration of C_2D_4 on the surface. That is, the D atom concentration should be about the same as is present in the exchange between the two ethylenes in the absence of deuterium. Consequently the recombination step (2) would be equally fast in the two reactions and the dissociative theory would predict a rapid exchange between C_2H_4 and C_2D_4 which did not occur. The authors therefore, adopt an associative mechanism. The arguments of Farkas and Farkas against this conclusion as well as experiments in which exchange between light and heavy olefins have been observed were discussed previously (pp. 272, 279).

Nonequilibration of H_2 and D_2 in Presence of Ethylene. The absence of equilibration of H_2 and D_2 during the exchange between D_2 and C_2H_4 in the experiments of Twigg and Rideal showed that the concentration of chemisorbed atomic hydrogen must be very small. Also, the fact that the hydrogen coming from the catalyst surface initially was low in deuterium showed that the actual exchange process must be fast compared to desorption of hydrogen. Therefore, they concluded that some stage in the adsorption or desorption of deuterium must be rate controlling, which is in agreement with the result that the rate is proportional to p_{D_2}. For this reason a study of kinetics will not give information about the mechanism of the actual exchange process because the exchange step is not the slow step in the overall reaction. These conclusions explain the non-fulfillment of the prediction of Horiuti and Polanyi[125] because the measured rate of exchange does not correspond to the steps of the associative mechanism that involve deuterium atoms. Both exchange and addition were first order with respect to deuterium pressure. Twigg and Rideal, accordingly, assume that the rate is related to a step involving deuterium molecules.

Twigg and Rideal Mechanism. In view of the above considerations, Twigg and Rideal arrived at an associative mechanism differing in some respects from the one of Horiuti and Polanyi. Their scheme is as follows: Ethylene is adsorbed on the catalyst by opening of the double bond. Deuterium is not chemisorbed on neighboring nickel atoms since it was shown that chemisorbed atoms were not present in large quantity. Instead, they assume that deuterium is held in the molecular state in a van der Waals layer above and between the ethylene molecules. Those deuterium molecules adsorbed above a hole in the ethylene layer are the ones that interact with the ethylene, thus:

(62) 

$$\underset{*}{CH_2}—\underset{*}{CH_2}\ \underset{*}{\overset{D_2}{\vdots}}\ \underset{*}{CH_2}—\underset{*}{CH_2} \rightarrow \underset{*}{CH_2}—CH_2D + \underset{*}{D} + \underset{*}{CH_2}—\underset{*}{CH_2} \tag{62}$$

(63) 

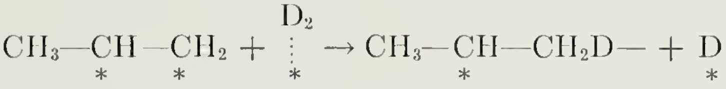
$$\underset{*}{CH_2}—CH_2D + \underset{*}{D} + \underset{*}{CH_2}—\underset{*}{CH_2} \rightleftharpoons \underset{*}{CH_2}—\underset{*}{CHD} + \underset{*}{H} + \underset{*}{CH_2}—CH_2D \tag{63}$$

Exchange results from the interaction of an adsorbed deuterium molecule with a chemisorbed ethylene molecule to give a chemisorbed deuterium atom and an ethyl radical. The deuterium can then react with a neighboring ethylene radical and the first ethyl radical forms chemisorbed ethylene and an adsorbed hydrogen. The slow step is reaction (62) which is associated with the activation energy of 18.6 kcal. Reaction (63) is rapid and a deuterium molecule can exchange by this process with six neighboring CH_2 groups. The deuterium content of the hydrogen after such exchange would be 14 per cent compared to the 20 per cent found experimentally.

Since the activation energy for the addition reaction is less than for exchange, they conclude that step (62) does not represent the activation of deuterium for this reaction. They suggest that a single deuterium molecule adds across the double bond of the ethylene molecule as postulated by Farkas and Farkas.[88, 89, 90] In a later paper, to be discussed presently, Twigg abandons this view of addition and presents a different one. The decrease in the rate of addition at the higher temperatures was attributed to desorption of deuterium held in the Van der Waals layer over the ethylene and over the holes in the ethylene layer. Zur Strassen[256] and Schwab[202] concluded this decrease in rate of addition to be due to desorption of ethylene. Farkas and Farkas[90] did not find the parallel behavior between exchange and addition on platinum that Twigg and Rideal found on the nickel wire. Farkas and Farkas had attributed the maximum in the addition reaction to an increase in the dissociation of adsorbed ethylene and reaction via exchange, thereby decreasing the concentration of the adsorbed ethylene that would otherwise undergo addition.

Using the mechanism of exchange given above, Twigg and Rideal formulated mechanisms for the migration of double bonds and for the complete exchange of all deuterium atoms in olefins. This is the subject of later papers by Twigg.

Interaction of Other Olefins with Deuterium. In a paper on the catalytic interaction of several olefins with deuterium, Twigg[236] reviewed the above arguments in favor of an associative mechanism of exchange. He also felt that complete exchange of the higher olefins was a strong argument in favor of this mechanism. Thus, for propylene:

(64) 

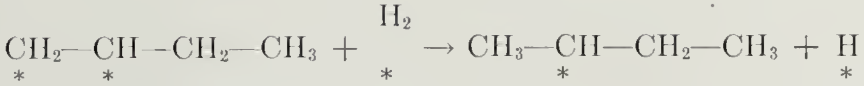
$$\mathrm{CH_3{-}\underset{*}{CH}{-}\underset{*}{CH_2}} + \overset{\mathrm{D_2}}{\underset{*}{\vdots}} \rightarrow \mathrm{CH_3{-}\underset{*}{CH}{-}CH_2D{-}} + \underset{*}{\mathrm{D}} \tag{64}$$

(65) 

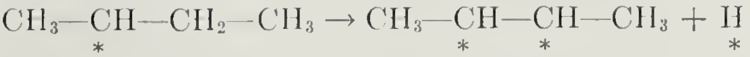
$$\mathrm{CH_3{-}\underset{*}{CH}{-}CH_2D} \rightarrow \mathrm{\underset{*}{CH_2}{-}\underset{*}{CH}{-}CH_2D} + \underset{*}{\mathrm{H}} \tag{65}$$

In the half-hydrogenated state the two methyl groups are identical and either may react with the catalyst to reform an adsorbed propylene molecule. If the dissociative mechanism were correct, the hydrogen atoms in the methyl group of $CH_3CH{=}CH_2$ should be as unreactive as in ethane and only the hydrogens attached to the double bonded carbon atoms should exchange. Deuterium and the following olefins, when heated at 97° on nickel wire until equilibrium is established, gave hydrogen with the per cents of deuterium listed in the parentheses: ethylene (32.4); propylene (25); butene-2 (18); isobutene (13), trimethyl ethylene (14). These observed values are near those expected for complete exchange rather than for exchange of only those hydrogens on the double-bonded carbon atoms. Under identical conditions, ethane did not exchange. The graphs for the course of the exchange reactions of the unsaturated hydrocarbons were smooth curves showing that all hydrogens were essentially equivalent with respect to exchange. This behavior, Twigg felt, could not be explained by the dissociative mechanism, but was a consequence of the associative mechanism.

The double bond in butene-1 was shown by vapor pressure measurements to shift, giving butene-2 on nickel wire at 133°C in the presence of hydrogen or deuterium. No transformation occurred in the absence of hydrogen. This double bond shift is readily accounted for by an associative mechanism:

(66) 

$$\mathrm{\underset{*}{CH_2}{-}\underset{*}{CH}{-}CH_2{-}CH_3} + \overset{\mathrm{H_2}}{\underset{*}{}} \rightarrow \mathrm{CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3} + \underset{*}{\mathrm{H}} \tag{66}$$

(67) 

$$\mathrm{CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3} \rightarrow \mathrm{CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3} + \underset{*}{\mathrm{H}} \tag{67}$$

Farkas and Farkas[82] have also explained such double bond shifts by a dissociative mechanism (p. 272) which could also be used to explain complete exchange.

The rates of exchange and addition for ethylene, propylene, butene-2 and isobutene were measured from 55 to 120°C, using equal volumes of deuterium and the olefin on a nickel wire. From plots of logarithms of the initial rates against $1/T$, the activation energies of the two reactions were obtained. These along with the ratio of the number of deuterium molecules undergoing exchange to the number undergoing addition are summarized in Table 3. The rather large activation energy for ethylene as compared to the higher hydrocarbons was not quantitatively explained on the basis of the assumed mechanism involving a deuterium molecule and chemisorbed ethylene. It was suggested that the effect may be due to lower heats of hydrogenation for the higher olefins[144] combined with less complete coverage of the surface so that deuterium molecules can penetrate and interact more readily with the carbon-nickel bond to form the half-hydrogenated complex.

TABLE 3. ENERGIES OF ACTIVATION, RELATIVE RATES, AND RATE OF ADDITION $(dp/dt)_0$ ON Ni WIRE[236]

	Energies of Activation			Relative Rates, (exchange)/(addition)			Rate of Addition
	Exchange	Addition	Difference	50°	84°	112°	84°
Ethylene	17.2 ± 0.5	8.2 ± 0.5	9.0	0.5	0.8	2.0	0.40
Propylene	13.7	6.0	7.7	0.8	1.7	3.8	0.27
Butene-2	10.0	3.3	6.7	1.1	2.2	4.7	0.18
Isobutene	10.0	3.3	6.7	1.1	2.2	4.7	0.1

The increase in the ratio of exchange to addition with increase in molecular weight was explained as arising from an increase in ratio of the number of exchangeable hydrogens to double bonds. From the energies of activation, the rate of exchange for propylene should be 10^2 times that of ethylene and that of butene should be 10^4 times that of ethylene. Instead, they are not greatly different. Similar discrepancies exist for addition. However, the ratios of exchange to addition (Table 3) are in the order expected from the values of the differences between activation energies for exchange and hydrogenation. Apparently, by taking the ratios of exchange to hydrogenation, the factor that disturbs the correlation between activation energy and absolute reaction rate is eliminated. This supports the view of some that all of the reactions take place on a uniform type of catalytically active center.

Geometrical Factors Affecting Reactions of Olefins. From geometrical considerations, Twigg and Rideal[241] found additional support for chemisorption of olefins through opening of the double bond. The nickel lattice consists of a face-centered cube having a unit cell side of 3.5 Å, with the closest nickel-nickel distance being 2.47 Å. Using the following bond lengths: Ni—Ni = 2.47 Å, C—C = 1.52 Å (single bond distance), Ni—C = 1.82 Å, they calculated that an adsorbed ethylene would fit on the 2.47 Å nickel-nickel spacing with a Ni—C—C angle of 105°4′. This is only slightly distorted from the normal tetrahedral angle of 109°28′. Actually, the distortion would be much less because the molecule can accommodate itself by twisting slightly so that the C—C axis lies at a small angle to the Ni—Ni axis. Alternate oxidation and reduction may also cause an increase in the interatomic distance of nickel atoms and allow an even better fit, although such treatment is not likely to increase the distance to 2.73 Å required for a normal tetrahedral angle. They pointed out that one group of hydrogenation catalysts, Fe, Ni, Co, and Cu have distances of closest approach ranging from 2.47 to 2.54 Å and another group ranging from 2.7 to 2.8 Å (e.g. Pd, Pt). Of the metals with spacings from 2.7 to 2.8 Å only those which have face-centered cubic lattices are active in hydrogenation. The greater effectiveness of face-centered cubic lattices in the group (Fe, Ni, Co, Cu) was demonstrated by Long, Frazer, and Ott[161] using several alloy systems for the hydrogenation of benzene. However, the body centered metals and alloys in this group were effective in ethylene hydrogenation.

Calculations were also made by Twigg and Rideal[241] on the geometrical factors related to completeness of coverage of the surface by ethylene and substituted ethylenes. Using 1.09 Å as the C—H bond distance, 0.78 Å as the radius of the hydrogen atom, and the tetrahedral angles for the carbon bonds, their calculations showed that the whole surface of 110 planes of nickel could be covered without interaction between neighboring ethylene molecules. A small amount of interaction would occur if the ethylene were adsorbed on the 111 planes. That ethylene can cover the surface of nickel rather completely is supported by the fact that ethylene almost completely inhibits the para-hydrogen conversion and the H_2—D_2 equilibration at temperatures below 160°C. The higher olefins with one or more —CH_3 groups (diameter taken as 3.06 Å) attached to the double-bonded carbon atoms interfere with each other and cannot completely cover the whole surface. Bare nickel sites are available with the higher olefins for chemisorption of hydrogen or deuterium as indicated by rather rapid para-hydrogen conversions and H_2—D_2 equilibration. The significance of the bare sites is not entirely clear in view of Selwood's[204a] recent experiments with magnetic measurements in which he found that hydrogen was adsorbed on an ethylene treated catalyst of nickel-silica. Jenkins and Rideal

(p. 301) find similar results on evaporated nickel films pretreated with ethylene.

Further considerations of the geometrical factors in hydrogenation reactions will be discussed in later sections.

Exchange, Addition and Double-bond Migration of 1-Butene. Twigg[237] studied the relative rates of exchange, addition, and double-bond migration of butene-1 on a nickel wire catalyst. Exchange was followed by measuring the deuterium content of the hydrogen during the course of the reaction. Addition was followed manometrically and the double bond migration was determined by vapor pressure measurements. In the absence of hydrogen or deuterium no double bond migration occurred in 20 minutes at 133°C. At 65°C, a study of the kinetics showed:

Table 4. Reaction Rates, Ratios of Rates, and Energies of Activation for Reactions of Butene-1 with Deuterium on Nickel Wire.[237]

T°C	Addition, $(1/a)\ (dp/dt)_0$	Exchange, $(1/a)(du/dt)_0$	DBM, $(1/a)(dy/dt)_0$	DBM/Exch	DBM/Add.	Add./Exch.
76.0°	9.4×10^{-2}	0.49×10^{-2}	3.01×10^{-2}	6.1	3.4	1.80
86.5	10.0×10^{-2}	0.57×10^{-2}	3.57×10^{-2}	6.2	3.8	1.64
101.5	10.9×10^{-2}	0.93×10^{-2}	5.05×10^{-2}	5.6	5.0	1.10
114.5	12.2×10^{-2}	1.39×10^{-2}	7.0×10^{-2}	5.0	6.2	0.82
126.0	15.9×10^{-2}	1.97×10^{-2}	7.5×10^{-2}	3.8	5.1	0.75
E	2.5 kcal	9.0 kcal	5.9 kcal			

p = total pressure, mm. Hg.; y = fraction of butene-2 in the butenes; u = fraction of H_2 in the hydrogens; t = times in min.

$$\text{Double bond migration: rate} \sim p_{\text{bu}}^{1/2} p_{H_2}^{1/2} \tag{16}$$

$$\text{Addition: rate} \sim p_{\text{bu}}^{1/2} p_{H_2}^{1/2} \tag{17}$$

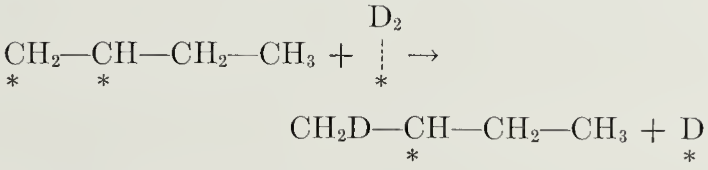
Previous studies with ethylene showed that exchange and addition had the same pressure dependencies. He concludes that the three reactions—exchange, hydrogenation, and double bond migration—all have identical kinetics and are therefore controlled by the same adsorption factors. Since the rates are not independent of the olefin pressure as in the case of ethylene, the surface is probably not completely covered as was shown by geometrical considerations in the previous paper.

All three reactions were examined simultaneously over the temperature range 76 to 126°C using 10.7 mm each of deuterium and butene-1 in a reaction vessel similar to that used for reactions of ethylene with deuterium (p. 290). The results for the initial rates of the reactions are summarized in Table 4. The rates were corrected for varying activity (a) of the catalyst by means of a standard hydrogenation reaction using ethylene. Values for the ratio of double bond migration to exchange, for example, were obtained from the equation:

$$DBM/E = (1/a)p_{\mathrm{Butenes}}(dy/dt)_0/(1/a)p_{\mathrm{D_2}}(du/dt)_0$$

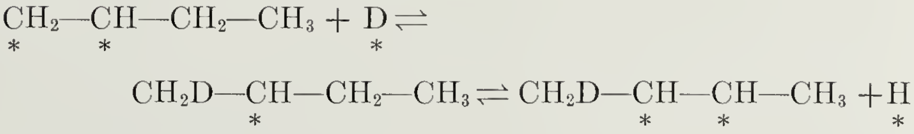
The ratio of the rate of double bond shift to the rate of exchange is equal to the ratio of the number of molecules isomerized to butene-2 to the number of deuterium molecules transformed to light hydrogen molecules. This would mean that approximately 12 molecules isomerized per deuterium atom transformed. Twigg explains this result as follows:

(68)



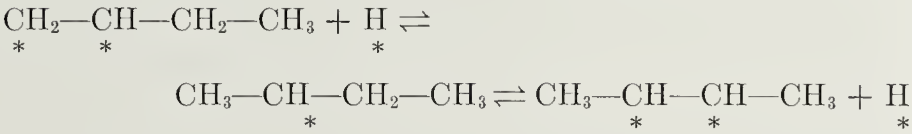
$$\underset{*}{CH_2}-\underset{*}{CH}-CH_2-CH_3 + \underset{*}{\overset{D_2}{\vdots}} \rightarrow CH_2D-\underset{*}{CH}-CH_2-CH_3 + \underset{*}{D}$$

(69a)



$$\underset{*}{CH_2}-\underset{*}{CH}-CH_2-CH_3 + \underset{*}{D} \rightleftharpoons CH_2D-\underset{*}{CH}-CH_2-CH_3 \rightleftharpoons CH_2D-\underset{*}{CH}-\underset{*}{CH}-CH_3 + \underset{*}{H}$$

(69b)



$$\underset{*}{CH_2}-\underset{*}{CH}-CH_2-CH_3 + \underset{*}{H} \rightleftharpoons CH_3-\underset{*}{CH}-CH_2-CH_3 \rightleftharpoons CH_3-\underset{*}{CH}-\underset{*}{CH}-CH_3 + \underset{*}{H}$$

The initial step involving the adsorption of deuterium is the slow one followed by fast reactions involving hydrogen and deuterium atoms. The rate of exchange is controlled by reaction (68) since this determines the rate at which the light hydrogen produced by the second reaction exchanges with deuterium in the gas phase. The double bond migration is controlled by the total hydrogen and deuterium in the adsorbed layer and is not dependent on the rate at which hydrogen enters or leaves the layer. The rate of double bond migration is controlled either by reactions (69a) and (69b) or by evaporation of butene from the surface.

It semed to him improbable that evaporation is the slow step for the following reasons. The half-power dependence on butene pressure indicates that the nickel wire surface is only partially covered with butene as geometric considerations showed also. With the supply of hydrogen atoms available on the surface, the butene-1 — butene-2 equilibrium should be established by reactions (69a) and (69b). The hydrogen pressure will not determine the type of molecule desorbed because the equilibrium is not affected by hydrogen. If desorption of butene were controlling, the rate of double bond shift would be independent of deuterium pressure, whereas it actually depends upon the square root of this pressure. This pressure dependence arises from the fact that the velocity of steps (69a) and (69b) depends on the surface concentration of hydrogen. Since hydrogen or deuterium enters the surface by reaction (68), this rate should depend upon the deuterium pressure. This accounts for the identical kinetics of exchange, hydrogenation and double bond migration. Twigg suggested that, if reactions of type (68) were the only ones operating, then a maximum of one butene molecule could be isomerized per deuterium atom exchanged. Actually, this is what Dibeler and Taylor[59, 60, 220] found in similar experiments on nickel wire using mass spectrometric and infrared analysis (see p. 370). The reason is not clear as to why the two sets of experiments should give such a large difference in double bond migration as compared to exchange. It may be related to a low rate of return of HD to the gas phase as was observed by Bond and Turkevich[40] for propylene. This low rate of return would show up as a low rate of exchange by Twigg's method of measurement. Further discussion of this problem will be given later.

Re-examination of Addition Reaction by Infrared Analysis. Twigg[239] has recently re-examined the hydrogenation reaction using mixtures of H_2 and D_2 and an infrared spectrometer to analyze the products. On the basis of these new experiments he has revised his mechanism of hydrogenation from one involving simultaneous addition of two atoms of a hydrogen molecule to one involving chemisorbed individual hydrogen atoms.

The simultaneous addition of a pair of hydrogen atoms to ethylene from a mixture of H_2 and D_2 should produce a mixture of about equal amounts of $CH_3—CH_3$ and $CH_2D—CH_2D$. On the other hand, dissociation of the hydrogen and deuterium into atoms before addition should yield $\frac{1}{4}CH_3CH_3$, $\frac{1}{2}CH_3CHD$, and $\frac{1}{4}CH_2DCH_2D$. In view of later work[231, 232, 252] to be described shortly, the method of preparing $C_2H_4D_2$ by addition of deuterium to ethylene at −78°C is open to question. Mass spectrometric examination of the products of addition of deuterium to ethylene show that all possible deutero-ethanes are obtained, even though very little exchange occurs. In spite of this uncertainty, Twigg's result that identical spectra were obtained in these experiments, supports his conclusions.

Using a nickel-Kiselguhr catalyst at −78°C two experiments were performed: One with 120 mm of an equal molar mixture of $H_2 + D_2$ plus 107 mm of ethylene for 18 hours, and the other with an equilibrated mixture of H_2 and D_2 (H_2, HD, D_2) for 6 hours. The product anticipated here is that expected from the first experiment if addition occurs atom by atom. Ethylene was admitted to the catalyst before the hydrogen mixture to prevent the equilibration of the $H_2 + D_2$ in the first experiment. That this equilibration was inhibited was shown by measuring the rate of para-conversion under similar conditions. Only 13 per cent conversion occurred in 85 minutes at which time 94.2 per cent of the ethylene was hydrogenated. In the absence of ethylene the half-life of the conversion was 13 minutes.

The infrared spectra of the ethanes from the two experiments were identical and different from an equal mixture of C_2H_6 and $C_2H_4D_2$. Twigg took this as proof that addition of hydrogen does not take place in a single act, but that the hydrogen and deuterium molecules are first split into atoms which then add one at a time.

Summary of Experimental Results. In the light of these experiments Twigg reviewed the relation of hydrogenation and exchange. The experimental results of this and his previous work were summarized as follows:

(1) The dependence of the rate of hydrogenation and exchange on pressures are identical and given by $p^{0}_{C_2H_4} \times p^{n}_{H_2}$ from −78 to +150°C where n is unity or slightly less.

(2) The energy of activation for exchange is greater than for hydrogenation.

(3) Above 100°C the energies of activation of hydrogenation and exchange decrease with increase in temperature, although the order of the reaction is unchanged and the H_2—D_2 equilibrium is still inhibited.

(4) Para-hydrogen conversion and the H_2—D_2 reaction are inhibited by ethylene except via exchange with ethylene.

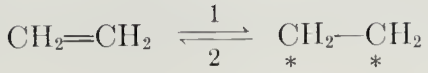
(5) During exchange between ethylene and deuterium the hydrogen returned to the gas phase is largely H_2 molecules.

(6) Hydrogen or deuterium is dissociated into atoms before hydrogenation.

Inhibition of para-hydrogen conversion and of H_2—D_2 exchange (item 4) indicates that the surface is almost entirely covered with ethylene. Since the reactions are zero order and not negative order with respect to ethylene, either the two gases do not compete for the same sites or adsorption equilibrium by the Langmuir mechanism is not achieved. Twigg accepts the second alternative. Up to 150°C he proposes that the rate of adsorption of ethylene is much faster than that of hydrogen (or deuterium) on the available bare surface. He considers the reaction $H_2 \rightarrow 2Ni{-}H$ to be of no significance because the free surface available is too small. Since, H_2 molecules (item 5) are returned to the gas phase, even when deuterium gas is used, interchange of ethylene between gas and catalyst is much faster than the interchange of hydrogen or deuterium. These considerations together with the fact (item 6) that hydrogen is dissociated, and therefore adsorbed, before hydrogenation led Twigg to propose the following mechanisms for exchange and hydrogenation in place of the earlier ones.

Reformulated Mechanisms:

(70)



$$CH_2{=}CH_2 \underset{2}{\overset{1}{\rightleftharpoons}} \underset{*}{CH_2}{-}\underset{*}{CH_2}$$

$$(71)\quad \underset{\theta_1}{\underset{*}{\mathrm{CH_2}}-\underset{*}{\mathrm{CH_2}}} + \underset{*}{\overset{\mathrm{D_2}}{\vdots}} \underset{4}{\overset{3}{\rightleftharpoons}} \underset{\theta_2}{\underset{*}{\mathrm{CH_2}}-\mathrm{CH_2D}} + \underset{\theta_3}{\underset{*}{\mathrm{D}}} \xrightarrow{7} \mathrm{CH_2D-CH_2D}$$

$$(72)\quad \underset{*}{\mathrm{CH_2}}-\mathrm{CH_2D} + \underset{*}{\mathrm{D}} \underset{3'}{\overset{4'}{\rightleftharpoons}} \underset{*}{\mathrm{CH_2}}-\underset{*}{\mathrm{CHD}} + \mathrm{HD}$$

$$(73)\quad \underset{*}{\mathrm{CH_2}}-\underset{*}{\mathrm{CH_2}} + \underset{*}{\mathrm{D}} \underset{6}{\overset{5}{\rightleftharpoons}} \underset{*}{\mathrm{CH_2}}-\mathrm{CH_2D} \underset{5'}{\overset{6'}{\rightleftharpoons}} \underset{*}{\mathrm{CH_2}}-\underset{*}{\mathrm{CHD}} + \underset{*}{\mathrm{H}}$$

$$(74)\quad \underset{*}{\mathrm{CH_2}}-\underset{*}{\mathrm{CH_2}} + \underset{*}{\mathrm{H}} \underset{6''}{\overset{5''}{\rightleftharpoons}} \underset{*}{\mathrm{CH_2}}-\mathrm{CH_3}$$

$$(75)\quad \underset{*}{\mathrm{CH_2}}-\mathrm{CH_3} + \underset{*}{\mathrm{H}} \underset{3''}{\overset{4''}{\rightleftharpoons}} \underset{*}{\mathrm{CH_2}}-\underset{*}{\mathrm{CH_2}} + \mathrm{H_2}$$

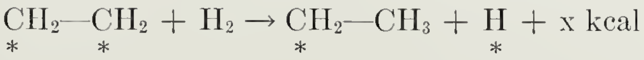
$$(76)\quad \underset{*}{\mathrm{CH_2}}-\mathrm{CH_3} + \underset{*}{\mathrm{H}} \xrightarrow{7'} \mathrm{CH_3-CH_3}$$

In Twigg's formulation, ethylene is chemisorbed by opening of the double bond (1). Van der Waals' adsorbed deuterium reacts with chemisorbed ethylene to produce the half-hydrogenated radical and a chemisorbed deuterium atom (3). This is not the rate determining step because exchange and addition have different activation energies. However, since he finds both reactions have the same kinetics, he assumes they both proceed from this same adsorbed state. Reactions (4) or (4′) and (4″) are assumed to be rate determining for exchange and reaction (7) or (7′) rate determining for addition.

It was found that H_2 (4″) rather than HD (4′) was returned to the gas phase during exchange between ethylene and deuterium. Reactions (5) and (6), which are assumed to be fast compared to the others, were therefore added. In his discussion of the results of Turkevich, Bonner, Schissler and Irsa[231, 232], Twigg[238] suggested that these reactions could also explain the initial high rate of formation of light ethane during the reaction of deuterium with ethylene. The chemisorbed ethylene and deuterium atoms exchange rapidly by reactions (5) and (6). The rate of the exchange, however, is not controlled by this reaction but by the return of adsorbed hydrogen to the gas phase (4″). The new deuterium coming to the surface by reaction (3) is rapidly equilibrated with the hydrogen of the ethylene by reactions (5) and (6). Thus, H atoms are more abundant than D atoms on the catalyst surface and the ethane in the initial stages of the reaction should be largely C_2H_6 as observed by Turkevich, *et al.* Also, the hydrogen returned to the gas phase should be largely H_2 .

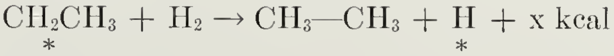
Twigg worked out some kinetic equations based on the above mechanism and found them to be consistent with his experimentally observed first order dependence of exchange and addition on deuterium pressure and independent of ethylene pressure since $\theta_{C_2H_4} \approx 1$. The ratio of exchange to hydrogenation k_4/k_7 and their difference in activation energies $E_4 - E_7$ should be constant over a wide temperature range as was found by Twigg and Rideal[240]. Using his kinetic expressions, he gave an explanation of the maximum observed in rates and for the decreasing activation energies for temperatures above about 90°C.

Using 17 kcal and 36 kcal for the heats of adsorption of hydrogen and ethylene, respectively, and the assumption that the heats evolved for



$$\underset{*}{\mathrm{CH_2}}\text{—}\underset{*}{\mathrm{CH_2}} + \mathrm{H_2} \rightarrow \underset{*}{\mathrm{CH_2}}\text{—}\mathrm{CH_3} + \underset{*}{\mathrm{H}} + \mathrm{x\ kcal}$$

and



$$\underset{*}{\mathrm{CH_2}}\mathrm{CH_3} + \mathrm{H_2} \rightarrow \mathrm{CH_3}\text{—}\mathrm{CH_3} + \underset{*}{\mathrm{H}} + \mathrm{x\ kcal}$$

are the same, he finds $x = E_4 - E_7 = 7$ kcal, and $E_5 - E_6 = 10$ kcal. These values are respectively 11 kcal and 1 kcal when the heats of adsorption for covered surfaces obtained by Beeck are used. If E_3 is taken as 11 kcal from low temperature hydrogenation data, he finds $E_4 = 18$ kcal and $E_7 = 9$ kcal by using Eley's values for heats of adsorption. By using Beeck's values for the heats of adsorption, he obtains $E_4 = 22$ kcal and $E_7 = 13$ kcal.

Best and Russell[30a] have used Twigg's mechanism outlined above to explain their results on the hydrogenation of ethylene on nickel-copper alloy systems.

Jenkins and Rideal's Re-examination of the Adsorption and Reactions of Ethylene. A Rideal type mechanism, which involves the reaction of gas phase or Van der Waals' adsorbed molecules with chemisorbed molecules, was used by Twigg and Rideal[240] (p. 292) to explain the interactions of ethylene and deuterium. Their mechanism at that time involved the interaction of a Van der Waals adsorbed hydrogen (or deuterium) with an associatively adsorbed ethylene. As a result of recent experiments on metal films[5, 6, 128, 180, 223], Jenkins and Rideal[128] have revised the mechanism to one involving gas phase ethylene and chemisorbed hydrogen (or deuterium). The experimental method, results, and conclusions are similar in many respects to those by Beeck[21] as will be described in the next section.

Jenkins and Rideal first studied the adsorption of ethylene and hydrogen on evaporated nickel films. These films (presumably about 50 mg) were prepared by evaporating a nickel hairpin spot welded to tungsten-"Pyrex" seals in a 30-ml vessel. The quantities of gas adsorbed were measured in units of 1 micron pressure change, which for the system used corresponded to 9.6×10^{15} molecules.

Their results on adsorption experiments may be summarized as follows:

(1) When small quantities of ethylene were admitted to the film at 20°C, the first 40 units were completely and very rapidly chemisorbed. Further addition of ethylene up to about 200 units resulted in rapid adsorption but a residual gas pressure remained which was shown to be all ethane. When more ethylene was added, both ethane and ethylene were found in the gas phase. Thus, two distinct phases as shown in Figure 1 were observed, the first one corresponding to complete chemisorption and the second one to adsorption plus ethane formation. When the vessel was evacuated after adsorption was complete, practically no ethylene was adsorbed on the film when more was admitted to the system.

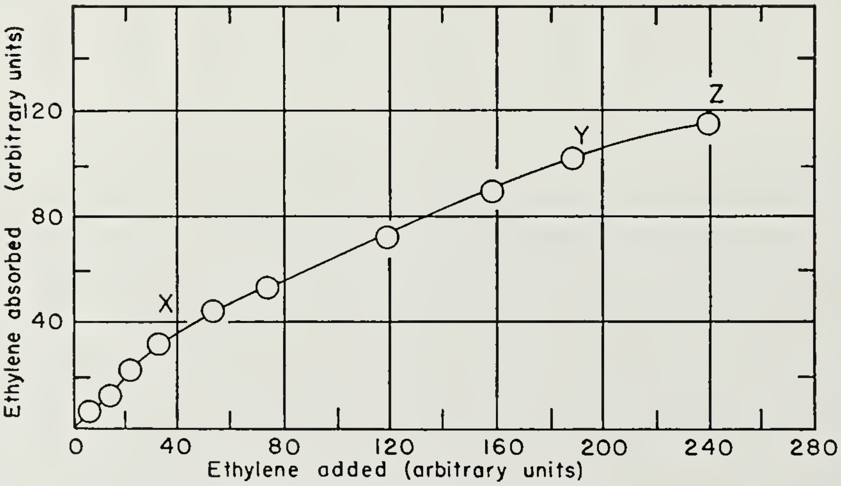


Figure 1. Phases in the adsorption of ethylene as successive amounts of ethylene are added to an evaporated nickel film.[28]

(2) From the quantity of hydrogen adsorbed at −183°C (2 lattice points per molecule) and from the quantity of ethylene adsorbed at the end of phase I it was concluded that one ethylene was adsorbed per 8 sites. Part of these sites were shown to be bare at the end of phase I by the irreversible adsorption of hydrogen at −78°C. They interpret the first phase as a reaction of ethylene to form acetylene complexes and chemisorbed hydrogen

$$CH_2{=}CH_2 \rightarrow \underset{*}{C}H{=}\underset{*}{C}H + \underset{*}{H}\underset{*}{H} \tag{77}$$

During the second phase, some of the chemisorbed hydrogen reacts with ethylene from the gas phase to form ethane, leaving more bare sites for the formation of acetylenic complexes.

(3) When ethylene was added in successive amounts to a nickel film on which hydrogen had been adsorbed, the residual gas up to the point Y (see Figure 1) was entirely ethane. The slope of this curve as compared to phase

H for the adsorption of ethylene alone indicated that both involved the reaction of gas phase ethylene with chemisorbed hydrogen.

(4) Hydrogen was admitted to the residues remaining after evacuation of the flask following complete adsorption of ethylene. An instantaneous decrease in pressure was observed followed by a slow continuous decrease whose rate was proportional to the initial hydrogen pressure. Further experiments indicated that the initial drop in pressure was due to adsorption on bare sites and the slow drop in pressure resulted from the formation of ethane and adsorption of hydrogen on the sites left vacant by this reaction.

(5) The low temperature irreversible adsorption of hydrogen on one of the nickel film catalyst was 145 units corresponding to 290 "sites". On a similar film, 121 units of ethylene was chemisorbed and a further 120 units of ethylene was converted to ethane. About 12 units of hydrogen could be adsorbed on the bare sites left. If the C_2H_2 residues occupy 2 sites each, $290-242 = 48$ bare sites on the complex-covered surface. Of these, the 12 units of hydrogen would occupy 24 leaving 24 unoccupied. Thus, they infer that a nickel surface in the presence of a mixture of ethylene and hydrogen is about 80 per cent covered with acetylene complexes, 10 per cent hydrogen on double sites and 10 per cent unoccupied single sites. These single sites can be occupied by hydrogen atoms or by diffusion of hydrogen atoms through the metal.

(6) When a surface covered with acetylenic complexes is heated to 170°C, it becomes carbided and the expected amount of hydrogen gas is evolved. The behavior of the surface after carbiding indicated to them that surface carbide migrates, leaving fresh nickel surface for adsorption of hydrogen. Such a carbided surface, like the complex-covered surface adsorbs hydrogen but not ethylene or ethane.

Jenkins and Rideal conclude from the above results that ethylene does not undergo "associative" adsorption by opening of the double bond. Instead, it is adsorbed irreversibly by dissociation into an acetylenic complex and two hydrogen atoms.

The slow reaction of hydrogen with the complex-covered surface was estimated to be less than $1/100$ of the normal hydrogenation rate of ethylene. Addition of hydrogen to the dissociatively adsorbed ethylene is, therefore, of secondary importance in the hydrogenation reaction. Because hydrogen is adsorbed on both the complex-covered and the carbided surface, and because of the observation that gaseous ethylene reacts rapidly with pre-adsorbed hydrogen, the authors suggest the following mechanism for hydrogenation. Gas-phase ethylene reacts with hydrogen adsorbed on vacant sites on a complex-covered surface producing ethane and leaving sites available for further adsorption of hydrogen.

The kinetics of the hydrogenation were determined on carbided nickel catalysts produced by exposing approximately 50 mg nickel films to ethylene and then heating them to 190°C for 30 min. Rates were determined for 5 cm each of hydrogen and ethylene in the temperature range from 20 to 180°C. The energy of activation was found to be 10.2 kcal/mole in the low temperature region with an inversion at 160 to 165°C.

Below the inversion temperature, the rate was found to be independent of ethylene pressure when it varied from 2.0 to 9.6 cm, and directly proportional to the hydrogen pressure. Thus,

$$\text{Rate} = kp_{H_2}p^{0}_{C_2H_4} \tag{18}$$

At 165°C the rate followed the equation,

$$\text{Rate} = Ap_{H_2}p_{C_2H_4}/(1 + Bp_{C_2H_4}) \tag{19}$$

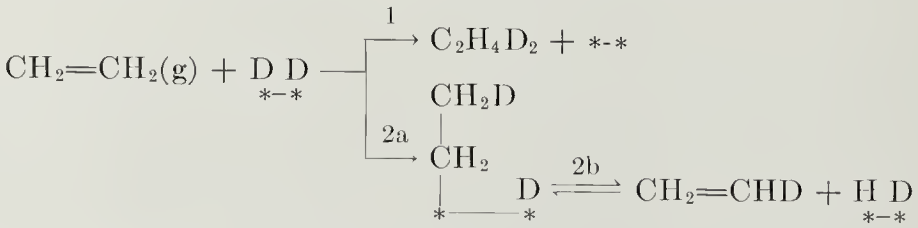
while at still higher temperatures

$$\text{Rate} = Kp_{H_2}p_{C_2H_4} \tag{20}$$

The authors derived a series of rate equations based on their mechanism that gaseous ethylene reacts with hydrogen chemisorbed on pairs of sites. Letting θ be the fraction of paired sites on which hydrogen is chemisorbed, the rate of chemisorption of hydrogen would be $k_1p_{H_2}(1 - \theta)$. Chemisorbed hydrogen can evaporate at a rate $k_2\theta$ or react with ethylene at a rate $k_3p_{C_2H_4}\theta$ so that at steady state $k_1p_{H_2}(1 - \theta) = k_2\theta + k_3p_{C_2H_4}\theta$. Using this approach they derived expressions that corresponded with the observed kinetics.

From the equations developed, they interpreted the change in order with respect to ethylene as the temperature is increased, as follows:
The rate of evaporation of hydrogen $k_2\theta$ increases more rapidly than the reaction of hydrogen with ethylene, $k_3p_{C_2H_4}\theta$. That is, the energy of activation of desorption is greater than the energy of activation of the hydrogenation. The inversion temperature of hydrogenation should also depend on pressure as has been observed.

The following equations were written by Jenkins and Rideal to illustrate their proposed mechanism of hydrogenation and exchange

(78)

$$CH_2{=}CH_2(g) + \underset{*-*}{D\ D} \xrightarrow{1} C_2H_4D_2 + *\text{-}*$$
$$CH_2{=}CH_2(g) + \underset{*-*}{D\ D} \xrightarrow{2a} \underset{*\text{———}*}{\overset{CH_2D}{\overset{|}{CH_2}}\quad D} \overset{2b}{\rightleftharpoons} CH_2{=}CHD + \underset{*-*}{H\ D}$$

(79)

$$\underset{*-*}{HD} \rightarrow HD + *\text{-}*$$

They give the following explanation of the results of Twigg and Rideal[240] in which it was found that the hydrogen returned to the gas phase was H_2 rather than HD, and the results of Turkevich, Schissler and Irsa[231, 232] (see p. 340) in which it was found that initially light ethane was an abundant product. The exchange reaction (2a) and (2b) is assumed to be considerably faster than the rate of desorption of hydrogen so that the deuterium adsorbed goes into the ethylene. At the lower temperatures where the exchange reaction (2) is also faster than hydrogenation (1), rapid replacement of deuterium will occur so that the surface will contain considerably more H than D. Thus, the ethane formed when C_2H_4 from the gas reacts with H on the surface will largely be C_2H_6 rather than C_2H_5D or $C_2H_4D_2$.
That is,

$$D_2(g) + *\text{-}* \rightarrow \underset{*-*}{D\ D} \tag{80}$$

$$2C_2H_4(g) + \underset{*-*}{D\ D} \xrightarrow[\text{fast}]{} \underset{*-*}{H\ H} + 2C_2H_3D(g) \tag{81}$$

$$\underset{*-*}{H\ H} + C_2H_4(g) \rightarrow C_2H_6 + *\text{-}* \tag{82}$$

One difficulty with this mechanism is that evidence from mass spectrometric examination to be described later (p. 352) indicates that in addition to light ethane there are also significant quantities of more highly deuterated ethanes up to C_2D_6 in the initial stages. No highly deuterated ethylenes are observed and it appears that the second and third deuterium gets into the ethylene by successive exchanges. On the other hand, the distribution of deuterium in the ethanes would indicate that multiple exchanges occur before the ethylene forms ethane and is desorbed. Thus, reaction (78) or (82) may not properly represent the detailed process of hydrogenation.

BEECK'S MECHANISMS AND EVAPORATED METAL FILMS

Ethylene Reactions on Oriented Nickel Films. Beeck, Smith and Wheeler[23] reported their initial work on an important series of researches on the catalytic activity of evaporated metal films. They devised methods of evaporating metals, such as nickel, under high vacuum to give unoriented films and under 0.5 to 2.0 mm pressures of inert gas to give oriented films. Evaporation of nickel and the other transition elements that have face-centered cubic structures in 1 mm of nitrogen or argon gave completely oriented films with the least dense 110 planes parallel to the glass surface. Iron, on the other hand, with a body-centered structure, gave films with their 111 planes (again the least dense ones) parallel to the glass. They studied the effect of the following: gas pressure during evaporation, treatment of the glass surface, temperature of the glass surface at time of dep-

TABLE 5. TYPICAL RESULTS ON EVAPORATED NICKEL FILMS FOR ETHYLENE HYDROGENATION AND GAS ADSORPTION

Kinetics

Rate of addition: $\sim p_{C_2H_4}{}^0 p_{H_2}$ for all nickel films. Excess ethylene lowers reaction rate.

Energy of activation: approx. 10 kcal.

Film Thickness and Orientation (values determined from curves given[28]; Temp. = 0°C; weights are mg./30cm²)

First order constants for oriented films: 10 mg = 0.74; 20 mg = 2.5; 30 mg = 4.6 min.$^{-1}$

First order constants for unoriented films: 10 mg = 0.18; 20 mg = 0.46; 30 mg = 0.83; 60 mg = 2.3 min.$^{-1}$

Ratio of rate constants, oriented to unoriented films: 20 mg = 5.5; 30 mg = 5.5. For completely unoriented film formed by evaporation on the surface at −183°C, ratio = 5.1. Above 15 mg the rate constant increases nearly linearly with the weight of the film.

Effect of Baking-out Temperatures of Glass Surface

Ratio of rate constant when glass surface is baked at temperature t to rate constant when baked at 480°C for 1 hr; 25°C = 0.45; 100°C = 0.55; 200°C = 0.72; 300° = 0.92

Effect Sintering on Activity and Adsorption (Values adjusted to film weights of 14 mg. /30 cm²)

Percent of activity when oriented films prepared at 23° were heated for 30 min. at temperature t°C; 23°C = 100%; 100°C = 40%; 200°C = 8%; 400°C ≅ 0%. Approximately the same results were obtained if the surface was maintained at the sintering temperature during evaporation of the nickel.

Adsorption (percent of that at 23°C) on films sintered at 100°C: H_2 = 73%, C_2H_4 = 100%. At 200°C: H_2 = 40%, C_2H_4 = 56%

Adsorption Measurements (Gas pressure = 0.1 mm)

Number of hydrogen atoms adsorbed at 23°C per 10 mg of film: oriented = 2.6×10^{18}; unoriented = 1.25×10^{18}

Number CO molecules adsorbed at −183°C per 10 mg of film: oriented = 2.6×10^{18}; unoriented = 1.25×10^{18}

Ratio of unoriented to oriented is 2 for adsorption but 5 for activity. Also, from 1 to 15 mg, the activity is not linear with weight but adsorption is.

One molecule of CO apparently occupies the same lattice space occupied by one hydrogen atom.

Adsorption Isotherms

Isotherms for fraction of surface covered at 0.1 mm were given for: CO at −183°C and 23°C; C_2H_4 at 23°C; N_2 at −183°C: H_2 at 23°C; O_2 at 23°C.

Irreversible chemisorption occurred in a few seconds for all except nitrogen which was not measurably adsorbed at room temperature.

Adsorption ratios relative to CO were: H atoms = 1; H_2 molecules = ½; N_2 = ½; C_2H_4 = ¼; O_2 = 2, corresponding to 1 lattice space for CO; 1 for H atoms; 2 for nitrogen; 4 for ethylene; and 2 molecules of O_2 per lattice space.

CO adsorption at 23°C was about 20% less than at −183°C.

H_2 adsorption was the same at 23°C and −183°C. About 20% of H_2 adsorbed at 0.1 mm could be pumped off at 10^{-4} mm.

N_2 adsorption (van der Waals) at 0.1 mm and −183°C is almost identical to H_2 adsorption.

TABLE 5.—*Concluded*

O_2 adsorption is twice that of CO or two molecules per lattice space. This increases with time, indicating a diffusion process.

C_2H_4 adsorption isotherm is different from the other gases in that the quantity adsorbed at 23°C and 1×10^{-3} mm is only about 50% that adsorbed at 0.1 mm, whereas hydrogen adsorbs about 80%, CO about 95%, and O_2 about 99% of the quantities adsorbed at 0.1 mm

Poisoning by CO and O_2

When the surface had adsorbed its maximum amount of CO, the hydrogenation reaction was practically completely inhibited. A smaller amount of O_2 than the maximum completely inhibited the reaction.

The activity of the films was proportional to the per cent of surface poisoned.

Films poisoned with CO still adsorb 20% of the hydrogen that a clean surface does, but it is readily pumped off.

Films poisoned with O_2 on standing one half day will chemisorb instantaneously the regular amount of H_2 indicating diffusion of oxygen into the interior of the lattice.

Other Metals

Films of iron, cobalt, palladium, platinum and copper were investigated and with the exception of copper similar results were obtained.

The enhanced activity of oriented films was associated with the larger distance in the 111 planes of iron and the 110 planes in nickel.

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osition, and the effect of gas pressure on the structure, electrical conductivity, catalytic activity, and adsorptive properties of the films.

The catalytic activity was measured with 100 to 500 mm of an equal molar mixture of ethylene and hydrogen in the vessel in which 5 to 50 mg of nickel had been evaporated on a 30 cm^2 area. The total volume was about 400 cc and the vessel was equipped with a glass turbine circulator to move the gases rapidly past the film. Comparison of the activities of the films was made at 0°C as a function of: (a) film thickness, (b) pressure of inert gas in which the film was evaporated, (c) temperature of the glass surface on which the metal was evaporated.

Summary of Experimental Results. Some of the results of the above and other measurements are summarized in Table 5.

Activity and Nature of Films. The authors discuss some possible mechanisms for the formation of the oriented films and their properties. They calculate that, for a 50 mg film, the total interior surface is about 10,000 cm^2, whereas, the apparent surface is only 30 cm^2. These films are therefore very porous. The unoriented ones have only half this interior surface. The increase in activity with the mass of the films as well as the poisoning experiments show that even for reactions completed in less than a minute the innermost layers participate in the reaction to the full extent of their inherent activity. The results indicate that diffusion into the pores or canals will allow the whole interior surface to be effective, but agitation is necessary to remove the ethane formed from the film.

Differences in surface areas between oriented and unoriented films cannot alone explain the differences in activity because the area differs by only a factor of 2 while the activities differ by a factor of 5. The authors discuss this problem in relation to atomic spacings in the planes and uniformity of surfaces. The surfaces are nonuniform in the sense that unoriented films expose a small fraction of the active 110 planes together with a large fraction of planes less active. Ordinarily, however, such films would be considered homogeneous crystal lattices, as distinguished from catalysts with nonuniform surfaces on which catalysis is assumed to be enhanced by active centers arising from crystal or field distortions.

No definite conclusions were reached as to why the 110 planes were more active. In this plane two spacings between nickel atoms are present equally, 3.51 Å and 2.48 Å. In the 100 plane twice as many have the 2.48 spacing as the 3.51 Å spacing, while in the 111 plane, they all have the 2.48 Å spacing. The experimental data were not sufficient to show whether the process of adsorption, evaporation, or reaction was faster on the 110 plane or not. Determination of the small differences in activation energies and heats of adsorption on the different planes would be of value. However, if it turns out that the reaction proceeds predominantly on the 110 plane and if this plane is five times more abundant in the oriented film, no difference in activation energy would be expected.

Detailed mechanisms of the hydrogenation mechanism were not discussed in this paper[28], although the authors did suggest that since ethylene covers four lattice spaces relative to carbon monoxide, it is presumably adsorbed at the four hydrogen atoms of the ethylene molecule. In the case of the adsorption of hydrogen, one molecule occupies two lattice spaces and consequently, for the most part, splits into atoms. Roberts[192], however, has shown that when a diatomic gas like hydrogen is admitted to a tungsten surface, 8 per cent of the lattice spaces are empty. This is in agreement with the observation that 20 per cent of the hydrogen adsorbed at 0.1 mm and 23°C can be readily pumped off. If molecules of H_2 are adsorbed relatively loosely on the 8 per cent vacant sites, it would account for at least 16 per cent of the total amount adsorbed.

Beeck[18, 21] reviewed his previous work and presented some new data on the relation of the rate constants to lattice spacing, heats of adsorption, and activation energies. On the basis of this work and kinetic considerations he presented a mechanism of hydrogenation different from those previously suggested.

Lattice Parameters and Rates of Hydrogenation. The rate constant for the hydrogenation of ethylene was reported for films of the following metals, all of which have the required property of chemisorbing hydrogen: Cr, Fe, Co, Ni, Rh, Pd, Pt, Ta, W. Copper has about the same lattice spacing as Ni, but since it does not chemisorb hydrogen it is not a good catalyst for the hydrogenation. In Figure 2, the logarithm of these rate constants (per cm^2 per sec.) are plotted as a function of lattice spacing. Rhodium is several hundred times more active than nickel and 10^4 times more active than tungsten, based on the same hydrogen adsorption. A maximum occurs for rhodium with a lattice spacing of 3.75 Å. This is approximately the distance between the hydrogen atoms in opposite methyl groups of the ethane molecule. The kinetics of the reaction (rate $\sim p^0_{C_2H_4}p_{H_2}$) indicates that the surface is sparsely covered with hydrogen, which might suggest that the rate determining steps involve hydrogen adsorption. Okamoto, Horiuti and Hirota[173], using Sherman and Eyring's[211] quantum mechanical treatment of hydrogen adsorption, calculated activation ener-

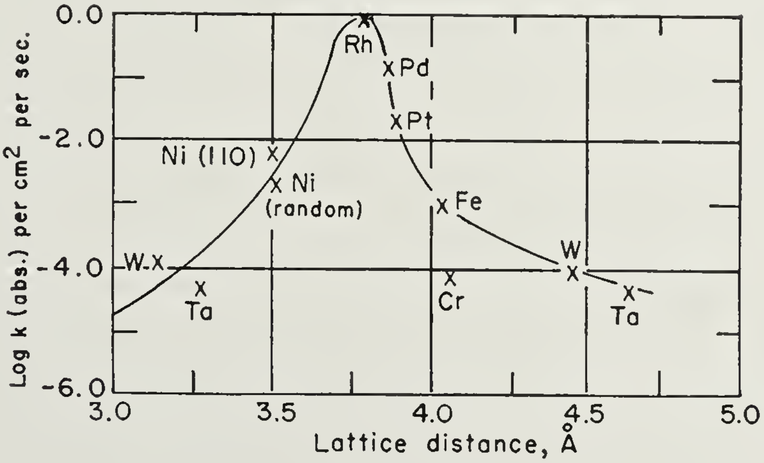


Figure 2. Activity of evaporated metal films as a function of lattice distances, 0°C[18, 28].

gies for pairs of adjacent nickel atoms in the different planes and came to the conclusion that the activation energy was lowest for the 110 planes. However, Beeck's results show that chemisorption of hydrogen is practically instantaneous for both oriented and unoriented films, either at −183°C or 23°C. Therefore, differences in activation energies of hydrogen adsorption cannot account for the differences in rates of hydrogenation. The activation energies for oriented and unoriented films of nickel as well as for iron, platinum, palladium and rhodium covering a thousand fold range in rate constant all gave about the same activation energy of 10.7 kcal for the temperature range −80°C to +150°C. In contrast to this group of elements, later results[21] showed that the activation energy for hydrogenation on tungsten and tantalum was only 2.4 kcal, although the rate was 20 times lower than on unoriented nickel. Initial rates were about ten times faster than the final rates.

Beeck concludes, therefore, that the differences in rate for the first group of metals (Ni, Fe, Pt, Pd, Rh) are governed by the constant A in the Arrhenius equation

$$k = Ae^{-E/RT} \tag{21}$$

with the same temperature coefficient for each metal. Not enough was known to explain the precise role of this "frequency factor" or "entropy of activation" which arises in part from "steric factors". The kinetic results of these experiments relating reaction rate to crystal parameter and showing such a marked separation of energy of activation and entropy of activation, are different from the results reported by Kemball[2, 137, 139, 140] (see p. 325) for the exchange of saturated hydrocarbons with deuterium.

Adsorption of Hydrogen. Heats of adsorption on oriented and unoriented films of nickel were measured at −183°C and room temperature for both hydrogen and ethylene as a function of the fraction of the surface covered. For hydrogen the following values were obtained for the percentage of the surface covered: 10% = 30 kcal; 40% = 27 kcal; 60% = 24 kcal; 80% = 20 kcal; 90% = 18 kcal; 95% = 15 kcal. Values for oriented films were not more than 2 to 3 per cent greater than the unoriented ones, both at −183°C and room temperature.

Similar results were obtained by Roberts[192] on tungsten using wires with small surface areas rather than evaporated films with areas 10^6 times larger. Roberts' results for tungsten were 45 kcal for the bare surface and 18 kcal for a nearly covered surface. In these experiments the hydrogen hits the wire at random, but with an evaporated metal film, the molecules must penetrate into the interior of the porous structure. The change in heat of adsorption implies that the adsorbed atoms or molecules are mobile; otherwise each increment of gas admitted would have the same heat of adsorption until the interior surface was filled. With CO and O_2 on all of the metals studied, the heats of adsorption for each increment of gas admitted was constant until the surface was nearly covered; then a sudden drop in the heat of adsorption occurred. Hydrogen on iron behaved similarly at −183°C, but at room temperature, its behavior was similar to that on nickel, indicating again mobility of the hydrogen. Mobility on tungsten seems to be somewhat impaired.

Curves were given[20, 21, 24, 26] for the heats of adsorption of hydrogen as a function of the fraction of surface covered for Fe, Ni, Rh, Ta and W. Curves for the first three were similar, but tungsten showed values that were rather high for small surface coverage and then decreased rapidly beyond 80 per cent coverage. Heats of adsorption for sparsely covered surfaces of tantalum, tungsten, and chromium were all 44–45 kcal; for Fe and Ni, they were 30–31 kcal; and for palladium and rhodium, 26–27 kcal. Tantalum showed strong exothermic absorption into the structure as well as adsorption onto the surface. A chemisorbed layer of nitrogen prevents the adsorption of hydrogen at room temperatures. If the surface is only partially covered with chemisorbed nitrogen, the rest of the surface can be covered with hydrogen. However, hydrogen can be adsorbed on tungsten covered with preadsorbed nitrogen, but the initial heat of adsorption is 27 kcal rather than 45 kcal for a clean tungsten surface. The quantity of hydrogen adsorbed on tungsten covered with nitrogen is less than one tenth of the total adsorbed and absorbed by clean tungsten. The slow absorption of hydrogen into the structure is blocked by the preadsorbed nitrogen.

Adsorption and Absorption of Hydrogen on Sintered Films. Some interesting experiments on adsorption and absorption of hydrogen on sintered nickel films by Beeck and his co-workers[25, 27] are of interest in explaining the differences between the behavior of evaporated nickel films and reduced nickel oxide. When evaporated nickel films are sintered at 100 to 400°C the quantity of hydrogen adsorbed rapidly in the initial stages is considerably reduced (see p. 306) and this reduction could be correlated with activity for hydrogenation, adsorption of CO, or BET surface areas. The ratio of the values of each of these measurements to their values for films sintered at 23°C, when plotted as a function of sintering temperature, fell on the same smooth curve. For example, when the sintering temperature was 100°C all of them were 35 to 45 per cent of their values for 23°C; at 200° they were 15 to 18 per cent; and at 400°C less than 1 per cent.

In addition to the fast adsorption, a slow "activated adsorption" of hydrogen occurred, which they concluded was actually "sorption" into the interior of the metal structure. It is of the activated type because it occurs with a measurable temperature dependent rate. The heat of sorption, i.e., absorption, must be considerably lower than the heat of adsorption, because absorption is more readily reversible at high temperatures than the adsorption process.

The ratio of the slowly "sorbed" hydrogen to the rapidly adsorbed hydrogen increased with the temperature of sintering. The areas occupied by the sorbed hydrogen are not accessible for chemisorption of CO or ethylene, or for Van der Waals' adsorption in BET surface area measurements with krypton. The activity of the film and therefore, the active surface is related only to the very rapidly adsorbed (chemisorbed) hydrogen. The authors suggest that many of the "activated adsorptions" reported for bulk or technical catalysts may have been sorptions into the catalyst rather than adsorption on the surface.

Adsorption of Ethylene. The heat of adsorption of ethylene at 23°C on nickel films falls from 58 kcal initially to appreciably lower values with increasing coverage. Initial values for the heat of adsorption of ethylene on other metals were, approximately: Ta = 135 kcal, W = 106 kcal, Cr = 98 kcal, Fe = 70 kcal, Rh = 50 kcal. Adsorption of ethylene is complicated by self-hydrogenation. On unoriented films of nickel at 23° about 5×10^{18} molecules are adsorbed on 100 mg nearly instantaneously and irreversibly. Addition of more ethylene results in the formation of ethane and when 12.5×10^{18} molecules of ethylene have been added, an equal number of ethane molecules appear rapidly in the gas phase leaving acetylenic residues on the surface. Further additions up to 80×10^{18} molecules resulted in additional self-hydrogenation. The residue on the surface then has the composition $C_nH_{0.4n}$ and this will polymerize to higher hydrocarbons. Beeck states that, at low temperatures (−39°C), ethylene does not self-hydrogenate.

Reactions of Preadsorbed Gases. When the residue from preadsorbed ethylene on nickel films reacts with hydrogen at 23°C, 20 per cent is removed in about one hour. The product is 10 per cent ethane and 90 per cent C_4 to C_8 and higher saturated hydrocarbons. Residues from preadsorbed ethylene on rhodium are nearly completely removed with long contact times and 60 per cent is lost in 1 minute, the product being principally ethane with a few per cent polymer.

If ethylene is preadsorbed on films of the metals, the rates of hydrogenation are reduced by the following factors: Ni = 0.6, Ta = 10, W = 5, Rh and Pt = 0.90–0.95 (reduced only few per cent). Preadsorbed acetylene cannot be reacted off nickel with hydrogen at 23°C but on rhodium 40 per cent is removed in 1 hour.

Although no data are given, Beeck states[21] that preadsorbed hydrogen reacts with ethylene practically instantaneously. This is an important consideration in arriving at the mechanism he proposes.

Thermal Considerations. In the course of the hydrogenation, the thermally important steps are: adsorption of reactants; rearrangements on the surface; desorption of products. The heats of the reaction must add up to 32.5 kcal, which is the heat of the over-all hydrogenation. For a sparsely covered surface, the heat of adsorption of hydrogen was found to be 30 kcal. Beeck assumes that hydrogen must be chemisorbed before reaction and consequently this accounts for most of the heat of reaction. The heat of desorption of ethane molecules is nearly zero, so that only 2.5 kcal remain for reaction between the adsorbed hydrogen and ethylene. Since he found the heat of adsorption of ethylene to be 58 to 60 kcal for a sparsely covered surface, he concludes that the reaction cannot be between the molecules of chemisorbed ethylene and chemisorbed hydrogen on the surface. Instead, his idea is that gaseous ethylene simultaneously picks up two hydrogen atoms from adjacent sites on the surface. Thus, the distance between hydrogen atoms as determined by lattice spacings will be important. From his experiments showing the rapid rate of reaction of ethylene with preadsorbed hydrogen and other experiments showing the rapid rate of adsorption of hydrogen, he concluded that neither of these can be the rate controlling step in the reaction.

Beeck's Mechanism. The above considerations together with his observations on the formation of acetylenic residues, Beeck[18] considers the rate of the reaction to be determined by the fraction of surface not covered by these residues. This is the surface available to adsorb hydrogen in a form suitable for hydrogenation. The thermal considerations above led him to the view that ethylene was not adsorbed in the main hydrogenation step itself; consequently, the rate should be proportional to the ethylene pressure. To come out with the observed kinetics, namely that the rate is proportional to the hydrogen pressure and independent of the ethylene pressure, he assumes that the surface available for the hydrogenation step must be proportional to the hydrogen pressure and inversely proportional to the ethylene pressure so that

$$\frac{dp_{\mathrm{C_2H_4}}}{dt} = kp_{\mathrm{C_2H_4}} \frac{p_{\mathrm{H_2}}}{p_{\mathrm{C_2H_4}}} = kp_{\mathrm{H_2}} \tag{22}$$

This means that the rate of removal of the poisoning acetylenic complexes by surface hydrogenation is the rate controlling process. That is, the rate of the very fast reaction of gaseous ethylene with adsorbed hydrogen is controlled by the rate of a second slow hydrogenation process because this latter process makes new surface available for chemisorption of hydrogen. A formulation of this mechanism might be somewhat as follows:

(1) Poisoning by formation of acetylenic residues and self-hydrogenation

$$\mathrm{CH_2{=}CH_2} \rightarrow \underset{*}{\mathrm{CH}}{=}\underset{*}{\mathrm{CH}} + \underset{*}{\mathrm{H}} + \underset{*}{\mathrm{H}} \xrightarrow{\mathrm{C_2H_4(g)}} \mathrm{C_2H_6} \tag{83}$$

(2) Reaction of adsorbed hydrogen removing acetylenic residues and providing surface.

$$\mathrm{H_2} + *\text{-}* \rightarrow 2\underset{*}{\mathrm{H}} \tag{84}$$

$$\underset{*}{\mathrm{CH}}{=}\underset{*}{\mathrm{CH}} + 4\underset{*}{\mathrm{H}} \xrightarrow[\text{slow}]{} \mathrm{C_2H_6} + *\text{-}* \tag{85}$$

(3) Reaction of chemisorbed hydrogen with gas phase ethylene

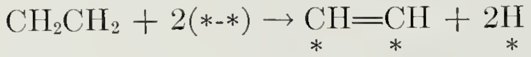
$$\mathrm{H_2} + *\text{-}* \rightarrow \underset{*-*}{\mathrm{H\ H}} \tag{86}$$

$$\mathrm{CH_2{=}CH_2(g)} + \underset{*-*}{\mathrm{H\ H}} \xrightarrow[\text{fast}]{} \mathrm{C_2H_6} + *\text{-}* \tag{87}$$

Beeck's Revised Mechanism. In a later paper Beeck[21] modified the above scheme somewhat. In this mechanism, the fast process is still the reaction of ethylene from the gas with adsorbed hydrogen. Instead of removal of acetylenic complexes, the rate controlling process is assumed to be removal of chemisorbed ethylene by reaction with chemisorbed hydrogen. Some acetylenic residues are formed but these are limited to areas where four adjacent sites are empty, two for the acetylenic residue and two for the hydrogen atoms. Thus, the initial step of poisoning now is the chemisorption of ethylene. The rate of reaction will be proportional to the surface not covered by such adsorbed ethylene and to the pressure of ethylene in the gas phase. The same kinetic expression as given above, therefore, still applies. However, the formulation of the reaction would now be:

(1) Initial poisoning of the surface and adsorption of ethylene:

(88)



$$CH_2CH_2 + 2(\ast\text{-}\ast) \rightarrow \underset{\ast}{CH}{=}\underset{\ast}{CH} + 2\underset{\ast}{H} \tag{88}$$

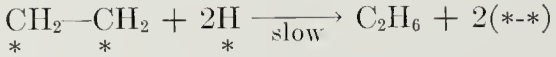
(89)

$$CH_2{=}CH_2 + \ast\text{-}\ast \rightarrow \underset{\ast}{CH_2}{-}\underset{\ast}{CH_2} \tag{89}$$

(2) Removal of adsorbed ethylene:

$$H_2 + \ast\text{-}\ast \rightarrow 2H \tag{90}$$

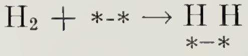
(91)



$$\underset{\ast}{CH_2}{-}\underset{\ast}{CH_2} + 2\underset{\ast}{H} \xrightarrow[\text{slow}]{} C_2H_6 + 2(\ast\text{-}\ast) \tag{91}$$

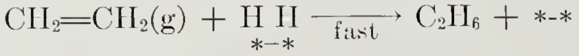
(3) Reaction of gas phase ethylene with adsorbed hydrogen:

(92)



$$H_2 + \ast\text{-}\ast \rightarrow \underset{\ast-\ast}{H\ H} \tag{92}$$

(93)



$$CH_2{=}CH_2(g) + \underset{\ast-\ast}{H\ H} \xrightarrow[\text{fast}]{} C_2H_6 + \ast\text{-}\ast \tag{93}$$

Because of the high heat of adsorption of ethylene on tungsten, and probably also tantalum, the original mechanism is retained. The poisoning by acetylenic residues proceeds to a point where four adjacent sites are no longer available, and the available surface remains constant. The rate is no longer controlled by removal of adsorbed ethylene, but primarily by the fast reaction of ethylene in the gas phase with the small amount of adsorbed hydrogen. The low activation energy of 2.5 kcal for tungsten as compared to 10.7 kcal for nickel is explained by this mechanism.

Intermediate cases, undoubtedly occur and the difference between oriented and unoriented films of nickel may be due to a greater tendency of unoriented films to form acetylenic complexes because of the higher metal atom density in these surfaces. When different metals are compared, it is seen that rhodium which has (a) the lowest heat of adsorption of ethylene,

(b) the least formation of polymers, and (c) the fastest removal of preadsorbed ethylene, has the greatest rate of hydrogenation. Plots of the logarithm of the first order constants against either the heat of adsorption of ethylene or heat of adsorption of hydrogen gave smooth curves in which the lower heats of adsorption had the greater activity.

Curves were also given correlating heats of adsorption and rates of reaction with such parameters as per cent d-character of the metallic bonds and the lattice spacing. A straight line relationship was obtained between the logarithm of the rate constant and the valence times the per cent d-character according to Pauling. Chromium did not fall on this curve or the curve for activity with respect to lattice spacing. According to Beeck's conclusions, two factors must be considered, nature of the chemical bonds between the adsorbate and adsorbent and geometric or electronic configuration which is reflected by the crystal parameters of the metals. The first is usually the more important consideration, but when different planes of the same metal are compared, the geometrical factors outweigh the purely chemical factors. In this case, Beeck considers the differences in binding of the adsorbate arise primarily from differences in crystal geometry.

Other Reactions on Metal Films. In addition to reactions of ethylene, Beeck and his co-workers[20, 21, 26] discussed some of their results on other systems, including the hydrogenation of benzene and acetylene, the dehydrogenation of cyclohexane, and the cracking of ethane.

Oriented films of nickel were only 1.24 times more active than the unoriented ones for hydrogenation of benzene at 58°C. The pressure dependencies were rate $\sim p^{0}_{C_6H_6} p^{0.44}_{H_2}$ and the activation energy was 8.7 kcal. The rates were low, of the order of 1 mm pressure decrease per minute for a benzene-hydrogen ratio of 1:3 at an initial total pressure of 240 mm. Nickel films were 2.3 times more active than iron under comparable conditions. Because of the zero order dependence on benzene they concluded that the hydrogenation proceeded through an adsorbed state of benzene. Recent studies on the interaction of benzene and deuterium on metal films will be described in a later section (p. 366).

Experiments on acetylene hydrogenation gave the following results: Iron and tungsten were inactive at 23°C; nickel was 200 to 1000 times less active than for hydrogenation of ethylene; rhodium and platinum were 10 times more active than nickel; and palladium was 20 times more active than nickel. The maximum occurs for palladium rather than for rhodium as found for ethylene hydrogenation. Activation energies for all four metals were between 6 and 7 kcal. In mixtures of acetylene and ethylene, selective hydrogenation of acetylene occurs.

Unoriented films of platinum at 325°C were 10 times more active for the dehydrogenation of cyclohexane than the partially oriented ones. This is the opposite of the relative activities for hydrogenation of ethylene. It was explained on geometrical grounds following the multiple adsorption hypothesis of Balandin[7, 8, 225] according to which simultaneous removal of 6 hydrogen atoms of cyclohexane is facilitated by the 111 planes of the face-centered cubic metal lattices. The unoriented films have more of these planes available which could account for their increased activity. During the initial stages of the reaction, it is first order in cyclohexane with an activation energy of 9.3 kcal but adsorption of benzene progressively poisons the catalyst. The initial rate for the second run on the same catalyst was 20 times slower. Palladium was active but tungsten was inactive for the dehydrogenation. Nickel and iron sintered too much for use at these temperatures.

When ethane is admitted to nickel films at 200 to 250°C cracking occurs but the rate decreases rapidly to zero. With equal molar mixtures of ethane and hydrogen, methane is formed with zero order and an activation energy of 48.4 kcal: $C_2H_6 + H_2 \rightarrow 2CH_4$. This reaction is 6 times faster on oriented than on unoriented films, and on rhodium it is 60,000 times faster than on unoriented nickel. Residues formed on the films at 225°C by ethane can be removed by addition of hydrogen at this temperature but not at 23°C. Methane is the principal product and this forms more rapidly from residues on rhodium.

The zero order dependence arises because the rate controlling step is the formation of methane on the surface from radicals produced from ethane. The high activation energy (48 kcal) for hydrogenation of these radicals is about five times greater than that for removal of adsorbed ethylene by hydrogenation. This indicated to Beeck that, during hydrogenation, ethylene is not adsorbed as a strongly held radical but instead it forms weaker partial bonds only. Similar conclusions were reached for the residues from the adsorption of ethylene, because here too, the acetylenic complexes behaved chemically different from adsorbed acetylene.

SELECTIVE HYDROGENATIONS—ACETYLENE REACTIONS

Selectivity of Nickel Catalysts for Ethylene and Ethane Formation. Actually the reactions of hydrogen or deuterium with acetylene are not always as simple as the formation of ethylene followed by further hydrogenation to ethane. During the formation of ethylene, ethane as well as higher hydrocarbons is frequently produced. The reactions occur in the presence of hydrogen at temperatures where acetylene alone does not polymerize or decompose. The "yield" of C_2 hydrocarbons and the "selectivity" for the formation of ethylene with respect to ethane varies considerably with the nature of the catalyst, the pressures of hydrogen and acetylene, and the temperature. These reactions have been studied rather thoroughly recently by Sheridan and his co-workers[35, 37, 39, 205-210] and by others[21, 58, 62, 129, 216, 222, 242]. Sheridan's papers, the review by Campbell and Campbell[49] and a number of books[30, 33, 54, 172] may be consulted for further references.

At 70° on a nickel catalyst supported on pumice[58, 205], the over-all initial rate law was $-dp/dt = k\ (H_2)(C_2H_2)^0$. However, under some conditions[58] the rate depended on $(H_2)(C_2H_2)^{-0.5}$ indicating inhibition by acetylene. The "selectivity" for formation of ethylene as compared to formation of ethane was 5 for equal molar mixtures at 80°, but a greater percentage of ethane was formed with increasing hydrogen pressure and increasing temperature. Yields of C_2 hydrocarbons varied from 65 per cent at 0° to 31 per cent at 126° with an activation energy of 10.9 kcal/mole. With excess hydrogen, the rate of hydrogenation of the ethylene after the acetylene has disappeared may be faster or slower than that of acetylene. This depends upon the temperature as would be predicted from the activation energies.

Mechanisms for Acetylene Reactions. The mechanisms proposed by Sheridan[206] for the polymerization of acetylene on a nickel catalyst supported on pumice are based on surface chain reactions initiated through a half-hydrogenated state of the associatively chemisorbed acetylene. He also discussed this mechanism in relation to the geometry of the catalyst and the stereochemistry of the reactants and products. He supports a mechanism for formation of ethylene through simultaneous addition of two atoms of the same weakly adsorbed hydrogen molecule to strongly adsorbed acetylene. This is similar to the mechanism suggested by Farkas and Farkas[82] in that it involves simultaneous addition of atoms from the same hydrogen molecule but it is nearer that suggested by Twigg and Rideal[186, 240] in which weakly adsorbed hydrogen is involved (see p. 292).

Acetylene Reactions on Other Metal Catalysts. Results similar to those on nickel were obtained for platinum[208] and palladium[209]. For platinum, the initial rate law was $-dp/dt = (H_2)(C_2H_2)^{-0.7}$ with a selectivity less than for nickel, but yields of C_2 products up to 70 to 80 per cent at 150°C. Palladium gave a similar initial rate law, but a selectivity of a factor of ten for formation of ethylene as compared to ethane. Other metal catalysts including iron, rhodium and iridium catalyzed the reactions in the order Pd > Pt > Ni > Rh. Iron, cobalt and iridium are weakly active and ruthenium and osmium are almost inactive. Copper promoted the formation of cuprene with excess acetylene, but with excess hydrogen it showed high selectivity for formation of ethylene and ethane. In general the orders with respect to pressures were similar for Pd, Pt, Ni, Rh, Fe, Ir and indicated strong adsorption for acetylene. Activation energies are all in the range 11 to 16 kcal indicating general similarity of mechanism. Beeck[21] also reported constant energies of activation for evaporated films of Pd, Pt, Ni and Rh but all were considerably lower (6–7 kcal). The relation of these reactions to structure, interatomic distances and d-character were also discussed by Sheridan[209] (see also p. 383). The work of Beeck[21] and of Douglas and Rabinovich[62] on the reactions of acetylene with deuterium will be reviewed later (pp. 315, 361, and 384).

Reactions of Methylacetylene. Methylacetylene[35] on nickel, platinum and palladium showed dependencies on pressures similar to those of acetylene, but the activation energies were somewhat higher. Selectivities for formation of the olefin were up to 14 at 90° on Ni. The yields of C_3 hydrocarbons were up to 87 per cent, compared to 40 to 50 per cent of C_2 hydrocarbons for acetylene. These results are explained as being due to the effect of the methyl group on the tightness of packing on the surface. Hydrogenation of mixtures of acetylene and methylacetylene showed that acetylene was more strongly adsorbed on both nickel and platinum catalysts[36, 37, 39]. They arrived at a figure of 1.5 for the ratio on nickel from studies on the exchange reaction between C_2D_2 and $CH_3C{\equiv}CH$. These experiments will be described in more detail later (p. 320).

STEREOCHEMICAL ADDITIONS

Cis-Addition to Acetylene Derivatives. Greenhalgh and Polanyi[111], as already discussed p. 288), have pointed out that *cis*-addition to acetylene derivatives was not proof of the simultaneous addition of a pair of hydrogen atoms, and that *cis*-addition can be explained on the basis of associative adsorption and formation of the half-hydrogenated state.

Campbell and Campbell[49] published an exhaustive review of catalytic reductions of carbon-carbon multiple bonds by chemical, electrolytic and catalytic means including problems of stereochemical addition. The reduction of acetylene compounds is also reviewed by Johnson[129]. In his discussions on geometrical isomerism Crombie[57] has referred to recent work on stereochemical addition of hydrogen. These will not be reviewed here because deuterium was not used as a tool in the investigations.

Stereochemical Addition of Deuterium to Aromatic Compounds. Linstead[160] and his co-workers made a rather detailed study of the stereochemistry of catalytic hydrogenations of aromatic ring systems over Adams platinum oxide in acetic acid. Of the nine compounds studied, all hydrogenated *cis* and *syn*. They explained the results using the hypotheses (1) that when one or more aromatic rings are hydrogenated during a single period of adsorption, the hydrogens add to one side of the molecule and further (2) that the orientation during adsorption of the aromatic molecule on the catalyst is affected by steric hindrance between the catalyst and the substituents of the molecule. Although they assumed the Farkas and Farkas mechanism of simultaneous addition of pairs of hydrogen atoms, this does not affect their conclusions because a mechanism via the half-hydrogenated state can lead to the same result, as Greenhalgh and Polanyi[111] have shown.

Stereochemical Reductions of Acetylene. Douglas and Rabinovitch[62] have recently attempted to prepare *cis*-ethylene-d_2 by addition of deuterium to acetylene. They obtained all possible deuteroethylenes at room temperature, but at −80°C they found a preference for the formation of *cis*-ethylene-d_2. Using chromous chloride reduction of DC≡CD, as described by Patterson and DuVigneaud[175], they prepared rather pure *trans*-ethylene-d_2, which was used for measurement of the rate of *cis-trans* isomerization.

Rabinovich and Looney[181] also carried out further miscellaneous experiments on the stereochemical reduction of DC≡CD, $CH_3C{\equiv}CD$, and tolane using a variety of reagents. With zinc and zinc promoted with either copper or with palladium in acid solution, reductions led the *cis*-compounds as did similar magnesium-acid reductions. Magnesium in ammonical ammonium chloride and chromous chloride in acid solution gave the *trans*-compounds. Appreciable exchange occurred during some of the reactions. The formation of *cis*-isomers by zinc-acid reduction is contrary to some previous views[49] on such chemical reductions. It had ordinarily been thought that chemical methods led to the thermodynamically stable isomer. The results of this work indicate that zinc-acid or magnesium-acid reduction behave more like heterogenous catalytic reductions than like the homogeneous reductions with chromous chloride. They also suggest an alternative stereospecific mechanism involving attachment of the acetylenic compound to the zinc metal followed by attack of hydrogen ions in two steps forming the olefin and zinc ions.

They conclude that *trans*-reduction by "chemical" means must also be stereospecific since for dialkyl acetylenes, Campbell and co-workers[49] have obtained 100 per cent yields of *trans*-olefins rather than equilibrium mixtures. Since *trans*-ethylene-d_2 was obtained from reduction with chromous chloride, the authors conclude that thermodynamic properties do not determine the product because the *cis-trans* equilibrium constant for ethylene-d_2 is near unity. They discuss the mechanisms of *trans* addition proposed by Farkas and Farkas[89] and by Greenlee and Fernelius[112, 115] but do not come to any definite conclusions.

It is clear that the hydrogen isotopes add to the information about stereochemical additions, but their use has not as yet completely clarified these complicated reactions.

THE QUESTION OF DISSOCIATIVE PROCESSES WITH UNSATURATED AND SATURATED HYDROCARBONS

Dissociative Adsorption. That dissociative processes do occur with unsaturated and saturated compounds on active catalysts has been well established by H. S. Taylor and his co-workers as well as by others. However, as the following will show, there is not general agreement that exchanges between unsaturated compounds necessarily proceed by a dissociative mechanism.

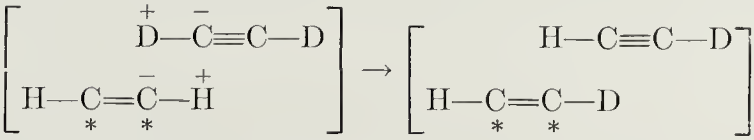
Turkevich and Taylor[235] and Howard and Taylor[127], for example, showed that, in the absence of hydrogen, ethylene gave ethane at 184°C on manganese chromate, at 0°C on active copper, and at 218°C on chromium oxide gel. Marikawa, Trenner and Taylor[171] found ethane as one of the products in the polymerization of ethylene on nickel. In the same series of experiments they also found that ethylene and propylene exchanged with deuterium at temperatures as low as $-80°C$. Exchanges were observed on catalysts under conditions where no activation of C—C or C—H bonds occurred in saturated hydrocarbons. They concluded that the presence of the double bond markedly weakens the C—H bonds so that exchange can occur more readily, possibly by the associative mechanism of Horiuti and Polanyi rather than by the dissociative mechanism.

Beeck[21] has summarized similar work that he and his co-workers have done on the behavior of ethylene and other hydrocarbons on evaporated metal films. When ethylene is slowly admitted to 100 mg of a nickel film at 23°C, they found that the first 0.2 cc-atm. was practically instantaneously and irreversibly adsorbed. When 1.0 cc-atm. had been added, 0.5 cc-atm. of ethane was formed and 0.5 cc-atm. remained on the surface as acetylenic residues. Only dissociation of the ethylene can explain such results. These interesting experiments were discussed more fully in an earlier section (312).

Exchange Between Unsaturated Hydrocarbons. Often cited against the dissociative mechanism of exchange for unsaturated compounds are the experiments of Conn and Twigg[52] in which they failed to detect exchange between C_2H_4 and C_2D_4 on a nickel wire under conditions where exchange between C_2H_4 and D_2 is rapid. Farkas[83] has suggested that these negative results arise because the concentration of H-atoms on the surface was low owing to reaction with ethylene. In this case, the rate controlling step in the exchange would be $\underset{*}{C_2H_3} + \underset{*}{D} \rightarrow C_2H_3D$ rather than $(C_2H_4)_{ads} \rightarrow \underset{*}{C_2H_3} + \underset{*}{H}$. Since the time of the experiments of Conn and Twigg, the exchange between two unsaturated hydrocarbons has been observed in a number of cases. Aman, Farkas and Farkas[1], for example, found that deuterobutene exchanged slowly (half period about 40 hrs) with ethylene on palladium and nickel catalysts.

Bond, Sheridan and Wiffen[39] studied the exchange between C_2D_2 and C_2H_2 and the exchange between C_2D_2 and $CH_3C{\equiv}CH$ on nickel-pumice catalysts at 40 to 120°C using infrared analysis. No exchange was observed in several hours between C_2D_2 and ethylene or allenes, whereas the exchange between C_2D_2 and C_2H_2 reached equilibrium in about 2 hours at 119°C with an equilibrium constant of 3.2. The formation of C_2HD was a first-order reaction and the rate varied as the 0.65 power of the total pressure with an activation energy of 10.7 kcal. The hydrogen attached to the triple-bonded carbon in methyl acetylene exchanged with C_2D_2 under similar conditions with a rate varying as the 0.47 power of the total pressure and an activation energy of 12.3 kcal at 74 to 133°C. From the rates as a function of the initial ratio of the reactants, they deduced as mentioned previously (p. 318), that acetylene was adsorbed 1.5 times more strongly than methylacetylene.

Bond, Sheridan and Wiffen present arguments against a dissociative mechanism for these exchange reactions and suggest one involving an acetylene molecule chemisorbed on the surface by the associative process and a physically adsorbed acetylene molecule:

(94) 

$$\left[\begin{array}{r} \overset{+}{D}-\overset{-}{C}\equiv C-D \\ H-\underset{*}{C}=\underset{*}{\overset{-}{C}}-\overset{+}{H} \end{array}\right] \rightarrow \left[\begin{array}{r} H-C\equiv C-D \\ H-\underset{*}{C}=\underset{*}{C}-D \end{array}\right]$$

Part of the driving force was attributed to the polarization of the C—H bond in acetylene. They cite the non-exchange between C_2D_4 and C_2H_4 reported by Conn and Twigg[52] as support for this mechanism because the C—H bond in ethylene is supposed to have no dipole[105].

Douglas and Rabinovitch[62], using mass spectrometric and infrared analysis, have found that exchange does occur between C_2H_4 and C_2D_4 in contrast to the results of Conn and Twigg. Similarly, they found exchange between C_2H_2 and C_2D_2. Thus, the arguments with respect to the significance of polarity may be doubtful. They found, for example, over 50 per cent exchange between C_2D_4 and C_2H_4 on a supported nickel catalyst at room temperature in 2 minutes and 90 per cent exchange on a nickel wire at 300°C in 3 hours. In 2 minutes on the supported nickel catalyst, 13 per cent exchange between C_2H_2 and C_2D_2 was observed at room temperature. They explain the results on the basis of the dissociative mechanism and suggest that the negative results of Conn and Twigg may have been due to poisoning of the relatively small surface of their nickel wire. The slowness of the exchange compared to addition, they suggest, results from relatively greater poisoning of the surface in the absence of hydrogen and reduction of the D-atom concentration in the surface because of simultaneous self-hydrogenation as observed by Beeck[21].

Bond and Turkevich[40] found that C_3H_6 and C_3D_6 on a platinum catalyst supported on pumice did not exchange in 11 minutes at 18°C. However when 3 mm of D_2 was present with 13 mm of approximately equal molar mixture of C_3H_6 and C_3D_6, propylenes with all possible deuterium contents were present. Propylenes other than those originally present constituted 20 per cent of the whole after 23 per cent of the possible addition had taken place. The deuterium content of the propylenes rose from 51.8 to 54.9 per cent. With excess deuterium, addition proceeded much faster than equilibration between the propylenes. The catalysis of the exchange between C_3H_6 and C_3D_6 by hydrogen or deuterium is explained in terms of the associative rather than the dissociative mechanism (see p. 345). This raises the question as to whether residual hydrogen on the catalysts used by Douglas and Rabinovitch[62] may not have been responsible for the rapid exchange reactions they observed, although Douglas and Rabinovitch do give arguments against this being the case.

The question as to whether or not the dissociative mechanism is the principal one operating in exchanges between light and heavy unsaturated compounds is apparently not settled. It is clear, however, that under certain conditions dissociative processes ean occur.

DEUTERIUM EXCHANGE WITH SATURATED HYDROCARBONS ON HYDROGENATION CATALYSTS

Methane Exchange. There seems to be little disagreement about a dissociative mechanism for the exchange of saturated hydrocarbons. In the experiments by Morikawa, Benedict, Trenner and Taylor[168-171] CH_4 was found to undergo exchange with D_2, CD_4 and D_2O on active nickel catalysts at 140°C and higher. At 184°C the rates of exchange were in the order $CD_4 > D_2 > D_2O$. Activation energies were approximately 19 kcal for the $CH_4—D_2$ exchange. The lower rate for the latter reaction was ascribed to the preferential adsorption of deuterium which thereby monopolized the surface. Similar exchanges ($CH_4—CD_4$) were also observed on alumina-silica cracking catalysts at 300°C which is below temperatures used for cracking and dehydrogenation[217].

Ethane and Other Hydrocarbons. With ethane and deuterium, on active nickel catalysts, two reactions occurred. One involved breaking of C—H bonds leading to exchange, and the other involved a breaking of C—C bonds leading to formation of methane:

$$C_2H_6 + D_2 \rightarrow C_2H_5D + HD \quad (110\text{–}138°C) \tag{95}$$

$$C_2H_6 + D_2 \rightarrow 2CH_3D \quad (150\text{–}184°C) \tag{96}$$

The breaking of the stronger C—H bond (97 kcal) occurs at a relatively lower temperature than the breaking of the C—C bonds (85 kcal). Both reactions are inhibited by deuterium, because it is adsorbed so much more strongly than the saturated hydrocarbons. It was suggested that the dissociative adsorption of the hydrocarbon through breaking of the carbon-hydrogen bonds is the mechanism of attachment of the hydrocarbon to the surface. Removal of two hydrogen atoms from adjacent carbon atoms establishes two carbon-metal linkages with the breaking of the carbon-carbon bond. These reactions have been studied more completely recently by Kemball and Taylor[142] using mass spectrometric analysis. In the presence of hydrogen the rate of ethane decomposition was proportional to $p_{C_2H_6}^{0.7}p_{H_2}^{-1.2}$, with an energy of activation of 52 kcal per mole. At low ratios of H_2 to C_2H_6, the rate depended on a high negative power of the hydrogen pressure which was ascribed to heterogeneity of the surface. Ethane alone decomposed with a rate dependent on $p_{C_2H_6}^{0.7}$ and an activation energy of 40 kcal per mole. The rate of formation of methane from ethylene was greater than from ethane indicating the formation of ethylene on the surface during decomposition of ethane followed by breaking of the C—C bond.

A study of the exchange rates for a series of saturated hydrocarbons on an active platinum catalyst was made by Farkas and Farkas[94, 95]. These results, as discussed in an earlier section, (p. 268) showed the rates to be in the order $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10} < C_6H_{14}$.

Exchange between CH_4 and CD_4. Wright and Taylor[253] re-examined the interaction of CD_4 and CH_4 on a nickel-chromia catalyst using a mass spectrometer to identify the products of the reactions. The kinetic data showed a first order dependence for the disappearance of CD_4 and for the appearance of CHD_3 and CHD_2 on the surface. The activation energy for the disappearance of CD_4 in its reaction with CH_4 was 20.9 kcal between 100 and 225°C. On twenty cylindrical pellets weighing 0.9 g with a gas volume of 44 cc and a temperature of 160°C, the per cent approach to equilibrium in one experiment, for example, was 83 per cent in 139 hours. At 98.5°C the initial rates of formation of CD_3H and CD_2H_2 showed that CD_3H formed more rapidly than CD_2H_2 in agreement with an assumption of consecutive reactions: $CD_4 \rightarrow CD_3H \rightarrow CD_2H_2$. They conclude that the desorption step $\underset{*}{CD_3} + \underset{*}{H} \rightarrow CD_3H$ is slower than the dissociation step $CD_4 \rightarrow \underset{*}{CD_3} + \underset{*}{D}$, the former controlling the rate of formation of CD_3H and the latter the disappearance of CD_4.

The reaction of hydrogen with the surface residues after an exchange reaction indicated that all possible fragments were present, CD_3, CD_2, CD and C including the corresponding ones with hydrogen in the place of deuterium. Increasing the temperature by steps showed sharp increases in the rate and quantity of products obtained. The results of this work again give strong evidence for dissociative mechanisms for the saturated hydrocarbons.

Exchanges of Saturated Hydrocarbons on Fischer-Tropsch Catalysts. Further experiments by Thompson, Turkevich and Irsa[221] on the exchange reactions between deuterium and saturated hydrocarbons on a Fischer-Tropsch catalyst show again how powerful the use of deuterium along with the mass spectrometer is in examining the details of reactions on catalysts.

Passing 6 volumes of D_2 and 1 volume of CH_4 at atmospheric pressure over a cobalt-thoria-magnesia catalyst at 183°C showed no exchange at space velocities of 140 to 150 per hour. However, after 17 hours of contact time, the products were 1.7% CD_4, 0.1% CD_3H, 0% CD_2H_2, 9% CH_3D and 89% CH_4. The 1.7% CD_4 and 9% CH_3D indicated two processes were occurring which they explained as follows: Methane dissociates on the surface as $\underset{*}{CH_3}$ and $\underset{*}{H}$ and on desorption from the large pool of $\underset{*}{D}$ on the surface becomes CH_3D. The CD_4 must arise from the rupture of all four C—H bonds followed by reaction with four adsorbed D atoms. Alternatively they suggest that there may be two types of sites, one on which the CH_4 is dissociated and remains for so short a time that only one C—H bond is broken. On the other type of center $\underset{*}{CH_3}$ is so strongly adsorbed that it exchanges several times with the large pool of D before being desorbed as CD_4.

In studies on iron Fischer-Tropsch catalysts, Browning, DeWitt and Emmett[44a] determined the equilibrium constant for the reaction

$$CH_4 + 2Fe \rightleftharpoons Fe_2C + 2H_2$$

and obtained values from 2×10^{-4} at 300°C to 1.3×10^{-3} at 350°C. These results support the idea that CD_4 might be formed by the complete dissociation of methane. Kummer and Emmett[153a] had also studied the behavior of methane on iron and cobalt Fischer-Tropsch catalysts using radioactive carbon as a tracer. It was found that the radioactive carbide on the catalysts was not a significant intermediate in the formation of higher hydrocarbons. Furthermore, carbon from radioactive methane in the synthesis gas did not appear in the higher hydrocarbons. On the other hand, radioactive carbon from ethanol and propanol appeared in one third to one half of the hydrocarbons containing from 2 to 10 carbon atoms[152a, 152b].

Thompson, Turkevich and Irsa[221], found the rate of exchange of CH_4 with CD_4 was about the same order of magnitude as that between CH_4 and D_2. After 22 hrs a mixture of 58% CH_4 and 42% CD_4 at 183°C. yielded 38.6% CD_4; 3.8% CD_3H; 0.0% CD_2H_2; 1.9% CDH_3 and 55.8% CH_4. The low yield of CD_2H_2 indicated that complete dissociation of CH_4 and CD_4 did not occur to an appreciable extent, because one would then expect a higher yield of CD_2H_2. This was taken as evidence, that during its lifetime on a surface relatively free of hydrogen or deuterium, CH_4 is present predominately as $\underset{*}{CH_3}$ and $\underset{*}{H}$, but in the presence of an excess of hydrogen it is present as $\underset{*}{CH_3}$, $\underset{*}{C}$ and $\underset{*}{H}$. It seems, however, on the basis of their alternative mechanism mentioned above, the higher concentration of $\underset{*}{D}$ on the surface might produce more exchanges before the $\underset{*}{CH_3}$ unites with $\underset{*}{D}$ and desorbs.

Under Fischer-Tropsch synthesis conditions of 183° and space velocities of 140 to 150 per hour, one volume of ethane with 6 volumes of deuterium at atmospheric pressure underwent 6.1 per cent exchange. The products were: 2.4% C_2D_6; 0.4% C_2D_5H; 0% $C_2D_4H_2$; 0.3% $C_2D_3H_3$; 2.7% $C_2D_2H_4$, 0.0% C_2H_5D and 93.9% C_2H_6. The large proportion of C_2D_6 is probably due to a process similar to that for methane and the high percentage of $C_2D_2H_4$ is due to the stability of the $\underset{*}{H_2C}—\underset{*}{CH_2}$ on the surface. One per cent of the original ethane underwent fission of the C—C bonds to produce methanes consisting of: 41% CD_4; 10% CD_3H, 0% CD_2H_2, 49% CH_3D and 0% CH_4.

Propane underwent similar exchanges forming 4% C_3D_8 and 1.4% C_3D_7H but no C_3H_7D to $C_3D_6H_2$. This indicated complete rupture of all C—H bonds or very rapid exchange of some of the adsorbed propane with deuterium. Methane (1–2%) but no ethane was observed. N-Butane underwent extensive exchange (42.5%) forming the more highly deuterated molecules but none with one to four deuterium atoms per molecule. Increasing the space velocity from 150 to 750 per hour dropped the exchange to 8.7 per cent giving only butanes with 8, 9, and 10 deuterium atoms while at 3000 per hour only a little exchange occurred with C_4D_{10} as the principal product. Isobutane similarly formed the more highly deuterated molecules at the higher space velocities. No ethane or propane was formed and the only degradation product was methane.

Thus, the authors[221] conclude that, on a Fischer-Tropsch cobalt catalyst, methane is relatively stable toward exchange with deuterium, ethane and propane less so and the butanes undergo rather extensive exchange. One formulation on the basis of radicals leads them to conclude that methane furnishes $\underset{*}{CH_3}$ and $\underset{*}{C}$ radicals; ethane, $\underset{*}{C_2H_4}$ and $\underset{*}{C_2}$ radicals; propane, $\underset{*}{C_3}$ radicals, and butane, $\underset{*}{C_4}$ radicals. Their alternative formulation seems attractive in which it is assumed that the methyl, ethyl, propyl and butyl radicals have a mean life on the surface long compared to the rate of exchange of individual C—H bonds so that most of the hydrogens exchange before the alkyl groups desorb as alkanes.

Exchange of Methane on Nickel Films. Simultaneous with the work of Thompson, Turkevich and Irsa[221], Kemball studied the interaction of methane with deuterium on nickel films and later extended his work to other hydrocarbons on films of several metals[2, 137, 139, 140].

In Kemball's experiments[137] on the reaction between deuterium and methane on evaporated nickel films at 206 to 255°C, the mass spectrometric analysis of the products showed that the initial rates of formation of products were in the order $CD_4 > CHD_3 > CH_3D > CH_2D_2$. At 230°C, for example, with 4.82 mm of D_2 and 3.26 mm of CH_4, the relative rates were 12.4, 3.7, 2.8 and 0.17 all in mm $\times\ 10^4$/min/mg of catalyst.

The activation energy for the formation of CH_3D was 24 kcal and the initial rate varied as $p_{CH_4}p_{D_2}^{-1/2}$. However, the activation energies for the formation of CD_4, CHD_3 and CH_2D_2 were all about 32 kcal with the rate dependent upon $p_{CH_4}p_{D_2}^{-1}$. The entropy of activation was also greater by 16 entropy units for the latter reactions. This he assumes accounts in part for the fact that, with 4.85 mm of D_2 and 3.26 mm of CH_4 at 227°C, the rate of formation of the sum of the three products (CD_4, CHD_3, CH_2D_2) was 5.7 times greater than the formation of CH_3D even though the activation energy of their formation was greater by 8 kcal.

The above results gave evidence that two types of reactions were taking place which he formulated as follows:

(97) $$\text{Type I: } \underset{*}{\overset{CH_4}{\vdots}} + \underset{*}{D} \rightarrow \underset{*}{CH_3} + \underset{*}{\overset{HD}{\vdots}}$$

(98) $$\text{Type II: } \underset{*}{\overset{CH_4}{\vdots}} + \underset{*-*}{DD} \rightarrow \underset{*-*}{CH_2} + 2HD$$

(99) $$\underset{*\ *}{CH_2} + \underset{*}{D} \rightarrow \underset{*}{CH} + \underset{*}{H} + \underset{*}{D} \rightarrow \underset{*\ *}{CHD} + \underset{*}{H}$$

The relative rates for the formation of the heavier methanes could be accounted for by assuming that methane leaving the surface after a type II reaction had a random collection of hydrogen and deuterium atoms. Increasing the deuterium pressure increased the amount of CD_4 relative to CHD_3 and $C_2H_2D_2$ as expected from this assumption. The results of this work on nickel is similar in some respects to those obtained by Thompson, Turkevich and Irsa[221] on a cobalt-thoria catalyst as described previously, but the mechanisms suggested are somewhat different.

Adsorption measurements for Kemball's films showed that, at 0°C, about 0.05 cc atmospheres (6.8×10^{18} molecules) of D_2 was adsorbed instantaneously per 100 mg of the nickel film with no further increase as the pressure was increased from 0.02 to 0.2 mm. No observable quantity of methane was adsorbed under the same conditions. However, at about 170°C, the mass spectrometer showed a slow decrease in the concentration of CH_4 as the total pressure rose, presumably due to formation of hydrogen. Measurements of the initial rates of this dissociative adsorption of methane at a series of temperatures gave an activation energy of adsorption of 11 kcal.

At 180°, the half-time of the reaction was of the order of 25 to 30 min. per 10 mg of catalyst and the quantity of methane that disappeared from the gas phase to form hydrocarbon radicals and carbide on the surface was about one-fifth that for deuterium at 0°C.

Exchange of Methane on Other Metal Films. In a later paper Kemball[139] compared the reaction of methane and deuterium on films of rhodium, platinum, palladium, tungsten and iron. He gave a detailed discussion of methods of calculating the rates, activation energies and frequency factors for type I and type II reactions based on different assumed mechanisms. Iron was inactive up to 420°C, but, on all of the other metals, there was evidence of two different mechanisms as had been found for nickel. Rhodium like nickel gave a high ratio of CD_4 to CH_3D, whereas with tungsten, palladium and platinum the rate of formation of CH_3D was higher than the rate formation of CD_4. The initial ratio of the rates of formation of the higher deuterated species were always closely related with the ratio of CD_4 to CHD_3, varying as shown in Table 6. The pressure dependencies, activation energies, and frequency factors for type I and type II reactions can be compared from the results recorded in Tables 6 and 7.

TABLE 6. PRESSURE DEPENDENCIES, ACTIVATION ENERGIES, AND FREQUENCY FACTORS FOR TYPE I REACTION. RATIOS OF RATES OF FORMATION OF CD_4 AND CHD_3 WITH EQUAL PRESSURES WHERE $r_I = kP_{CH_4}{}^a P_{D_2}{}^b$ [139]

Catalyst	a	b	CD_4 rate/ CHD_3 rate	E_I kcal/ mole	log A_I	Temp. Range
Ni	1.0	−0.5	3.3	23.8	24.2	206–255°C
Rh	1.0	−0.5	3.1	20.0	24.4	138–217°C
W	0.6	−0.4	1.5	8.9	19.3	92–174
Pt	0.4	−0.2	1.3	20.8	24.3	159–275
Pd	0.3	−0.1	1.0	22.0	24.6	243–308

TABLE 7. PRESSURE DEPENDENCIES, ENERGIES OF ACTIVATION AND FREQUENCY FACTORS FOR TYPE II REACTION WHERE $r_{II} = kP_{CH_4}{}^a P_{D_2}{}^b$ [139]

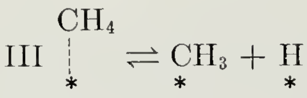
Catalyst	*a*	*b*	E_{II} kcal mole	log A_{II}	Temp. range
Ni	1.0	−1.0	29.4	27.3	206–255°C
Rh	1.0	−0.9	24.4	27.4	138–217
W	0.8	−0.8	11.3	20.0	92–174
Pt	0.4	−0.7	24.5	25.9	159–275
Pd	0.3	−0.5	34.2	28.6	243–308

Mechanism of Methane Exchange on Metal Films[139]. These results could be explained on the basis of the mechanisms given above if the rate determining step for type I reaction is the adsorption of methane as methyl radical and a hydrogen atom. This rate is equal to the rate of desorption of methyl radicals as methane molecules. The rate of type II reaction is controlled by the rate of adsorption and desorption of methylene radicals.

The change in the orders of reaction for the series Ni, Rh, W, Pt, Pd shows that the relative strength of deuterium adsorption decreases and the strength of adsorption of methane increases in the order listed. This also correlates well with the ratios of the amounts of CD_4 and CHD_3 formed. That is, for stronger adsorption of deuterium by Ni and Rh and consequently higher surface concentration of $\underset{*}{D}$, the chance of forming CD_4 is greater. Similarly the pressure dependence on methane for type I and type II reactions, shows that the same number of methane molecules are involved in each. Also, the nearly constant difference of -0.5 between type I and type II, in dependences on deuterium pressure indicate that the type II reaction involves one less deuterium atom than type I reaction. Orders of reactions in Table 6 are in agreement with the mechanisms if it is assumed that the chance of finding a bare site for Ni and Pt, for example, is proportional to $p_{D_2}^{-0.5}$ and $p_{D_2}^{-0.35}p_{CH_4}^{-0.3}$, respectively.

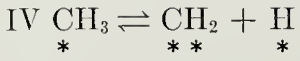
A second formulation (compare with the alternative mechanism suggested by Thompson, Turkevich and Irsa, p. 324) was also considered:

(100)



$$\text{III}\ \underset{*}{\overset{CH_4}{\vdots}} \rightleftharpoons \underset{*}{CH_3} + \underset{*}{H}$$

(101)



$$\text{IV}\ \underset{*}{CH_3} \rightleftharpoons \underset{**}{CH_2} + \underset{*}{H}$$

Reaction (IV) alone will not account for the relative rates of formation of the four deuteromethanes. In order to give a high yield of CD_4, the dissociation and re-combination for reaction (IV) would have to be rapid, in which case little CH_3 would be returned to the gas phase as CH_3D. However, if this dissociation is the slow step for formation of the higher deuterated species, and if the desorption or adsorption of methyl radicals is the slow step in the formation of CH_3D, then Kemball shows that the rates of reactions (III) and (IV) are:

$$r_{\text{III}} = r_{\text{I}} + r_{\text{II}} = x_{CH_4}N_{CH_3} \tag{23}$$

$$r_{\text{IV}} = \frac{r_{\text{II}}}{r_{\text{I}}}(r_{\text{I}} + r_{\text{II}}) = x_{CH_2}N_{CH_3} \tag{24}$$

Here r_{I} is the rate of return of CH_3D to the gas phase and r_{II} is the rate of return of the higher deuterated species. x_{CH_4} is the probability that a CH_3 radical will be returned to the gas phase as a methane molecule; x_{CH_2} is the probability that a CH_3 radical will dissociate into a methylene radical in unit time; and N_{CH_3} is the number of methyl radicals. A second set of activation energies, frequency factors and pressure dependencies were tabulated for this mechanism. The orders of the reaction were in agreement with these mechanisms provided the chances of finding a bare site on nickel and platinum, for example, are proportional to $p_{D_2}^{-0.45}$ and $P_{D_2}^{-0.175}p_{CH_4}^{-0.275}$, respectively. Since reaction (IV) requires a methyl radical and two bare sites, its rate depends on

$$(p_{CH_4}p_{D_2}^{-0.5})(p_{D_2}^{-0.175}p_{CH_4}^{-0.375})^2 = p_{CH_4}^{0.45}p_{D_2}^{-0.85} \tag{25}$$

It was concluded that more precise measurements of rates as a function of temperature, pressure, and extent of adsorptions would be needed to decide which of the two formulations is the better and which set of activation energies and frequency factors were the correct ones. If methylene radicals are formed both by direct adsorption of methane and dissociation of methyl radicals (reactions II and IV), the values would be intermediate between the two sets. By either formulation, however, activation energies were in all cases higher for formation of the more highly deuterated species than for CH_3D. This arises because the heat of adsorption of a deuterium atom is included. Some correlation with lattice parameters could be made for the formation CH_3D but not for the formation of the other species. The low value of the activation energy for both types of reactions on tungsten was attributed to the ease of adsorption of methane on tungsten at 0°C whereas adsorption on nickel occurred only above 100°C and then with an activation energy of 11 kcal.

It is well known that the apparent activation energy will be increased by an amount equivalent to the heat of adsorption of a strongly adsorbed inhibiting gas, but Kemball also derives an expression for its influence on the frequency factor following the treatment by Everett[75]. In this work it was shown that entropies and heats of adsorption were often related in a linear manner. Where this relationship is valid, there is a linear relationship between the logarithm of the frequency factor and the energy of activation, as is often found in catalytic reactions. Under Kemball's experimental conditions 5×10^{23} molecules per second strike 100 cm^2 of surface, but, with the exception of tungsten, the frequency factors are all greater than 10^{24}. This he explains as being due to an enhancement of the frequency factor by an inhibiting gas. For the metals showing the greatest differences between the activation energies there is also the greatest difference between the frequency factors, which is in qualitative agreement with the above relationship. Markham, Wall and Laidler[163] have discussed Kemball's results and have derived some kinetic equations based on a proposed mechanism, but no experimental work was reported.

Exchange of Ethane on Metal Films. Ethane exchange with deuterium was studied in a similar manner by Anderson and Kemball[2] over evaporated films of a number of metals. The results are summarized in Table 8. All values relating to the effect of temperature were obtained in a 180 ml reaction vessel with an 8 fold excess of deuterium except for tungsten where a 4-fold excess was used. The pressures of ethane were from 2.3 to 2.9 mm. Values of A are in molecules per second per 10 mg of the metal and M is the mean number of deuterium atoms reacting per ethane molecule.

Ethanes with deuterium atoms from one to six were obtained. The initial distribution of deuterium atoms as measured by the ratio of molecules with six deuterium atoms to whose with one deuterium (D_6/D_1) fall into three groups: (1) principal product C_2H_5D (W, Mo, Ta); (2) principal product C_2H_5D and C_6D_6 (Zr, Cr, V, Ni (high temp), Pt); (3) principal product C_2D_6 (Pd, Rh, Co). Manganese, silver and iron were inactive up to 370°C, but iron did produce some highly deuterated methane from 310–365 as expected from the studies of Browning, DeWitt and Emmett[44a] on equilibria in such systems as $Fe - Fe_2C—CH_4—H_2$. Cobalt showed simultaneous cracking and exchange at 300°C, the main product of the cracking being CD_4 .

TABLE 8. REACTION RATES, ACTIVATION ENERGIES, AND FREQUENCY FACTORS FOR EXCHANGE OF ETHANE WITH DEUTERIUM[2]

Catalyst	Temp. Range	Temp. where *ke* = 1%/min. 10 mg.	*E kcal.*	log *A*	D_6/D_1	M
W	−80–29°C	−54°C	8.2	23.7	0.008	1.3
Mo	−50–0°	−12°	7.0	21.5	0.0	1.16
Ta	−94–0°	−14°	7.8	21.9	0.0	1.15
Zr	158–192	145	15.4	23.5	0.27	2.3
Cr	149–215	136	13.9	23.4	0.32	2.5
V	102–160	125	20.7	26.8	0.35	2.6
Ni (high temp.)	162–195	192	18.0	23.8	0.75	3.1
Ni (low temp.)	0–75	—	6.5 to 2	—	0.03	1.3
Ni (oriented)	0–75	—	6.5 to 2	—	0.0	1.05
Pt	134–192	142	12.5	22.3	1.3	3.5
Pd	145–207	177	21.4	25.8	10.4	4.8
Rh	0–70	26	11.7	24.0	13.4	5.0
Co	—	—	—	—	15	—

Significant exchange rates for unoriented films of nickel (approx. 10 mg) occurred only above 160°C and this was accompanied by cracking to methanes with a distribution of 0 to 4 deuterium atoms. With heavier unoriented films or with oriented nickel films similar to those prepared by Beeck, Smith and Wheeler[28], the exchange proceeded in the temperature range 0 to 75°C. However, the activation energy fell from 6.5 kcal at 0 to

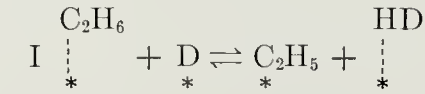
25°C to 2 kcal at 50 to 75°C. This behavior was explained by a shift in equilibrium between adsorbed species on the surface, possibly involving adsorbed ethylenic or acetylenic residues. Twigg[239] suggested that a similar phenomenon in the hydrogenation of ethylene was due to a shift in the equilibrium between adsorbed ethyl radicals and ethylene.

For tungsten, rhodium, and palladium the pressure dependencies were respectively $p_{C_2H_6}^{0.1}p_{D_2}^{0.1}$, $p_{C_2H_6}^{0.8}p_{D_2}^{0.7}$ and $p_{C_2H_6}^{0.9}p_{D_2}^{-0.8}$. Contrary to the results of Beeck[21] on hydrogenation of ethylene where the activation energy for hydrogenation of ethylene was nearly constant, the activation energies for exchange of ethane for Kemball's experiments vary from 7.0 to 21.4 kcal per mole. The lower values are probably associated with a low activation energy of adsorption of ethane. There is a rough proportionality between E and log A as was found for the exchange with methane. No correlation was found between activation energy and crystal structure, except perhaps the three metals (W, Mo and Ta) having low values of E. They have a body-centered cubic structure although others also have this structure. Some correlation between structure and the distribution of deuterium was found. Thus, W, Mo, Ta, Cr and V with body-centered cubic structures have the lower values for the ratio of C_2D_6 to C_2H_5D. The face-centered cubic metals Rh, Pd and Pt have the higher values for the ratio of C_2D_6 to C_2H:D. Nickel was an exception, but comparison of the products from oriented and unoriented nickel films gave some evidence that different crystal faces had different catalytic activities. A high ratio of C_2D_6 to C_2H_5D might be expected for those metals whose surface atoms have spacings that closely fit those of ethane. However, the authors state that considerations of adsorption of an ethylene residue on the various metals as was done by Twigg and Rideal[241] for ethylene shows no correlation with spacing, provided the spacing is somewhere in the range 2.4 to 3.1 Å. Variations in M—M distance is compensated by change in M—C distance and slight twisting of the C—C bond.

Mechanism of Ethane Exchange. The following mechanism is suggested by the authors. There is little doubt that the exchange reaction involves dissociative adsorption of the ethane as suggested by Morikawa, Benedict and Taylor[170] and later by others. However, a simple mechanism involving only the reaction $C_2H_6 \rightleftharpoons \underset{*}{C_2H_5} + \underset{*}{H}$ would lead primarily to C_2H_5D. With Rh, Pd and Pt the principal product is C_2D_6. A mechanism is suggested involving the formation of an ethylene residue followed by reformation of an ethyl radical containing deuterium. This process is then repeated to give the various higher deuterated ethyl radicals which are ultimately desorbed as ethane. Thus, an adsorbed ethyl radical can either (a) desorb as C_2H_5D into the gas phase or (b) adsorb further to give an adsorbed ethylene residue leading to the formation of the more highly deuterated products. The number of deuterium atoms in the molecule will be determined by statistical considerations.

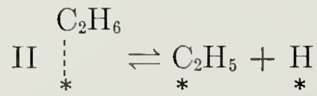
The authors assign a parameter P to the ratio of the chance that (b) will occur to the chance that (a) will occur and discuss its value as a function of temperature pressures, etc. In general, the large values of P have larger values for the ratio of C_2D_6 to C_2H_5D. The general mechanism proposed here is again similar to one of the mechanisms proposed by Thompson, Turkevich and Irsa[221] except that they suggested two types of sites, one on which reaction (a) occurred and the other for reaction (b). On the latter site the alkyl radical was so strongly held that it underwent several exchanges with the large pool of adsorbed D before being desorbed. Anderson and Kemball write the detailed mechanism for the exchange of ethane with deuterium as follows:

(102)



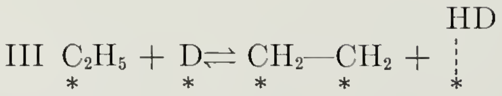
$$\text{I}\quad \underset{*}{\overset{C_2H_6}{\vdots}} + \underset{*}{D} \rightleftharpoons \underset{*}{C_2H_5} + \underset{*}{\overset{HD}{\vdots}}$$

(103)



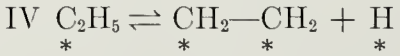
$$\text{II}\quad \underset{*}{\overset{C_2H_6}{\vdots}} \rightleftharpoons \underset{*}{C_2H_5} + \underset{*}{H}$$

(104)



$$\text{III}\quad \underset{*}{C_2H_5} + \underset{*}{D} \rightleftharpoons \underset{*}{CH_2}—\underset{*}{CH_2} + \underset{*}{\overset{HD}{\vdots}}$$

(105)



$$\text{IV}\quad \underset{*}{C_2H_5} \rightleftharpoons \underset{*}{CH_2}—\underset{*}{CH_2} + \underset{*}{H}$$

The exchange may occur by a combination of (I) and (II) with either (III) or (IV) thus giving four possible combinations. They discuss these combinations using kinetic expressions involving terms for each radical or molecule and a term representing the chance of finding the required number of free sites. They find processes (I) and (III) fit the data best for tungsten and processes (II) and (IV) are best for rhodium and palladium. Thus the exchange on tungsten, for which the principal product is C_2H_5D, appears to proceed by a different mechanism than the exchange on rhodium and palladium where the principal product is C_2D_6 and the more highly deuterated products. This, they infer, may be related to the observations of Beeck[21] in which he found Rh, Pd and Pt to be more efficient hydrogenation catalysts than tungsten and tantalum.

Exchange of Propane and Isobutane on Metal Films. Kemball[140] has recently completed additional studies on the exchange reaction of propane and isobutane with deuterium on evaporated films of tungsten (−80 to −20°C) rhodium (−25 to 20°C), and nickel (−47 to 30°C). Energies of activation, frequency factors, and temperature ranges for the exchange (Table 9) show that for tungsten and rhodium the values are similar for isobutane, propane and ethane, but the temperatures required for methane exchange were much higher. Nickel films were about equally effective for isobutane and propane but ethane required somewhat higher temperatures and methane considerably higher. There was a decrease in the energy of activation for exchange of the secondary hydrogen in propane and the tertiary hydrogen atom of isobutane on nickel above 0°C similar to that observed for ethane. It was again suggested that this behavior may be due to a change in the nature of adsorbed species, perhaps an increase in the number of adsorbed olefin residues at the expense of alkyl radicals. Similar results were observed by Farkas[95] for the exchange of propane on platinum catalysts on which the activation energy changed from 26 to 11 kcal/mole in the temperature range 26 to 126°C. Higher frequency factors on rhodium, for example, are associated with higher energies of activation.

Table 9. Exchange of Propane with Deuterium[140]

Catalyst	Gas	Temp. Range	*E*(kcal./mole)*	log *A*	$P_{C_nH_{2n+2}}$[a]	P_{D_2}[b]	Temp.
					a	*b*	
W	C_3H_8	−82 to −24	9.0	21.8	−0.4	−0.4	−75
Rh	C_3H_8	−25 to −16	13.3	25.0	0.5	−0.8	−24
Ni	C_3H_8(2°H)	−47 to 0	10.4	21.7	1.0	−0.6	−25
W	*i*—C_4H_{10}	−80 to −27	7.9	20.1	—	—	—
Ni	*i*—C_4H_{10}(3°H)	−47 to 0	9.0	20.5	—	—	—

* Activation energies and frequency factors are from $x = Ae^{-E/RT}$, where x is the initial rate of disappearance of light hydrocarbon in molecules/sec/cm² of surface.

The orders of the reactions with respect to propane and deuterium on the three metals are similar to those for ethane and methane, but it does become somewhat less positive with increasing size of the hydrocarbon. Tungsten differs from the other metals in that it shows stronger adsorption for the hydrocarbon.

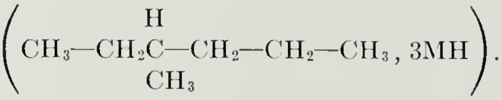
On tungsten and nickel the initial products were C_3H_7D and C_4H_9D followed by small amounts of molecules containing two or more deuterium atoms, the proportion of these increasing with increase in temperature and pressure of deuterium. These higher deuterated species probably arise from successive replacement of hydrogen atoms. With rhodium the completely deuterated hydrocarbons were the most abundant initial species although some of all possible compounds appeared simultaneously, giving average deuterium contents of about 5.4 atoms of deuterium per molecule for propane and 5.8 for isobutane. For tungsten at the lower temperatures, the average was 1.2 to 1.4. This again indicates two different mechanisms as was found for ethane and methane, one mechanism leading primarily to mono-deuterated hydrocarbon and the other leading to the highly deuterated molecules. The extent of the multiple exchange and the similarity between the initial products for isobutane, propane and ethane indicates that multiple exchange is a characteristic property of rhodium as contrasted with tungsten which leads to single successive exchanges.

Results with tungsten and nickel showed that the exchange of the secondary hydrogen on propane and the tertiary hydrogen on isobutane to give CH_3CHDCH_3 and $(CH_3)_3CD$ was more rapid than exchange of the primary hydrogens. At low temperatures on nickel, for example, they found 90 per cent of the mono-deuterated propane was CH_3CHDCH_3. A similar preference for the secondary hydrogen to exchange with deuterium over a platinized platinum catalyst between 20 and 40°C was indicated in the experiments of Kauder and Taylor[133]. The mass spectrometer data indicated that propane on this catalyst underwent single successive exchanges rather than multiple exchanges.

A comparison of metal films with other catalysts indicates some significant differences in behavior, as has been discussed by H. S. Taylor[218]. However, the use of metal films combined with mass spectrometric examination of the products has done much to clarify the processes that occur in catalytic reactions with hydrogen and deuterium with saturated hydrocarbons. Similar techniques to be described in a later section have likewise added much detailed information on the reactions of deuterium with unsaturated hydrocarbons.

Simultaneous Exchange and Racemization. A study of two or more simultaneous reactions is frequently advantageous in elucidating the mechanism of catalytic reactions. Burwell and Briggs[46], and Gordon and Burwell[107] have done this for the exchange and racemization of the optically active saturated hydrocarbon

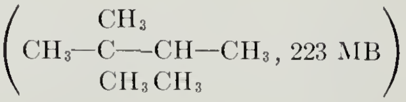
(+) 3-methyl hexane



$$\left(CH_3—CH_2\overset{H}{\underset{CH_3}{C}}—CH_2—CH_2—CH_3,\ 3MH\right).$$

They have also studied the isotopic exchange when deuterium and vapors of this compound as well as those of heptane

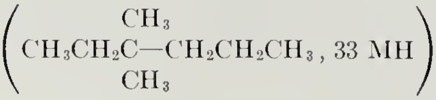
$(CH_3CH_2CH_2CH_2CH_2CH_2CH_3)$, 2,2,3-trimethyl butane



$$\left(CH_3—\overset{CH_3}{\underset{CH_3}{C}}—\underset{CH_3}{CH}—CH_3,\ 223\ MB\right)$$

and

3,3 dimethyl-hexane



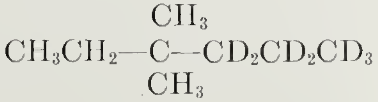
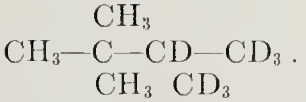
$$\left(CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}—CH_2CH_2CH_3,\ 33\ MH\right)$$

are passed over a nickel-kieselguhr catalyst at 90 to 130°C. At these temperatures no measurable skeletal isomerization or hydrogenolysis of the carbon-carbon bond occurred. The relative degrees of exchange at comparable conditions are given in Table 10.

The variation in rates is more analogous to radical reactions than carbonium ions since in the latter case 3-methyl hexane would be expected to react much faster than heptane. The rate of appearance of the multiply exchanged species was considerably greater than could be accounted for by successive single atom exchanges occurring through repeated successive absorptions. Thus, at low conversions (below 10%), if a fraction x has exchanged once, the fraction subjected to exchange twice by a process of successive adsorptions would be $x^2/2$ and the number of molecules with two deuterium atoms would be 0.01 per cent or less. Instead, when 8.5 per cent of the heptane molecules had exchanged, the percentage of the molecules with one deuterium, was 0.95 per cent, with two 1.10 per cent, with three 0.70 per cent, with four 0.47 per cent, etc. Molecules containing up to sixteen deuterium atoms were present (0.16 per cent with sixteen). Apparently, once these alkane molecules are adsorbed, they have a high probability of undergoing reactions leading to extensive exchange before they evaporate. These multiple exchanges are similar to those described above by Thompson, Turkevich and Irsa[221] and Kemball[140].

TABLE 10. EXCHANGE OF HYDROCARBONS WITH DEUTERIUM[46, 107]

Hydrocarbon	Relative No. of Molecules Exchanged Per Unit Time	Ave No. of D Atoms per Mol.	Max. No. D Atoms per Mol.
H (heptane)	1.00	6.3	16
3 MH	.75	6.5	16
33 MH	.36	4.1	7
223 MB	.13	2.7	7

In the case of heptane and 3-methyl hexane, all molecules containing from one to sixteen deuterium atoms are present, while for 3,3-dimethyl hexane and 2,2,3-trimethylbutane very little exchange occurred beyond seven deuterium atoms, presumably giving:  $CH_3CH_2—\overset{CH_3}{\underset{CH_3}{C}}—CD_2CD_2CD_3$ and  $CH_3—\overset{CH_3}{\underset{CH_3}{C}}—\underset{CD_3}{CD}—CD_3$. It appears that the process of multiple exchange following the initial adsorption does not propagate past a quarternary carbon atom. On the other hand, the complete exchange of 3-methyl hexane and the exchange of the isopropyl side chain in 2,2,3-trimethyl-butane shows that it can proceed past the tertiary carbon atom.

On some of the least active catalysts there was an exponential decline in relative abundance of the higher deuterated species indicating a process in which exchange with adsorbed alkane occurs one atom at a time. At the end of each such single exchange there are fixed probabilities of desorption or undergoing another exchange. As in the exchange reactions discussed previously, more than one type of process must be assumed to account for the distribution of products. This distribution will also be affected by the possibility that hydrogen atoms which dissociate from the hydrocarbon may not come to equilibrium with the deuterium on the surface before recombining. Thus the dissociation rate may be greater than the exchange rate.

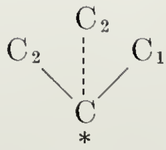
When optically active 3-methyl hexane along with hydrogen or deuterium is passed over nickel-kieselguhr catalyst at about 120°C, racemization occurs with a rate expressed by

$$R = k_0 e^{-(26000/RT)} {p_{H_2}}^{-0.5\text{ to }-0.7} {p_{3MH}}^{0.33} \tag{26}$$

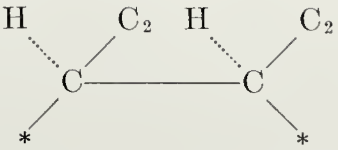
In the absence of hydrogen the catalyst is poisoned, but it may be regenerated by prolonged treatment with hydrogen at 120° or more completely at 300°C. Within experimental uncertainty (±20%), the rate of racemization was the same with deuterium as with hydrogen. The rate determining step, therefore, probably does not involve hydrogen or deuterium atoms adsorbed on the surface. Thus the breaking of a C—H bond to give alkyl radicals by dissociative adsorption would not involve participation of previously adsorbed hydrogen or deuterium, and would therefore be consistent with this result.

The ratio of the numbers of molecules exchanged to those racemized was about 1.6. They suggest that the excess molecules exchanged may be associated with the exchange process causing the exponential decline. In this process, some of the molecules adsorbed at the propyl and ethyl side chains of the 3-methyl hexane would be desorbed before the exchange propagated to the optically active center. Thus it appears that racemization accompanies exchange in the tertiary position and the rate is the same in the presence of hydrogen or deuterium. Any proposed mechanism should take these conditions into consideration.

Mechanism of Exchange and Racemization. Burwell and Briggs point out that a dissociatively adsorbed alkane molecule is identical with the half-hydrogenated stage of Horiuti and Polanyi[125] in olefin hydrogenation by the associative mechanism. Partial reversal of the process involved in the hydrogenation of olefins, coupled with double bond isomerization may offer an explanation of exchange. However, they conclude that adsorption as an alkyl radical or as a olefin-like radical plus two hydrogen atoms will not necessarily lead to racemization since such radicals are asymmetric:



and

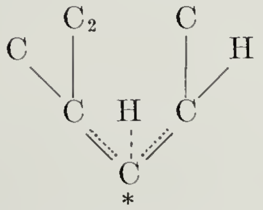


By microscopic reversibility the alkane regenerated should have the original configuration. Similarly the associative mechanism involving double bond migration in which carbon atom 3 is attached to the surface by dissociation of the C—H bond would not lead to racemization.

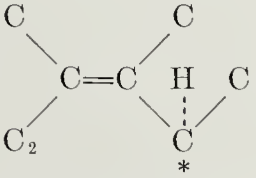
A two step dissociative mechanism, one involving retention and one inversion of configuration could lead to partial racemization. Only if the rates of the two processes were, by chance, the same would complete racemization occur. Thus, the authors state that simple dissociative adsorption will not cause racemization as suggested by Farkas[82] unless the two stereochemically opposite processes occur at the same rates. They cite their observation that exchange if only 60 per cent greater than racemization would require the rates of both stereochemical reactions to be practically the same. Since this does not seem likely, they do not favor the dissociative mechanism.

Instead of either the dissociative or associative mechanism, Burwell and Briggs proposed a mechanism involving a symmetric adsorbed intermediate such as an allylic free radical[131, 220] or a non-adsorbed double bond:

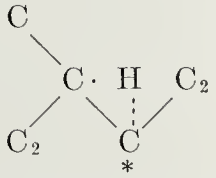
(I)



(II)



(III)



These permit migration of point of attachment of the hydrocarbon molecule with accompanying isotope exchange. Such intermediates would not permit exchange to be propagated past the quarternary carbon atom, in agreement with observations.

When optically active 4-methyl-2 hexene was hydrogenated on a nickel-kieselguhr catalyst at 45°, negligible racemization occurred. If the species proposed above can be derived from either olefins or alkanes, the relative probability of hydrogenation and migration of the double bond would have to vary with conditions. The relationships proposed here involving a common type intermediate for alkane exchange and olefin exchange and hydrogenation are interesting. Further experiments on such factors as type of catalyst, relative adsorbabilities, surface coverage, differences in products of exchange, and relative rates of concurrent reactions will aid in establishing those relations that may exist between the behavior of saturated and unsaturated hydrocarbons.

Interaction of Deuterium with Alkanes and Cycloalkanes on Nickel Catalysts. The work described in the preceding section has been extended by Rowlinson, Burwell and Tuxworth[193] to include eleven alkanes and cycloalkanes. In addition to nickel-kieselguhr catalysts, they used evaporated nickel films and reduced nickel oxide. The films were prepared by evaporating 50 to 75 mg. of nickel on the walls of a 45 mm inside diameter glass tubing. Gas mixtures, consisting in most cases of a ratio of 3 moles of deuterium to one of alkane, were prepared by bubbling the deuterium through the liquid alkane maintained at the appropriate temperature. This mixture was passed through the reactor at the rate of from 0.3 to 0.7 cc of liquid hydrocarbon per hour and then into a trap cooled with liquid nitrogen. Procedures for reactions with reduced nickel oxide and nickel-kieselguhr catalysts were similar to those described previously by Burwell and Briggs[46]. Analyses of the products were made with a mass spectrometer and infrared spectrometer. The 4.6 μ band for C—D was employed to estimate the approximate degree of exchange before taking the mass spectra.

Typical distribution curves were given showing the per cent of each deuterated species obtained by reaction of deuterium with the following: (A) heptane on nickel-kieselguhr (96°C); (B) heptane on reduced nickel oxide (176°C); (C) 3-methyl hexane on reduced nickel oxide (210°C); (D) 3,3-dimethyl pentane on reduced nickel oxide (210°C); (E) 2,3-dimethylbutane on nickel film (200°C); (F) cyclohexane on reduced nickel oxide (176°C); (G) 1,1-dimethylcyclohexane on nickel film (201°C); (H) cyclopentane on nickel film (200°C).

Molecules containing from 1 to all hydrogens exchanged were produced. With heptane and 3-methyl hexane, the most abundant species were those of extensive but not complete exchange. The fully exchanged species were most abundant for the cyclopentanes, cyclohexanes, and 2,3-dimethylbutane, although a comparatively large abundance of d_1 molecules was also present. No anomaly appears in the concentration of species in which one-half of the hydrogen atoms of the cyclohexanes are exchanged. This was taken as evidence that these molecules are not adsorbed flat at these temperatures (175 to 200°C) and that exchange does not occur on one side only during their residence on the surface. However, in later experiments the exchange between deuterium and cycloalkanes on nickel and palladium catalysts at temperatures between $-50°$ and 75°C, Burwell[46a] found a discontinuity in the concentrations of $C_nH_nD_n$ and $C_nH_{n-1}D_{n+1}$. At 50°C, for example, the exchange with cyclopentane is confined to a considerable degree to the hydrogen atoms on one side of the molecule.

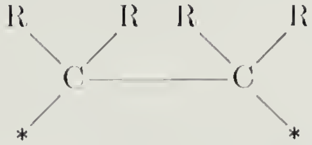
With 3,3-dimethylpentane, significant exchange does not proceed beyond five deuterium atoms in the molecule. This indicated, as previously found,[46] that a gem-dimethyl group blocks the propagation of the exchange. The propagation of the exchange is not affected by a single branch, nor by two branches on separate carbon atoms as shown by the results with 2,3-dimethylbutane. Similarly, the exchange of 1,1-dimethylcyclohexane is limited to 10 deuterium atoms which is the number of hydrogen atoms attached to the ring. Neopentane exchanges very slowly yielding primarily $C_6H_{11}D$ with very small amounts with $-d_2$ and $-d_3$.

The authors take these results to mean that propagation of the exchange does not occur to any appreciable extent by $\alpha - \alpha$ exchange. Also, if $\alpha - \gamma$ migration occurred, exchange should proceed past a double branch on the same carbon atom. Further, cyclohexane should show a higher probability of six exchanges rather than complete exchange. Multiple exchange does occur up to the double branch of 3,3-dimethylpentane. If multiple exchange resulted from diffusion into a pore where several single exchanges occurred before the molecule diffused out, some molecules with complete exchange should be observed. From the above arguments, the authors conclude that $\alpha - \beta$ migration is primarily responsible for multiple exchange, that is from one carbon atom to the adjacent one.

The exchange patterns in general fell into two groups, those such as 3-methylhexane resembling heptane, and the cycloalkanes resembling 2,3-dimethylbutane. The differences between the two groups could be accounted for by differences in probabilities for propagation of exchange and desorption after one or two exchanges. Steric factors involved in the primary adsorption and propagation are undoubtedly involved here.

Further experiments on the rates of exchange and racemization confirmed previous results that racemization accompanies practically every exchange on the tertiary carbon atom.

The authors do not feel that the propagation of exchange by the mechanism suggested by Anderson and Kemball[2] will explain racemization. This mechanism involved an intermediate of the type

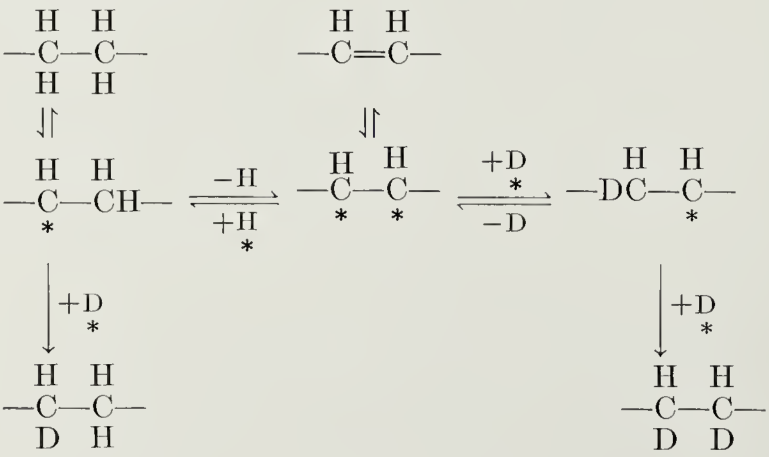


which is essentially an associatively adsorbed alkene. Rowlinson, Burwell and Tuxworth[193] suggest that an adsorbed free radical intermediate such as type (III) illustrated previously (p. 337) could account for racemization and $\alpha - \beta$ propagation of exchange.

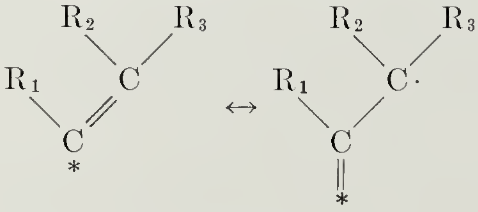
A special type of planar alkyl group adsorbed with the plane of the radical perpendicular to the surface was also suggested as a possible intermediate. This is equivalent to a free radical in which the *p*-orbital interacts with surface orbitals. Addition of deuterium to the central carbon atom would result in desorption while simultaneous removal of a hydrogen atom from one of the adjacent carbon atoms would result in propagation of the exchange. This is not totally different from the adsorbed free radical (III) above since its plane must be perpendicular to the surface or there must be free rotation about the central C—C bond.

In a review of stereochemistry and heterogeneous catalysis, Burwell[46a] used conventional type mechanisms to represent the predominant *cis*-exchange of saturated and unsaturated hydrocarbons and *cis*-additions of unsaturated hydrocarbons:

(105a)



Repetition of the sequence in (105a) could account for any degree of exchange in the saturated alkanes. However, for *trans*-addition, for racemization, and for complete exchange of cyclic alkanes he uses an intermediate with a carbon atom having a three-fold coordination:



Other possibilities were also considered.

MASS SPECTROMETRIC INVESTIGATIONS OF UNSATURATED HYDROCARBONS

Reactions of Ethylene and Propylene with Deuterium

Redistribution During Ethylene Hydrogenation. The discovery by Turkevich, Bonner, Schissler and Irsa[231, 232] that much of the ethane formed by the reaction of deuterium with ethylene on a nickel wire catalyst contained no deuterium has rather significant consequences with respect to the detailed processes occurring during hydrogenation. The results of this and other similar researches by Wagner *et al.*[243, 244, 252], Dibeler and Taylor[59, 60, 220] and Weiss and Taylor[247] will be described in the following sections. A review of the other aspects of the catalytic hydrogenation of ethylene has been published by Eley[68a].

Turkevich *et al.*[231, 232] used a mass spectrometric method of analysis to determine the deuterated species at various stages of the reaction between deuterium and ethylene. To facilitate the interpretation of the data, the mass spectra were obtained first for the ethane plus ethylene and then for the ethane portion alone after removal of ethylene. This separation was accomplished by reaction of the ethylene with bromine vapor followed by distillation. The mass spectra of the deuteroethylenes was obtained by difference. Results of the mass spectrometric analysis of samples taken during the reaction of a mixture of 9.9 mm of ethylene and 20.5 mm of deuterium at 90°C are given in Table 11. Curves were given for the compositions of the ethylene and ethane fractions as a function of the extent of reaction. Up to about 20 per cent reaction, completely light ethane was the major component of the ethane fraction. Its partial pressure then remained nearly constant during the remainder of the reaction because of the increasing concentration of deuteroethylenes. Similarly, the partial pressure of C_2H_5D remained constant after about 70 per cent reaction for the same reason. The partial pressure of the other deuterated ethanes continued to rise throughout the reaction.

TABLE 11. COMPOSITION OF ETHANE AND ETHYLENE FRACTIONS AS A FUNCTION OF PERCENTAGE ADDITION TO THE DOUBLE BOND*[231, 232]

Component	Ethane Fraction				Component	Ethylene Fraction	
	% Completion					% Completion	
	20%	40%	73%	97%		20%	40%
C_2H_6	38.4	21.0	12.5	9.5	C_2H_4	54.8	39.0
C_2H_5D	35.8	43.0	32.5	23.5	C_2H_3D	32.6	29.0
$C_2H_4D_2$	19.9	21.0	25.5	26.0	$C_2H_2D_2$	11.6	21.0
$C_2H_3D_3$	4.7	10.0	16.5	18.0	C_2D_3H	1.0	7.0
$C_2H_2D_4$	1.2	3.0	9.0	12.5	C_2H_4		4.0
C_2HD_5		1.0	3.5	7.5			
C_2D_6			1.0	3.0			
Total pressure mm	2.0	4.0	7.3	9.7		8.0	6.0

* Values at 40, 73 and 97% reaction were estimated from curves presented by the authors.

The rate of exchange to form deuteroethylenes was apparently two to three times the rate of addition. The concentration of light ethylene decreased exponentially while the partial pressure of each of the deuterated species passed through maxima at successively later stages of the reaction. This suggests that the higher deuterated species might arise through successive exchanges rather than multiple exchanges during a single adsorption as observed for the saturated hydrocarbons (see p. 324).

An important result of these experiments is the proof that, at 90°C on a nickel wire catalyst, ethane formation did not occur through the simultaneous addition of two deuterium atoms as proposed by Farkas and Farkas[82] and at one time supported by Twigg and Rideal[240] but later also disproved by Twigg[239]. The experiments also suggest that ethylene hydrogenation is effected by hydrogen that was previously on another ethylene molecule. In other words, a hydrogen redistribution must occur among the adsorbed molecules. No detailed mechanism was proposed in this paper, but a mechanism for such redistributions was suggested later by Wagner, Wilson, Stevenson and Otvos[243] (see p. 349) and by Bond and Turkevich[40] for propylene. Additional results on the ethylene-deuterium reactions on several catalysts have been described recently by Schissler, Thompson and Turkevich[195a].

Reaction of Propylene with Deuterium. In a later paper, Bond and Turkevich[40] made a more complete mass spectrometric investigation of the interaction of propylene with deuterium on a pumice supported platinum catalyst. Except for experiments on the effect of temperature, 1 g of a 5 per cent platinum-pumice catalyst was used at 18°C. The products of the reaction were analyzed with a mass spectrometer using ionizing voltages of 15 to 23 volts, at which voltages the contributions of the lower fragments are small. This facilitated analysis of the mass spectra. A summary of the results of their experiments follows.

Kinetics of Addition of Hydrogen to Propylene. With a fixed pressure of propylene (50 mm), the initial rate of decrease in pressure was determined for varying pressures of hydrogen from 25 to 500 mm. Similarly, for a fixed pressure of hydrogen (75 mm) the initial rate of decrease in pressure was measured for propylene pressures varying from 50 to 500 mm. Values read from the curves given in their paper are summarized in Table 12. In the lower pressure ranges these results are approximately of the form $dp/dt = k(C_3H_6)^{-1/2}(H_2)^{1/2}$. A rate expression approximating the data was derived using Langmuir's isotherm with the assumption that both reactants compete for the major part of the surface. Some of the hydrogen was assumed to be adsorbed on a small fraction of the surface without competition even at high pressures of olefin owing to geometrical considerations[241]. The adsorption coefficient of propylene was taken to be about ten times that of hydrogen.

Effect of Pressures on Distribution of Final Products. A series of experiments was run to determine the effect of relative pressures of deuterium and propylene on the distribution of the deutero-compounds in the final product. The average deuterium content per molecule is listed as the "deuterium number," i.e., $C_3H_{8-x}D_x$. Table 13 summarizes the results for a number of initial pressures. The following composition was obtained for

TABLE 12. KINETICS OF HYDROGEN ADDITION TO PROPYLENE[40]

Propylene Pressure (50 mm)		Hydrogen Pressure (75 mm)	
Hydrogen Pressure	Initial Rate of Pressure Drop (mm/min.)	Propylene Pressure	Initial Rate of Pressure Drop (mm/min.)
50	12	50	14
100	21	100	10
200	30	200	7.7
300	34.5	300	6.6
400	37.5	400	6.3
500	37.5	500	6.0

TABLE 13. DISTRIBUTION OF DEUTEROPROPANES FROM THE INTERACTION OF DEUTERIUM WITH PROPYLENE[40]

Product	Propylene Pressure 13 mm			Deuterium Pressure 16.5 mm		
	16.5 mm D_2	109 mm D_2	521 mm D_2	13 mm C_3H_6	166 mm C_3H_6	541 mm C_3H_6
C_3H_8	13.5	2.1	1.4	13.5	32.3	45.2
C_3H_7D	26.7	21.8	19.6	26.7	32.4	28.4
$C_3H_6D_2$	24.2	37.6	44.9	24.2	19.5	15.8
$C_3H_5D_3$	14.8	18.8	18.4	14.8	8.9	5.6
$C_3H_4D_4$	8.6	8.8	7.5	8.6	3.6	2.4
$C_3H_3D_5$	5.5	4.5	3.7	5.5	2.0	1.4
$C_3H_2D_6$	3.7	2.7	1.8	3.7	1.2	0.8
C_3HD_7	2.2	2.2	1.5	2.2	0.4	0.3
C_3D_8	0.7	1.4	1.0	0.7	0.0	0.1
D-number	2.25	2.54	2.43	2.25	1.32	1.01

the excess propylene of the last two experiments of Table 13: With 166 mm of propylene: C_3H_6 = 96.0%; C_3H_5D = 3%; $C_3H_4D_2$ = 1.0%. With 541 mm of propylene: C_3H_6 = 97.0%; C_3H_5D = 3.0%; $C_3H_4D_2$ = 0.0%.

The increase in concentration of light propane with increase in propylene pressure is significant because it shows that, under these conditions, much of the hydrogen added to the olefin does not come directly from the hydrogen in the gas phase, but from the hydrogen of another olefin molecule. That is, a redistribution reaction must be occurring between adsorbed olefin molecules on the surface or between adsorbed and gaseous olefins. The authors showed that the excess hydrogen in the propane was balanced by the deuterium in the unreacted propylene. Excess deuterium has the effect of increasing the yield of $C_3H_6D_2$ and an increase in the average deuterium content of the propane at the expense primarily of C_3H_8 and C_3H_7D. The yield of propanes containing from 4 to 8 deuteriums does not vary much.

Similar experiments were made with about 100 mm of propylene and the following pressures of deuterium: (a) 91 mm, (b) 140 mm, and (c) 307 mm. The distribution of the products during the course of the reaction was determined. With 91 mm of deuterium the distribution at 57 per cent reaction was about the same as at the end. Apparently no results were obtained for the earlier stages. The deuterium number changed only from 1.86 at 57 per cent reaction to 1.91 at the end. At 57 per cent reaction the composition of the propylene was: $C_3H_6 = 95\%$, $C_3H_5D = 4\%$ and $C_3H_4D_2 = 1\%$. The composition of the residual propylene at the end was: $C_3H_6 = 66\%$; $C_3H_5D = 26\%$; $C_3H_4D_2 = 8\%$. A material balance indicated that little hydrogen was returned to the gas phase. Apparently exchange is much slower than addition as contrasted with the behavior of ethylene on nickel[231, 232]. These observations indicate that when propylene is adsorbed on the platinum catalyst, most of it remains until it forms propane.

With 98 mm of C_3H_6 and 140 mm of D_2 the product distribution was initially constant, but toward the end of the reaction the proportions of highly deuterated propanes increased. At 57 per cent reaction the deuterium contained only about 3 atom per cent hydrogen, but toward the end of the reaction the hydrogen content increased rapidly to about 25 to 30 atom per cent. As the reaction proceeds, the ratio of deuterium to propylene increased and the return of hydrogen was accelerated. This behavior will be discussed in connection with the author's proposed mechanisms.

Reactions with H_2, HD, and D_2. A slight excess of an equilibrated mixture of $H_2 + D_2$ with 66 mm of propylene gave a product distribution essentially constant throughout the reaction with about 35 to 36 per cent of C_3H_7D. A similar experiment with non-equilibrated $H_2 + D_2$ also yielded about 35 to 36 per cent of C_3H_7D, but the initial rate of formation of C_3H_8 was slightly greater. The initial rate was slightly less for $C_3H_6D_2$ as well as for the other deuterated propanes. The rate of equilibration of H_2 and D_2 was measured simultaneously with addition in this experiment. This equilibration rate was rather slow, about 25 per cent of the rate of addition. After 1.5 min. when addition was 63 per cent complete, the composition of the hydrogens in the gas phase was: 14.8 mm of D_2, 12.2 mm of H_2 and 10.8 mm HD, or 28.6 per cent HD. After 7.0 min. when the reaction was 98.5 per cent complete, the composition was: 3.8 mm D_2; 4.7 mm H_2, 5.8 mm HD or 40.6 per cent HD. In the absence of propylene the equilibration was complete in less than a minute. These results confirm the experiments of Twigg[239] from which it was concluded that two atoms from the same molecule of hydrogen did not add simultaneously to an olefin.

Exchange between C_3H_6 and C_3D_6. In order to learn more about the redistribution reaction between adsorbed olefin molecules that must certainly be occurring on the catalyst during hydrogenation, Bond and Turkevich did the following experiment. A mixture of propylenes consisting of 51.5% C_3H_6, 41.5% C_3D_6 and 7.0% C_3HD_5 was admitted to the catalyst. After 11 min. no exchange was observed. However, when deuterium was admitted with the mixture, the exchange was catalyzed. Excess deuterium as shown in Table 14 decreased the extent of the exchange.

The absence of $C_3H_3D_5$ and $C_3H_2D_6$ indicates that addition is more rapid than equilibration between the propylenes at the higher deuterium pressures. At the lower deuterium pressures equilibration between the propylenes was more extensive because all the propanes were obtained. After the addition was 23 per cent complete, about 20 per cent of the propylenes were other than those initially present, during which time the deuterium content of the propylene increased only from 51.8 to 54.9 per cent. Apparently desorption of propylene from the surface occurs during hydrogenation conditions, but it is suppressed by high deuterium to propylene ratios.

TABLE 14. EXCHANGE OF C_3H_6 AND C_3D_6 IN THE PRESENCE OF DEUTERIUM[40]

Component	Propanes		Component	Propylenes
	10 mm C_3H_6 15 mm D_2	10 mm C_3H_6 3 mm D_2		13 mm C_3H_6 3 mm D_2
C_3H_8	2.2%	7.2%	C_3H_6	29.4
C_3H_7D	11.7	13.3	C_3H_5D	10.9
$C_3H_6D_2$	14.1	12.1	$C_3H_4D_2$	4.5
$C_3H_6D_4$	11.5	8.2	$C_3H_3D_3$	0.9
$C_3H_4D_4$	9.1	6.0	$C_3H_2D_4$	4.2
$C_3H_3D_5$	0.0	2.3	C_3HD_5	11.6
$C_3H_2D_6$	0.0	6.2	C_3D_6	38.6
C_3HD_7	22.2	23.2		
C_3D_8	29.2	21.5		

Effect of Temperature. The apparent activation energy for addition of hydrogen (200 mm) to propylene (200 mm) from −18 to 130°C was found to be 6.3 ± 0.3 kcal.

The distribution of deuteropropanes during the reaction of about 50 mm of propylene with 50 mm of deuterium was determined at temperatures of −18°C, 18°C, 75°C and 129°C. The concentration of the more highly deuterated products increased somewhat with an increase in temperature; the concentration of the lower deuterated products are given in

Table 15. The composition of the propylenes after 50 per cent addition at −18°C was C_3H_6 = 88%, C_3H_5D = 10%, $C_3H_4D_2$ = 2%, and at 129°C the composition was: C_3H_6 = 92%, C_3H_5D = 5%, $C_3H_4D_2$ = 2%, $C_3H_3D_3$ = 1% at 72 per cent reaction. Also at 129°C it was found that H_2 or HD was returned to the gas phase in appreciable amounts, 28% at 72% reaction.

In order to obtain more information about the exchange reaction they studied the effect of temperature on reaction mixtures containing 10-fold excess deuterium. The yield of propanes with 4 to 8 deuterium atoms increased with temperature, but the percentages of C_3H_8, C_3H_7D and $C_3H_5D_3$ passed through a maximum. The yield of $C_3H_6D_2$ progressively fell as the temperature rose. A nearly linear increase in deuterium number from 2 at −18°C to about 4 at 129°C and a corresponding increase in the return of hydrogen to the gas phase occurred with increase in temperature.

Table 15. Distribution of Deuterated Products as a Function of Temperature[40]

Temp. °C	C_3H_8	C_3H_7D	$C_3H_6D_2$	$C_3H_5D_3$	$C_3H_4D_4$
−18	6.8	33.1	34.3	15.2	5.6
18	14.5	31.2	27.0	14.1	6.6
75	21.0	26.2	20.4	13.4	8.3
129	18.7	26.1	22.0	15.0	8.7

From the effect of temperature on the over-all addition reaction and from the temperature dependence of the rate of formation of propanes other than $C_3H_6D_2$, the authors arrive at an energy of activation of 15 kcal for the redistribution reaction.

Summary of Experimental Results. The following conclusions derived from the experimental work described above should be considered in formulating a mechanism:

(1) During the addition reaction appreciable redistribution of hydrogen atoms occurs giving rise to completely light propane and deuteropropanes containing up to 8 deuterium atoms.

(2) The excess hydrogen in the propanes is balanced by the deuterium in the exchanged propylene.

(3) With about equal pressures of deuterium and propylene, little HD or exchanged propylenes are returned to the gas phase and the relative concentrations of the deuteropropanes remain approximately constant throughout the reaction.

(4) With a large excess of propylene, the proportion of light propane, C_3H_8 and exchanged olefin increased; that of $C_3H_6D_2$ and higher deu-

terated species decreased, and only small amounts of HD was returned to the gas phase. The deuterium number decreases with excess propylene.

(5) With excess deuterium, the yield of light propane, C_3H_8, decreased markedly while the yield of $C_3H_6D_2$ increased. Above a 5-fold excess of deuterium, the return of HD to the gas phase increased appreciably and the deuterium number did not change much.

(6) Increasing the temperature has the following effects: increases the yield of light propane, increases appreciably the return of HD to the gas phase, but does not increase the extent of exchange appreciably. An increase of the more highly deuterated species occurs at the expense of $C_3H_6D_2$ with increase in temperature. With a 10-fold excess deuterium, the deuterium number increases from 2 at −18°C to about 4 at 129°C.

(7) Experiments with H_2 and D_2 mixtures show that molecular addition does not occur. H_2—D_2 equilibration does occur but at a much lower rate than in the absence of propylene, indicating a small H or D atom concentration.

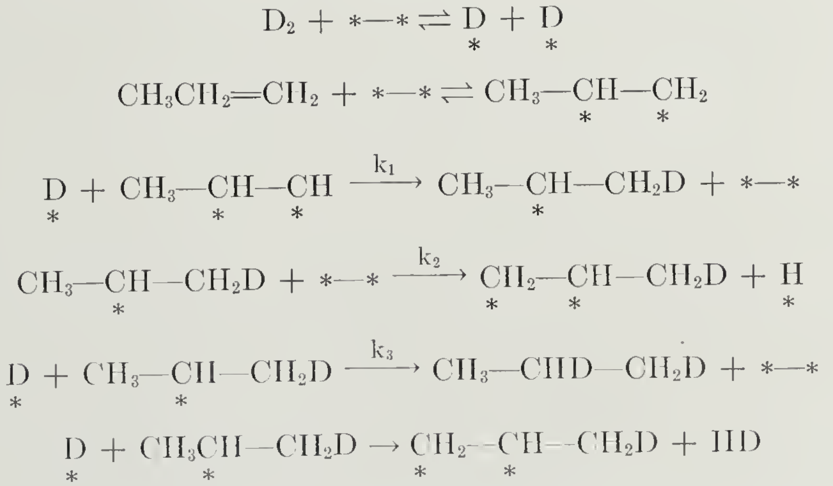
(8) Equilibration of C_3H_6 and C_3D_6 by redistribution is catalyzed by small amounts of deuterium but this catalysis is slower with higher pressures of deuterium.

(9) The activation energy for hydrogenation is 6.3 kcal and that for the redistribution reaction is 15 kcal.

(10) The exchange of D_2 with propane on the platinum catalyst was relatively slow under the conditions of the experiments.

Mechanisms. The scheme of reactions used by the authors to explain their observations are based upon an associative adsorption and types of reactions proposed by others previously[239, 240].

The reactions inferred from their discussions are:



(106) $$\mathrm{D_2} + *{-}* \rightleftharpoons \underset{*}{\mathrm{D}} + \underset{*}{\mathrm{D}} \qquad \text{(a)}$$

(107) $$\mathrm{CH_3CH_2{=}CH_2} + *{-}* \rightleftharpoons \mathrm{CH_3{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}}\underset{*}{\mathrm{CH_2}} \qquad \text{(b)}$$

(108) $$\underset{*}{\mathrm{D}} + \mathrm{CH_3{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}}\underset{*}{\mathrm{CH}} \xrightarrow{k_1} \mathrm{CH_3{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2D} + *{-}* \qquad (1)$$

(109) $$\mathrm{CH_3{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2D} + *{-}* \xrightarrow{k_2} \underset{*}{\mathrm{CH_2}}\mathrm{{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2D} + \underset{*}{\mathrm{H}} \qquad (2)$$

(110) $$\underset{*}{\mathrm{D}} + \mathrm{CH_3{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2D} \xrightarrow{k_3} \mathrm{CH_3{-}CHD{-}CH_2D} + *{-}* \qquad (3)$$

(111) $$\underset{*}{\mathrm{D}} + \mathrm{CH_3}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2D} \rightarrow \underset{*}{\mathrm{CH_2}}\mathrm{{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2D} + \mathrm{HD} \qquad (4)$$

Similar reactions in which the half-hydrogenated state is the normal propyl radical, $CH_3\text{—}CH_2\text{—}\underset{*}{CH_2}$ can also occur. Repetition of the appropriate reactions can account for the distribution of species produced under various conditions. All possible isotopic propylenes and half-hydrogenated states as well as H and D may be on the surface in concentrations determined by the partial pressures, relative adsorbabilities, and rate constants. The relative concentrations remain constant when neither HD nor deuterated propylenes are returned to the gas phase. This is nearly true when propylene and deuterium pressures are about equal, thus accounting for item 3 above.

At the lower deuterium pressures, the very low rate of formation of HD presumably occurring by reaction (4), indicates small D atom concentration. Under these conditions propylene and half hydrogenated states will be the main reactants, thus accounting for the formation of the lighter propanes. The excess hydrogen in the propanes is balanced by the deuterium that appears in the exchanged propene since little HD is returned to the gas phase.

Large pressures of deuterium will increase the concentration of D atoms so that the main reactants will be half-hydrogenated states and deuterium atoms. This will increase the proportion of $C_3H_6D_2$ and the formation of HD as found in item 5. Since there are a limited number of effective sites which a deuterium atom can occupy adjacent to a propylene molecule, all of these will be filled even when the deuterium and propylene pressures are about equal. Increase of deuterium pressure will not affect reactions (2) and (3) much because they are controlled by half-hydrogenated states, consequently the deuterium number will not be increased greatly as found in item 5. Very high ratios of deuterium to propylene will increase the formation of HD owing to the higher coverage by deuterium under these conditions.

The equilibration of C_3H_6 and C_3D_6 in the presence of D_2 is assumed to occur by a sequence of reactions like (1) and (2), but the equilibration is suppressed by increasing the deuterium/propylene ratio because of reaction (4).

When both reactants, either separately or combined as half-hydrogenated states, are present in equal amounts, the distribution of products will be determined by the total hydrogen/deuterium ratio and the velocity constants. A fraction $k_3/(k_2 + k_3)$ of the half-hydrogenated states will become hydrogenated. Since the yield of $C_3H_6D_2$ is never greater than 45 per cent they assume that k_2 is somewhat greater than k_3 at room temperature.

The authors show from relative strengths of adsorption that increasing the temperature in the presence of excess deuterium increases the coverage by deuterium, but this would not explain the decrease in yield of $C_3H_6D_2$. They conclude that this must be due to the fact that the activation energy of reaction (2) is greater than of reaction (3). Using their value of 15 kcal for the redistribution reaction along with the change in deuterium concentration they can account for the increase in deuterium number with increase in temperature.

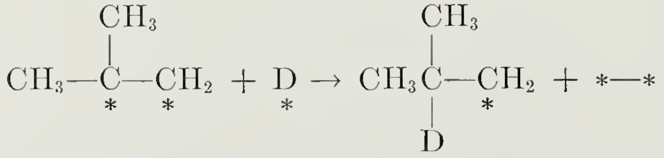
Another scheme of reactions has been used by Wagner *et al.* to explain the rather high concentration of light alkane[252]. Their mechanism, as will be discussed in the following section, involves an interchange of hydrogen between adsorbed propylene and alkyl radicals or between alkyl radicals themselves. In a later paper Bond[32] does include such steps along with steps that involve van der Waals adsorbed deuterium molecules in addition to chemisorbed deuterium atoms. Cyclopropane[34a, 38] yields propane with 0 to 8 D atoms, but with a different distribution than propylene gives. Apparently cyclopropane does not isomerize to propylene before reaction with deuterium.

Redistribution During Hydrogenation of the Olefins.

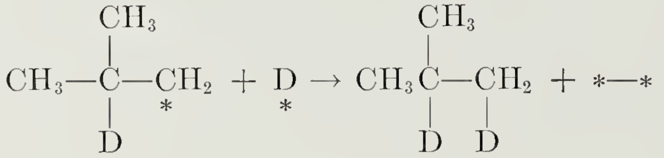
Wagner, Wilson, Otvos and Stevenson[243, 244, 252] reported some important mass spectrometric investigations of the addition of deuterium to *cis*-2-butene, isobutene, and ethylene similar to those of Turkevich, Bonner, Schissler and Irsa[231, 232]. They circulated deuterium and the olefin through a tube containing a reduced nickel catalyst (Harshaw No. 78). The total volume of the system was about 300 ml and the circulation rate was approximately 500 cc per minute. Deuterium was first admitted to the desired pressure, followed by the olefin, after which circulation was started. Mass spectrometric analysis of the resulting butanes was done with 8 volt ionizing electrons to avoid the necessity of correcting for ion fragments from species of higher molecular weights. Deuterobutenes were analyzed with 5-volt electrons and deuteroethanes and deuteroethylenes were determined with 5.5- and 7.5-volt electrons, respectively. The reaction products of isobutylene could be analyzed with the usual 75-volt electrons.

Reaction of Isobutylene with Deuterium. The products obtained after 20 minutes reaction between 9 millimoles of deuterium and 1 millimole of isobutene with 10 pellets of the nickel catalyst at −46°C were: isobutane-d_0 = 18%; isobutane-d_2 = 70%; isobutane-d_3 = 7%; isobutane-d_4 = 1.3%. In another experiment at −78°C they obtained in 20 min.: isobutane-d_0 = ~0.0%; isobutane-d_2 = 97%; isobutane-d_3 = 2.4%; isobutane-d_4 = 0.5%. It appears that isobutene at −78°C yields $C_4H_8D_2$ almost quantitatively and from the mass spectrometer patterns they concluded that it was largely isobutane-1,2-d_2. Under the conditions of these experiments isobutanes with less than two deuterium atoms were not formed and no exchanged isobutene was observed. The authors suggest that this hydrogenation occurs by addition of two chemisorbed deuterium atoms to a physically adsorbed isobutene similar to the mechanism originally suggested by Beeck[18] (p. 313).

Another possibility is that the isobutane-1-2-d_2 could be formed by the reactions:

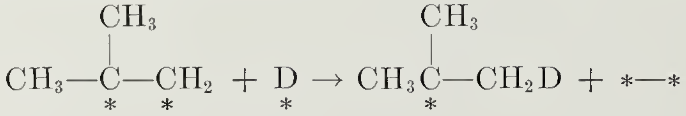
(112) 

$$CH_3-\underset{*}{\overset{CH_3}{C}}-\underset{*}{CH_2} + \underset{*}{D} \rightarrow CH_3\underset{D}{\overset{CH_3}{C}}-\underset{*}{CH_2} + *-*$$

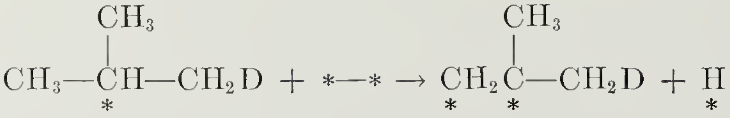
(113) 

$$CH_3-\underset{D}{\overset{CH_3}{C}}-\underset{*}{CH_2} + \underset{*}{D} \rightarrow CH_3\underset{D}{\overset{CH_3}{C}}-\underset{D}{CH_2} + *-*$$

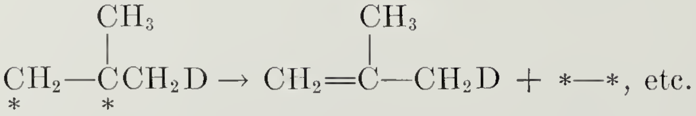
If the following alternative alkyl radical were formed in appreciable amounts, the reactions would be:

(114) 

$$CH_3-\underset{*}{\overset{CH_3}{C}}-\underset{*}{CH_2} + \underset{*}{D} \rightarrow CH_3\underset{*}{\overset{CH_3}{C}}-CH_2D + *-*$$

(115) 

$$CH_3-\underset{*}{\overset{CH_3}{CH}}-CH_2D + *-* \rightarrow \underset{*}{CH_2}\underset{*}{\overset{CH_3}{C}}-CH_2D + \underset{*}{H}$$

(116) 

$$\underset{*}{CH_2}-\underset{*}{\overset{CH_3}{C}}CH_2D \rightarrow CH_2{=}\overset{CH_3}{C}-CH_2D + *-*, \text{ etc.}$$

In this case more exchange would be expected[32] since the methyl groups are equivalent. The reverse of reaction (112) can lead only to the original reactants and would not lead to exchange on desorption of the olefin.

Reaction of cis-2-butene with Deuterium. A few of the results of similar experiments with *cis*-2-butene are summarized in Table 16. The experiments at −78°C were carried out with 10 pellets of the catalyst, 1 millimole of 2-butene and 10 millimoles of deuterium. In all of the other experiments the same quantities of butene and deuterium were used with one pellet of catalyst. The per cent of H gained by the deuterium in three of the experiments were: −48°C = 2.05% H; 0°C = 4.9% H; 50°C = 10.2% H.

These results show that all possible deuterobutanes were produced at the low temperatures. Very little exchange was observed in contrast to the results on nickel wire at higher temperatures[40, 220, 231, 232, 236]. No deuterobutenes with more than one deuterium atom was observed so that the highly deuterated butanes did not arise from addition to exchanged butene. Also no exchange occurred between butane and deuterium at these temperatures.

At the lower temperatures, very little HD was produced so that the average composition of the deuterobutanes was that corresponding to two deuterium atoms per molecule. At the higher temperatures more exchange occurred and more HD was returned to the gas phase resulting in an average deuterium content greater than two deuterium atoms per molecule. In all cases the exchange was of minor importance. The distribution of the deuterated species were quite different in the butenes than in the butanes indicating different processes. The relative proportions of the deuterated butanes changed slightly during the course of the reaction.

TABLE 16. REACTIONS OF CIS-2-BUTENE WITH DEUTERIUM[252]

Component	50 min. −78°C	5 min. −48°C	35 min −48°C	150 min. −48°C	60 min. 0°C	55 min. 50°C
Butenes						
C_4H_8	3.1	91	38	0.8	1.8	3.9
C_4H_7D	0.0	0.7	2.2	0.2	0.2	0.07
Butanes						
C_4H_{10}	7.1	1.0	6.0	7.5	5	2
C_4H_9D	20.2	1.8	12	20	17	9
$C_4H_8D_2$	35.5	2.9	20	33	25	21
$C_4H_7D_3$	21.3	1.4	12	21	22	21
$C_4H_6D_4$	8.7	0.8	6.0	11	15	19
$C_4H_5D_5$	2.7		2.2	4	9	14
$C_4H_4D_6$	0.6		1.0	2	2	9
$C_4H_3D_7$	0.3		0.8	1	1	5
$C_4H_2D_8$	0.1					2
$C_4H_1D_9$	0.1					1
C_4D_{10}	0.1					

The over-all kinetics of the hydrogenation of *cis*-2-butene was found to be first order in olefin from both pressure measurements and mass spectrometer analyses. The authors point out, however, that this may be due to diffusion in and out of the catalyst pellets, particularly since the vapor phase is saturated at −78°C and nearly so at −50°C.

The principal effect of increasing the temperature was to decrease the butanes with 0, 1, and 2 deuterium atoms; those with 3 deuterium atoms were unchanged and those with more than three were increased.

Reactions of Ethylene with Deuterium. The results obtained in these experiments were similar to those reported by Turkevich *et al.*[231, 232]. Some of the results obtained with 1 millimole of ethylene, and 10 millimoles of deuterium are summarized in Table 17. At −50°C the deuterium gained 0.45 per cent H corresponding to 35 per cent D in the hydrogens of the ethanes while at 50°C the deuterium gained 5.2 per cent H corresponding to 50 per cent D in the hydrogens of the ethanes. From the analysis of the isotopic species, the per cent D in the hydrogens of the ethanes was 31 per cent D at −50°C and 42 per cent D at 50°C. Here again exchange was of minor importance at the lower temperatures and all possible deuterated ethanes were obtained. The proportions of the lighter ethanes were not as high as those observed by Turkevich *et al.*[231, 232] at 90°C. The exchange reaction was also considerably greater than addition at 90°C on the nickel wire catalyst used by Turkevich *et al.*

TABLE 17. PRODUCTS FROM REACTION OF ETHYLENE WITH DEUTERIUM[252]

Component	5 min. −50°C	35 min. −50°C	185 min. −50°	5 min. 50°C	60 min. 50°C
Ethylenes					
C_2H_4	78	13.0	0	61	6.0
C_2H_3D	0.0	0.0	0.0	0.0	0.0
Ethanes					
C_2H_6	4.7	15.6	17.8	1.8	7.2
C_2H_5D	6.6	22.2	25.6	5.8	16.5
$C_2H_4D_2$	6.5	24.0	27.4	11.9	26.4
$C_2H_3D_3$	3.3	13.6	16.1	7.3	17.0
$C_2H_2D_4$	0.9	7.0	7.8	6.1	10.0
C_2HD_5		3.5	3.6	3.8	9.1
C_2D_6		1.3	1.5	2.3	7.9

Redistribution Reaction. The results of the above experiments by Wagner *et al.* indicate clearly that addition can occur without appreciable exchange and that the redistribution of hydrogen and deuterium atoms results in the formation of all possible deuterobutane molecules. The random distribution was shown not to be due to exchange of butanes with deuterium. This was checked further by circulating 1 millimole of C_4H_9D, 0.5 millimole of 2-butene and 10 millimoles of hydrogen over the catalyst. Neither the formation of $C_4H_8D_2$ nor a reduction in the quantity of C_4H_9D occurred.

In order to determine whether or not the redistribution occurred by dissociation of the 2-butene

$$C_4H_8\ (\text{ads}) \rightarrow \underset{*}{C_4H_7}\ (\text{ads}) + \underset{*}{H}, \tag{118}$$

they did the following experiments: 5 millimoles of H_2, 5 millimoles of D_2 and 1 millimole of *cis*-2-butene was circulated over the catalyst at $-50°C$. The results were:

Kinetics of addition: first order in butene
Rate constant for addition: 0.020 min.^{-1}.
Kinetics of H_2—D_2 exchange: first order
Rate constant for H_2—D_2 exchange: 0.025 min^{-1}.

In the absence of 2-butene the rate constant for the H_2—D_2 exchange was 0.063 min^{-1}. These results indicate that at low temperatures the exchange reaction

$$D_2 + \underset{*}{H} \rightarrow HD + \underset{*}{D} \tag{119}$$

occurs during the addition reaction. However, since the rate of the exchange is much slower than in the absence of butene, the surface must be largely covered with adsorbed butene and a smaller but significant amount of adsorbed deuterium atoms. During the reaction of deuterium with 2-butene at low temperatures very little HD was formed. This indicates that the number of hydrogen atoms adsorbed on sites suitable for exchange with D_2 is small during the reaction.

Mechanism of Redistribution. The above observations led the authors to conclude that the redistribution must occur by direct transfer of hydrogen and deuterium atoms among the adsorbed hydrocarbon molecules and radicals before desorption as butane occurred: For example,

$$\begin{aligned} &CH_3\text{—}\underset{*}{C}H\text{—}\underset{*}{C}H\text{—}CH_2D + CH_3\text{—}\underset{*}{C}H\text{—}CHD\text{—}CH_3 \rightleftharpoons \\ &\qquad CH_3\text{—}\underset{*}{C}H\text{—}\underset{*}{C}H\text{—}CH_3 + CH_3\text{—}CHD\text{—}\underset{*}{C}H\text{—}CH_2D \end{aligned} \tag{120}$$

The final formation of butane might be represented as:

$$\begin{aligned} &CH_3\text{—}\underset{*}{C}H\text{—}CHD\text{—}CH_3 + CH_2\text{—}CHD\text{—}\underset{*}{C}HCH_2D \rightarrow \\ &\qquad CH_3\underset{*}{C}H\text{—}\underset{*}{C}H\text{—}CH_3 + \underset{\text{butane}}{CH_3\text{—}CHD\text{—}CHD\text{—}CH_2D} \end{aligned} \tag{121}$$

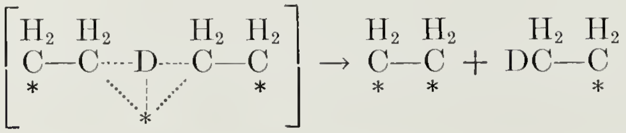
The authors write these reactions in general terms to indicate that two hydrocarbons entities of any deuterium content may react. The number of bonds to the surface and the deuterium content will be determined by the deuterium to olefin ratio as well as other factors. These general reactions will be summarized later.

Reactions involving adsorbed deuterium atoms, such as

$$CH_3\text{—}\underset{*}{C}H\text{—}CHD\text{—}CH_3 + \underset{*}{D} \rightarrow \underset{\text{butane}}{CH_3CHD\text{—}CHD\text{—}CH_3} \uparrow \tag{122}$$

are considered to be of minor importance in the formation of butane from the straight chain butenes at the lower temperatures. While deuterium or hydrogen atoms attached to the catalyst are not important in the transfer reactions, the attraction of bare nickel sites for hydrogen or deuterium may aid the interchange by lowering the activation energy through formation of a transition state such as

(123)



$$\left[\underset{*}{\overset{H_2}{C}}-\overset{H_2}{C}\cdots\underset{*}{D}\cdots\overset{H_2}{C}-\underset{*}{\overset{H_2}{C}}\right]\rightarrow \underset{*}{\overset{H_2}{C}}-\underset{*}{\overset{H_2}{C}}+D\overset{H_2}{C}-\underset{*}{\overset{H_2}{C}}$$

Distribution of Deuterium in Products. An examination of the distribution of the deuterated butanes indicates that these redistribution reactions are more rapid than the final transfer step responsible for butane formation. That is, the average residence time of the adsorbed molecules and radicals is sufficiently long to establish random distribution of deuterium before desorption as butane occurs. A small concentration of alkyl or half-hydrogenated complexes compared to adsorbed butenes would lead to this result.

For a random distribution of deuterium in the butanes the mole fraction F_n of a species containing n deuterium atoms is given by

$$F_n = \frac{10!}{n!(10-n)!}\,x^n(1-x)^{(10-n)} \qquad (27)$$

where x is the fraction of hydrogen positions which, on the average, are occupied by deuterium atoms. A comparison between the observed values at −78°C and the calculated distribution are shown in Figure 3. This is for a mixture of 10.5 mole per cent of specific species $C_4H_8D_2$ and 89.5 mole per cent of a butane containing on the average 2.13 deuterium atoms per molecule randomly distributed among the available positions on the molecule. The agreement is reasonably good except for species with two deuterium atoms. They suggest that the excess 10.5 per cent of $C_4H_8D_2$ over that expected probably arises from direct addition of deuterium atoms to the double bond as in the case of isobutene.

Other distribution curves were given for the deuterobutanes from *cis*-2-butene at 50°C and for deuteroethanes from ethylene at −50 and 50°C. At −78°C with 2-butene and at −50°C for ethane the concentration of the highly deuterated species was somewhat greater than that predicted from random distribution. The authors suggest that these highly deuterated species may arise from more or less isolated alkyl radicals which have longer residence times on the surface. During this time they might undergo a larger number of reversible exchanges with adsorbed deuterium than the average:

$$(124)\quad \mathrm{CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 + \underset{*}{D} \rightleftharpoons CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 + *{-}*}$$

Effect of Temperature. At the higher temperatures the distribution of the isotopic species differs appreciably from that calculated for random distribution. The curves are broader and both the lighter and heavier species are more abundant than predicted for the observed deuterium content. They give alternative suggestions to explain this, but favor the idea that the residence time of a given molecule may be longer or shorter than the average, with a corresponding greater or lesser chance to exchange. The distribution of extra deuterium to other molecules by the redistribution reaction will depend on the opportunities to react before final desorption as alkane. The increased extent of the exchange reaction forming deuteroalkanes at the higher temperatures will also have an effect on the composition of the products.

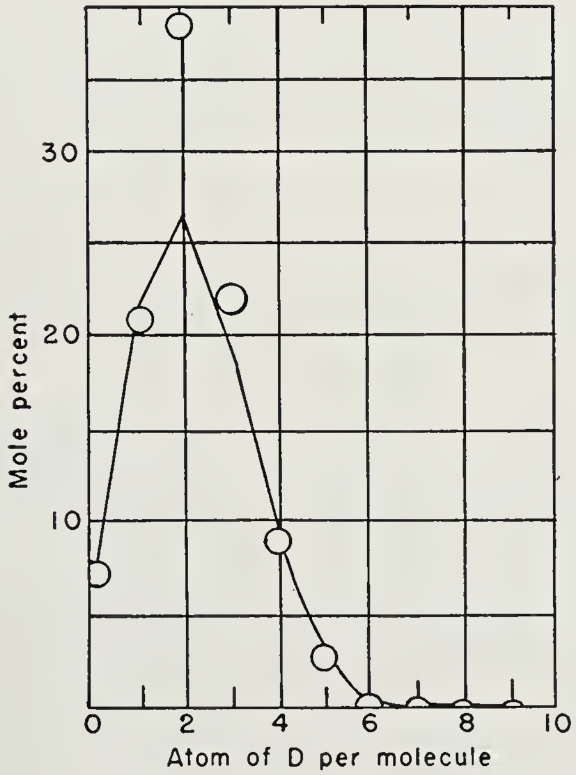
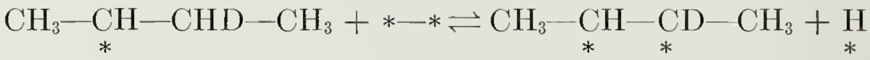
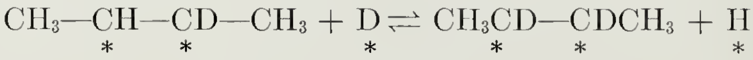


Figure 3. Calculated and observed distribution of deuterobutanes at −78°C[243].

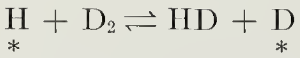
Exchange Reaction. The rate of the exchange reaction forming deutero-olefin was found to be first-order in 2-butene as was the over-all hydrogenation reaction. The authors develop equations for the ratio of light to deutero-olefin as a function of time in terms of the rate constants for exchange, k_E and the addition, k_H . At $-48°C$ the rate constant for 2-butene exchange was 0.00157 min.^{-1} while that for hydrogenation was 0.0268. At 0°C the rates were 0.0024 and 0.054, respectively; at 50°C the rate constant for hydrogenation was 0.156. They showed that the average number of deuterium atoms per butane molecule introduced into the deuterobutanes by intermediate formation of deuterobutene was given by $k_E/(k_E + k_H)$. The excess deuterium atoms introduced by this mechanism was found to be much smaller than the total observed excess, particularly at the higher temperatures. Thus the value of $k_E/(k_E+)k_H)$ at 0°C was 0.042 while the excess deuterium atoms per molecule was found experimentally to be 0.90. It was suggested that the excess deuterium arises from reactions such as

(125) 

$$CH_3—\underset{*}{CH}—CHD—CH_3 + *—* \rightleftharpoons CH_3—\underset{*}{CH}—\underset{*}{CD}—CH_3 + \underset{*}{H}$$

(126) 

$$CH_3—\underset{*}{CH}—\underset{*}{CD}—CH_3 + \underset{*}{D} \rightleftharpoons CH_3\underset{*}{CD}—\underset{*}{CD}CH_3 + \underset{*}{H}$$

(126a) 

$$\underset{*}{H} + D_2 \rightleftharpoons HD + \underset{*}{D}$$

Reactions such as these were used in the mechanisms proposed by Horiuti and Polanyi[125] and by Twigg[239]. However, the results summarized above indicate that these reactions cannot account for the redistribution in the butanes or for the distribution of the deuterobutenes at the lower temperatures. These reactions combined with the return of HD to the gas phase can account for the excess deuterium which can then be spread among the molecules and radicals on the surface by the redistribution reaction.

The distribution of deuterobutenes and deuterobutanes was entirely different in that no more than one deuterium was observed in measurable quantities in the deuterobutenes. This indicated that the desorbed deuterbutene had not been chemisorbed in the same way as those molecules that participated in the redistribution reaction. The authors conclude that the butene undergoing exchange to form butene-d_1 was not on the surface very long. They suggest a mechanism involving a cyclic interchange between butene molecules in a physically adsorbed second layer with chemisorbed deuterium atoms.

Summary of Reactions and Mechanisms. Without specifying the mode of adsorption of the olefin, the authors wrote a series of general equations which might contribute to the observed reactions in varying amounts depending on the conditions of the experiments. Rather than a list of these general reactions given by the authors,[252] similar ones using deuterium and 2-butene with chemisorption through openings of the double bond are given here:

(1) Hydrogen exchange:

$$H_2 + \underset{*}{D} \rightarrow \underset{*}{H} + HD \qquad Q = 0 \tag{127}$$

$$D_2 + \underset{*}{H} \rightarrow \underset{*}{D} + HD \tag{128}$$

(2) Hydrogen or deuterium chemisorption:

$$D_2 + *{-}* \rightarrow \underset{*}{D} + \underset{*}{D} \qquad Q = +16 \tag{129}$$

(3) Hydrogen or deuterium chemisorption and alkyl formation:

$$D_2 + CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 \rightarrow CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 + \underset{*}{D} \qquad Q = +16 \tag{130}$$

(4) Hydrogen or deuterium chemisorption and alkane formation:

$$D_2 + CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 \rightarrow CH_3{-}CHD{-}CHD{-}CH_3 + \underset{*}{D} \qquad Q = +16 \tag{131}$$

(5) Olefin chemisorption:

$$CH_3{-}CH{=}CH{-}CH_3 + *{-}* \rightarrow CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 \qquad Q = +25 \tag{132}$$

(6) Olefin chemisorption to form alkyl radical:

$$CH_3{-}CH{=}CH{-}CH_3 + \underset{*}{D} \rightarrow CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 \qquad Q = +25 \tag{133}$$

(7) Addition:

$$CH_3{-}CH{=}CH{-}CH_3 + 2\underset{*}{D} \rightarrow CH_3{-}CHD{-}CHD{-}CH_3 + *{-}* \qquad Q = +25 \tag{134}$$

(8) Redistribution

$$CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 + CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 \rightleftharpoons CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3 + CH_3{-}\underset{*}{CD}{-}\underset{*}{CH}{-}CH_3 \qquad Q = 0 \tag{135}$$

(9) Alkane formation

$$CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3 + CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_3 + CH_3{-}\underset{*}{CH}{-}\underset{*}{CD}{-}CH_3 \qquad Q = 0 \tag{136}$$

(10) Alkane formation:

(137) $\mathrm{CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3 + \underset{*}{D} \rightarrow}$

$$\mathrm{CH_3{-}CHD{-}CH_2{-}CH_3 + *{-}*} \quad Q = 0 \pm 3$$

(11) Exchange

(138) (a) $\mathrm{CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 + \underset{*}{D} \rightarrow}$

$$\mathrm{CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 + *{-}*} \quad Q = 0 \pm 3$$

(139) (b) $\mathrm{CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 + *{-}* \rightarrow}$

$$\mathrm{CH_3{-}\underset{*}{CH}{-}\underset{*}{CD}{-}CH_3 + \underset{*}{H}} \quad Q = 0 \pm 3$$

(140) (c) $\mathrm{CH_3{-}\underset{*}{CH}{-}\underset{*}{CD}{-}CH_3 \rightarrow}$

$$\mathrm{CH_3{-}CH{=}CD{-}CH_3 + *{-}*} \quad Q = -25$$

(141) (d) $\mathrm{\underset{*}{D} + \underset{*}{H} \rightarrow HD + *{-}*} \qquad Q = -16$

Other reactions such as the following can be added to explain the formation of excess H_2 as observed by Twigg[239].

(12) Formation of H_2 or HD without exchange

(142) (a) $\mathrm{CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 + CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3 +}$

$$\mathrm{*{-}* \rightarrow CH_3{-}\underset{*}{CH}{-}\underset{*}{CD}{-}CH_3 + CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 + H_2} \quad Q = +16$$

(143) (b) $\mathrm{CH_3{-}\underset{*}{CH}{-}CHD{-}CH_3 + CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3 +}$

$$\mathrm{*{-}* \rightarrow CH_3{-}\underset{*}{CH}{-}\underset{*}{CH}{-}CH_3 + \underset{*}{CH_3}{-}\underset{*}{CH}{-}CH{-}CH_3 + HD} \quad Q = +16$$

The calculated heats evolved, Q, in kcal per mole for the above reactions were obtained by the authors using the following estimated values for bond energies: H—H = 103; C—H = 97; C—C = 85; C=C = 135; Ni—Ni = 15; Ni—H = 67; Ni—C = 45. Where hydrogen or deuterium is involved in the reaction, the values for hydrogen only were used. The value of Q is not a measure of the activation energy but it does indicate which reactions may be readily reversed at low temperatures.

Because of the high heats of chemisorption of hydrogen and alkene and because of the negligible activation energy for adsorption on bare nickel sites, they suggest that the rate determining reactions are those that produce vacant sites for entry of more deuterium or hydrogen and olefin into the pool of adsorbed reactants. These are the addition reaction (7) which becomes less important at higher temperatures and step (10) and (11a) of the exchange reaction.

Since a nearly theoretical random distribution of the deuterobutanes was obtained, the surface concentration of alkene is much higher than alkyl radicals. This indicates that formation of chemisorbed deuterium or hydrogen occurs more frequently by reaction (2) than by reactions (3) and (4).

Also reactions (3) or (4) followed rapidly by (11b) would have resulted in the formation of more HD than was observed. Similarly if the alkyl radical concentration is small, reaction (5) must be more important than reaction (6). The principal reactions in the over-all addition on this basis are then (2) and (5) followed by (7), (9) and (10). Redistribution occurs largely by reaction (8) and is terminated by reaction (9) or (10).

The relative contributions of these competing reactions will be sensitive to reaction conditions such as deuterium to olefin ratio in the gas; relative adsorbabilities or surface concentrations; nature or structure of the olefin; temperature; catalyst, etc.

Exchange and Hydrogenation Reactions of Acetylene, Ethylene and Benzene

Douglas and Rabinovitch[62] have made a series of qualitative experiments on the catalytic reactions of acetylene and ethylene using both mass spectrometric and infrared analysis of the products. Their experiments were initiated by an attempt to prepare *cis*-ethylene-d_2 by addition of deuterium to acetylene. Farkas and Farkas[89] (p. 270) had pointed out that catalytic addition of hydrogen to disubstituted acetylenes usually gave the *cis*-ethylenic derivative. Mixtures of C_2H_2 and D_2 varying from 1:1 to 24:1 were allowed to flow over nickel and palladium at pressures varying from 3.5 to 60 cm with space velocities from 50 to 0.08 sec^{-1}. After removal of unreacted acetylene by absorption in alkaline mercuric cyanide and ammoniacal silver nitrate solution, mass spectrometric and infrared analysis showed that in all cases, all possible deuteroethylenes were obtained. *Cis*- and *trans*-ethylene-d_2 were formed in about equal amounts but in excess of simple statistical equilibrium, the two species accounting for 20 to 25 per cent of the total ethylenes. No appreciable variations in product distribution was observed for the various experimental conditions.

Rather pure (~98 per cent) *trans*-ethylene-d_2 for infrared calibration was prepared by reduction of $CD{\equiv}CD$ with chromous chloride by the method of Patterson and DuVigneaud[175]. The failure to obtain the *cis*-ethylene-d_2

by heterogenous catalysis as predicted, led the authors to examine such reactions in more detail. A summary of their results are given in the following sections without a detailed description of the experimental conditions.

Results of Experiments with Ethylene[62]**.** (1) Over 50 per cent exchange occurred between C_2H_4 and C_2D_4 in 2 minutes at room temperature on a nickel-kieselguhr catalyst prepared by final evacuation at 400°C. Under similar conditions 80 per cent of t-$C_2H_2D_2$ was converted to *cis*- and all other deuteroethylenes in 15 minutes. The exchange reactions were much slower on a nickel wire since 3 hours at 300°C were required to produce 90 per cent exchange. The half-time of hydrogenation with an equal molar mixture of hydrogen and ethylene at 25°C was about one minute on the nickel-kieselguhr catalyst and 3 hours on the nickel wire. Acetylene inhibited interethylenic exchange as shown by the following experiment. First, 6 cm of acetylene was admitted to the catalyst; then 6 cm of t-$C_2H_2D_2$ was added. No isomerized or exchange ethylenes were produced at room temperature in 15 minutes.

(2) When 0.8 cm of C_2D_4 was admitted to a freshly reduced nickel-kieselguhr catalyst that had been evacuated at room temperature, the ethanes formed after 15 minutes were: C_2D_6 , C_2HD_5 , $C_2H_2D_4$, $C_2H_3D_3$ in the ratios: 2.1: 1.8: 1.1: 1.1, respectively. However, when the catalyst was pumped at 400°C there was very little reaction with the hydrogen remaining on the catalyst since no exchanged ethylenes or ethanes were observed in 2 min. After 15 min. a small amount of C_2HD_3 (1%) and C_2D_6 (19%) were formed, but no other ethanes with hydrogen were present. The C_2D_6 was undoubtedly formed by the self-hydrogenation reaction of Beeck[21]. Other experiments also confirmed the conclusion that the residual hydrogen on a catalyst pumped at 400°C did not complicate the results of the interethylenic exchanges.

(3) *Trans*- to *cis*-isomerization of t-$C_2H_2D_2$ was found to be more rapid than interethylenic exchange on both the supported nickel catalyst and the nickel wire.

(4) After 5 min. with 9 cm of C_2H_4 and 3.5 cm of D_2 on a nickel-kieselguhr catalyst, the ethylene fraction consisted of 70 per cent C_2H_4 and 30 per cent deuteroethylenes, predominantly C_2H_3D. Unfortunately, no analysis of the ethane fraction was made for comparison with the results of Turkevich *et al.* [231, 232] and Wilson *ct al*[252].

The above results show that, contrary to the results of Conn and Twigg[52] (p. 290), intermolecular exchange does occur with ethylenes. This has also been shown by others[1, 40, 147] (p. 281). Douglas and Rabinovitch suggest that the negative results of Conn and Twigg may have been due to poisoning of the relatively small surface of the nickel wire used in the experiments. These experiments of Conn and Twigg have been frequently cited as evidence against the dissociative mechanism of Farkas and Farkas[82] (p. 291) in favor of the associative mechanism[111] advocated by Polanyi and his co-workers as well as by others (p. 282). Douglas and Rabinovitch favor a dissociative mechanism such as that suggested by Farkas (p. 269) or by Beeck in which acetylenic residues are formed. Both mechanisms involve donation of hydrogen to the catalyst which may subsequently bring about inter-ethylenic exchange. The authors write equations combining these mechanisms.

Although the authors present evidence that residual hydrogen on the catalyst was small and therefore was not responsible for the observed ethylenic exchanges, Bond and Turkevich[40] (p. 345) found that deuterium or hydrogen catalyzed the exchange between C_3D_6 and C_3H_6 on a supported platinum catalyst. These latter authors suggested a mechanism of the inter-exchange involving half-hydrogenated states or alkyl radicals rather than a dissociative process (p. 347). It thus appears that the results of Douglas and Rabinovitch are not necessarily conclusive in support of the dissociative mechanism.

Results of Experiments with Acetylene. (1) Self-hydrogenation of acetylene was found by Douglas and Rabinovich to occur on a nickel-kieselguhr catalyst pumped at 400°C. In 15 minutes about 50% of 0.6 cm of C_2D_2 reacted to form 10% C_2H_2, 45% C_2HD, 41% $C_2H_2D_2$, 10% C_2HD_3 and 30% C_2D_4. These results also show that appreciable quantities of hydrogen remain on the nickel catalyst evacuated at 400°C and that acetylene is much more effective is reacting with it than is ethylene. However, the production of appreciable quantities of C_2D_4 shows that extensive self-hydrogenation occurs.

(2) Appreciable inter-acetylenic exchange occurred at temperatures as low as $-80°C$ on a nickel-kieselguhr catalyst previously evacuated at 400°C. In 2 min. at room temperature 10 cm of C_2H_2 and 10 cm of C_2D_2 formed 13 per cent C_2HD while at $-80°C$ with 5 cm of each, 13 per cent of C_2HD was formed in 5.5 hours. They suggest that this inter-exchange did not result because of the hydrogen remaining on the catalyst because the amount of exchange with C_2D_2 with the hydrogen on a catalyst evacuated at room temperature was much less than the exchanges between C_2H_2 and C_2D_2. Thus 10 cm of C_2D_2 on a nickel-kieselguhr catalyst evacuated at room temperature produced only 2 per cent of C_2HD and 2 per cent of C_2H_2 in one hour.

(3) The addition of deuterium to acetylene at $-80°C$ resulted in the formation of a preponderance of *cis*-ethylene-d_2 as compared to the reaction at 25°C. In 20 hrs at $-80°C$, 44 cm of C_2H_2 and 29 cm of D_2 gave an ethylene product consisting of 50% *cis*-$C_2H_2D_2$, 20% *trans*-$C_2H_2D_2$, 15% C_2H_3D, and 10% C_2HD_3. These results are in accord with conclusions of

Farkas and Farkas[89]. The authors suggest that the *trans*-compound results from isomerization of newly formed *cis*-ethylene-d_2.

(4) The products obtained from the reaction of acetylene with a mixture of H_2 and D_2 at −80°C are nearly the same as those obtained from the reaction of acetylene with equilibrated H_2, HD and D_2. For example, with 45 cm of C_2H_2, 15 cm H_2 and 15 cm of D_2 at −80°C for 22.5 hrs, the ethylenes obtained consisted of: 10% *cis*-$C_2H_2D_2$, 15% *trans*-$C_2H_2D_2$, 20% C_2H_3D, and 35% C_2H_4. The equilibrated mixture gave 10% *cis*-$C_2H_2D_2$, 10% *trans*-$C_2H_2D_2$, 25% C_2H_3D, and 40% C_2H_4.

If addition had been by independent hydrogen and deuterium molecules, the H_2—D_2 mixture should have yielded *cis*-ethylene-d_2 and light ethylene. The similarity in the products obtained in the two experiments indicates a scrambling of the hydrogen and deuterium and therefore rules out a mechanism involving simultaneous addition of two atoms of the same molecule, whether adsorbed or in a van der Waals layer or not. The mechanism of addition must involve hydrogen or deuterium atoms as has also been shown by Twigg[239], Turkevich *et al.*[231, 232], Wilson *et al.*[252], Bond and Turkevich[40], and Taylor and Dibeler[220]. A general review of the addition of hydrogen to triple bonds has been written recently by Bond[33].

Deuterium Reactions with Ethylene on Metal Films. Kemball[141] examined the interaction of deuterium and ethylene on evaporated films of nickel, tungsten, rhodium and iron at −100°C. The procedure was similar to that used in his studies of the exchange of deuterium with saturated hydrocarbons described in a previous section (p. 325). The investigation was undertaken to compare the behavior of unsaturated and saturated hydrocarbons. Comparison could also be made with the results obtained by Turkevich, *et al.*[231, 232] on a nickel wire at 90°C and by Wilson *et al.*[252] on a nickel-kieselguhr catalyst between −50 and 50°C.

The preparation of the metal films and the reaction system were similar to that described by Kemball previously[137, 138]. In most of the experiments about 2.7 mm of ethylene and 8.1 mm of deuterium were admitted to the 180 ml reaction vessel at −120°C. After the temperature was adjusted to −100°C, the mass spectra were taken at intervals during the reaction using 11.0 and 13.4 v electrons for the ionization. From the mass spectrometer data, he was able to calculate the concentration of all deuterated ethane and ethylene species.

A series of curves were given showing the change in percentage of each ethylene and each ethane with time on each of the four metals. These will not be reproduced here, but the general behavior on nickel, for example, was similar to the results by Turkevich *et al.*[231, 232] and Wilson *et al.*, although with a somewhat different distribution. The initial distributions of the deuteroethylenes and deuteroethanes are given in Table 18 and the final distribution in the ethanes are shown in Table 19. Rates (R_1) of deuteration at −100°C on Fe, Ni, Rh, and W in per cent per min per 10 mg of catalyst were, respectively, 1.54, 2.30, 18.0, and 3.42. The exchange rates (R_2) in D atoms per 100 molecules per min per 10 mg of catalyst were 3.60, 5.25, 18.3 and 2.6 for each of the above metals, respectively. From these values, the ratio of the rate of exchange to rate of deuteration were: 2.34 for Fe, 2.28 for Ni, 1.02 for Rh and 0.08 for W.

TABLE 18. INITIAL DISTRIBUTION OF PRODUCTS DURING THE REACTION OF DEUTERIUM WITH ETHYLENE ON METAL FILMS[141]

Catalyst	Ni	Fe	Rh	W
Ethylene				
d_1	46.7	55.5	34.4	7.0
d_2	13.2	9.4	7.0	—
d_3	2.7	1.3	1.7	—
d_4	0.7	0.2	0.9	—
Ethane				
d_0	7.8	13.7	8.4	3.1
d_1	12.5	9.2	14.4	14.7
d_2	9.5	6.6	15.8	69.8
d_3	4.0	2.4	7.4	4.5
d_4	2.0	1.0	5.0	0.7
d_5	0.8	0.5	3.6	0.2
d_6	0.2	0.2	1.4	—

TABLE 19. DISTRIBUTION OF FINAL PRODUCTS IN THE REACTION OF DEUTERIUM WITH ETHYLENE[141]

Ethane	Random Dist.	Rh −104°C $3D_2:1C_2H_4$	Fe −100°C $3D_2:1C_2H_4$	W −100°C $3D_2:1C_2H_4$	Ni −100°C $3D_2:1C_2H_4$	Ni −92°C $9D_2:1C_2H_4$	Ni* −50°C $10D_2$: $0C_2H_4$	Ni† 90°C $2D_2:1C_2H_4$
d_0	8.8	11.5	20.1	4.8	17.9	12.4	17.8	8.0
d_1	26.3	27.2	28.4	15.5	26.8	29.9	25.6	29.5
d_2	32.9	29.1	22.1	70.5	23.2	25.4	27.4	25.1
d_3	22.0	13.7	12.7	6.7	14.0	14.3	16.1	16.7
d_4	8.2	9.1	8.6	1.6	9.6	9.7	7.8	11.8
d_5	1.7	6.8	5.2	0.5	5.9	5.9	3.6	6.9
d_6	0.4	2.6	2.9	0.14	2.6	2.4	1.5	2.0
Ave D per molecule	2.00	2.10	1.89	1.89	1.99	2.06	1.87	2.24

* Results of Wilson *et al.*[252] on nickel-Kieselguhr.

† Results of Turkevich *et al.*[231, 232] on nickel wire.

The rates of exchange were determined as follows. Although the percentages of deuteroethylenes vary in a complicated manner with time, the over-all rate of exchange was obtained by reducing the values to a linear relation. Thus, a quantity ϕ at any time was defined by $\phi = (1)(\%d_1) + (2)(\%d_2) + (3)(\%d_3) + (4)(\%d_4)$. A plot of the results according to the integrated form of the equation $d\phi/dt = k(\phi_\infty - \phi)/\phi_\infty$ where t is the time and k is the initial rate of entry of deuterium atoms into 100 ethylene molecules, gave a straight line. Because very little H was returned to the gas phase (1.5% HD for Ni and Fe, and 5% for Rh), a value of 400 was taken for ϕ_∞. This corresponds to the ultimate value of ϕ if ethylenes had not been removed by deuteration. With tungsten where the rate of exchange was small, this rate of exchange could be obtained from the rate of change of ethylene-d_1.

The approximate value of the energy of activation between −120 and −100°C was 7 kcal/mole for both exchange and deuteration on Fe, Ni, and Rh, while on W it was 5 to 6 kcal/mole. Both reactions were independent of ethylene pressure and proportional to the square root of the deuterium pressure.

Of special interest was the distribution of the initial products. Keii[134, 135] has worked out a set of equations based on Horiuti's[121] associative reaction scheme involving hydrogen (or deuterium) atoms, ethyl radicals and ethylene molecules, and applied them to the results of Turkevich *et al.*[231, 232]. The scheme of equations used by Keii was:

$$(144)\qquad \left.\begin{array}{l} \left.\begin{array}{l} C_2H_4(g) \underset{1'a}{\overset{1a}{\rightleftharpoons}} \underset{*}{CH_2}-\underset{*}{CH_2} \\ H_2(g) \underset{1'b}{\overset{1b}{\rightleftharpoons}} \left\{\begin{array}{l} \underset{*}{H}\cdots\cdots\cdots \\ \\ \underset{*}{H} \end{array}\right. \end{array}\right\} \underset{2'}{\overset{2}{\rightleftharpoons}} \underset{*}{CH}-CH_3 \end{array}\right\} \xrightarrow{3} C_2H_6(g)$$

At the lower temperatures reaction 1b was considered to be rate determining with the other rates in the order: $1b \ll 1'b \simeq 3 \ll 2 \simeq 2'$. Most of the D(ads) formed by adsorption of D_2 was assumed to be replaced instantly by H(ads.) from reaction 2′, thus explaining the predominance of C_2H_6 in the initial stages of the reaction. Using the details of this mechanism Keii obtained agreement between predictions from his equations and the results of Turkevich *et al.*[231, 232].

Kemball chose to develop a set of equations for the distribution of the initial products without specifying detailed reactions. He used a set of four parameters related to the probabilities of the various changes that the adsorbed entities may undergo. The acetylenic complexes formed by the dissociative adsorption of ethylene on nickel was shown by Jenkins and Rideal[128] to react too slowly to play an important role in either exchange or hydrogenation. Kemball considers the important adsorbed entities to be only adsorbed ethylene and adsorbed ethyl radicals, and thus, in a sense, he does select a general mechanism for the reactions.

The reactions to which his probability parameters refer are: (a) adsorbed ethylene may either form adsorbed ethyl or desorb; (b) when ethylene reacts with adsorbed hydrogen (or deuterium) to form adsorbed ethyl radical, there is an equal chance for either end to react and a probability that it may either be deuterium or hydrogen; (c) adsorbed ethyl radicals may either revert to ethylene or leave as ethane, but in reverting to ethylene the chances of any of the three hydrogens (or deuteriums) on the methyl carbon being lost are equal; (d) there is a certain probability that the ethyl radical reacts with either deuterium or hydrogen to form ethane.

He worked out a series of eighteen simultaneous equations for the fractions of the six possible ethylenes and twelve possible ethyl radicals. These were solved using selected probability parameters to determine agreement with the experimental results. For nickel, the probabilities referred to above that gave reasonable agreement with his experiments were: $a = 3/4$ and $1/4$; $b = 2/3$ and $1/3$; $c = 12/13$ and $1/13$; $d = 1/2$ and $1/2$. Reasonable agreement in the case of tungsten was obtained when the following values were used: $a = 3/4$ and $1/4$; $b = 5/6$ and $1/6$; $c = 0.4/1.4$ and $1/1.4$; $d = 5/6$ and $1/6$.

Kemball concludes that there must be a close relation between deuteration and exchange, both of which are fast even at −100°C on all of the four metals. On the other hand, these four metals showed widely different activities for exchange of ethane with deuterium (p. 329). Iron films, for example, were inactive up to 370°C. With the metal films, he found a correlation between the production of ethanes with more or less than two deuterium atoms and the extent of the ethylene-deuterium exchange. This correlation was not found by Wilson *et al.*[252] on a nickel-kieselguhr catalyst since they observed very little exchange and a larger spread in the distribution of deuterium in the ethanes. Thus, a close relation between exchange and hydrogenation does not seem to be general for all nickel catalysts[40, 220, 231, 232].

The results for the reaction of ethylene with deuterium or tungsten showed little exchange and a high percentage of ethane-d_2. A comparison of these results with those obtained by the exchange of ethane with deuterium (p. 331) indicated to him that an ethyl radical, whether formed from dissociative adsorption of ethane or by half hydrogenation of ethylene, has little chance of forming a chemisorbed ethylene molecule. The distribution of products on tungsten is considerably different from that on Ni, Fe and Rh, and in neither case did they follow a random distribution of two deuterium atoms per molecule. Differences between the mean number of deuterium atoms in the deuterated ethanes and two is accounted for by the production of HD which remains in the excess deuterium at the end of the reactions. Higher temperatures favor the production of HD, as illustrated by the results at 90°C on a nickel wire.

Other than the implications involved in Kemball's calculation of the distribution of deuterated products, he does not write a detailed scheme of equations for a mechanism. However, he doubts that Jenkins and Rideal's[128] conclusion (p. 301) with respect to the absence of chemisorbed ethylene is valid during hydrogenation conditions. He also points out that Horiuti's[121] mechanism does not provide for a Rideal type reaction between a gas molecule and a chemisorbed entity as used by Twigg[239] to explain the kinetics.

Further, he questions some of the arguments of Wilson *et al.*[252] for the re-distribution of hydrogen and deuterium by direct transfer between adsorbed olefin and adsorbed alkyl radicals. In particular, he doubts their argument, that if appreciable quantities of hydrogen atoms are on the surface HD should be returned to the gas phase by the mechanism of Couper and Eley[55]. This mechanism involves a complex of three hydrogen atoms on a single site. On this basis, Wilson *et al.* concluded that reactions involving chemisorbed hydrogen atoms were unimportant. The experiments of Jenkins and Rideal, however, show that appreciable quantities of chemisorbed hydrogen can be present on a surface covered with dissociatively adsorbed ethylene. By assigning one probability for the entry of deuterium when an adsorbed alkyl was converted to alkane, and another when adsorbed alkene is converted to adsorbed alkyl, the observed percentages of d_0 and d_1 molecules could be accounted for. Wilson *et al.* had used the same probability for the two reactions in support of their re-distribution mechanism.

Thus, it still appears that there is no general agreement on the mechanism of such a simple reaction as that between ethylene and deuterium. Even with instruments such as the mass spectrometer, which can give detailed information on all the products of the reaction, the mechanism cannot be deduced with certainty. Further experiments are needed on the effect of pressure, temperature, and nature of the catalyst. In the end, it may be found that certain aspects of the several mechanisms proposed may be involved.

Deuterium Reactions with Benzene on Metal Films. Anderson and Kemball[3a] have reported some results on the mass spectrometric examination of the distribution of products from exchange and addition reactions of deuterium with benzene on metallic films of W, Pt, Pd, Ag. Silver was not active for deuteration although some exchange ocurred. The relative activities of these films were in the order given for both exchange and deuteration. In the deuteration reaction, the major product in the initial stages was cyclohexane-d_6 together with other highly deuterated cyclohexanes. It thus appears that deuteration is essentially the addition of six deuterium atoms to each benzene molecule with little redistribution as occurs with the aliphatic unsaturated hydrocarbons.

Exchange of benzene with deuterium on the metal films apparently occurs by a process separate from deuteration, since relatively large amounts of benzene-d_1 appear in the initial stages. They suggest that an adsorbed phenyl radical is important in the process and that it undergoes exchange like the saturated hydrocarbons retaining its resonance structure. Multiple exchanges are assumed to occur by a process of repeated second point adsorptions involving further dissociative adsorption of the phenyl radicals to form adsorbed phenylene radicals. These are then converted back to phenyl radicals, which on leaving the surface, contain more than one deuterium atom.

Pressure dependencies for the two reactions were found to be

$$\text{Deuteration rate} \sim P_{C_6H_6}^{0.2} P_{D_2}^{0.8}$$

$$\text{Exchange rate} \sim P_{C_6H_6}^{0.1} P_{D_2}^{0.5}$$

with uncertainties in the exponents of about 0.2. Equations were given to explain distribution of deuterium in the exchanged benzenes.

Reaction of Butenes with Deuterium

One of the first applications of mass spectrometric methods to the study of the interaction of deuterium with olefins was by Dibeler and Taylor[59, 60, 220]. They re-examined certain aspects of the exchange, addition, double bond migration, and *cis-trans* isomerization reactions of 1-butene and 2-butene. A nickel wire catalyst was used in an apparatus very similar to that described by Twigg[237] for an earlier investigation of these same reactions.

Types of Reactions. When butene and hydrogen interact on a nickel wire catalyst below 150°C the following reactions occur: addition, double bond migration, and *cis-trans* isomerization of butene-2. However, when deuterium is used in the place of hydrogen, the complexity of the reactions increases, but also the information obtainable increases. For this system, the following reactions can now be investigated with modern instrumental methods: (1) addition; (2) double-bond migration; (3) *cis-trans* isomerization of butene-2; (4) exchange; (5) position at which exchange occurs; (6) composition of exchanged butenes; (7) composition of deuterobutanes; (8) return of HD or H_2 to gas phase; (9) equilibration between $H_2 + D_2$; (10) reaction products with mixtures of $H_2 + D_2$. In addition to these we can now add the hydrogen redistribution reaction found by Turkevich *et al.*[40, 231, 232], Wagner *et al.*[243, 244, 252], and Weiss and Taylor[247].

Analytical Methods. Dibeler and Taylor attempted to follow a number of reactions either simultaneously or under as nearly the same conditions as practicable. The analytical methods used to follow these reactions were:

- Mass spectrometer
  - Hydrogenation: butane-masses 58, 57, 43
  - Deuteration: butane-d_2—mass 60, etc.
  - Exchange: butene-d_1, d_2, d_3—masses 57, 58, 59 etc.
  - Position of deuterium: increase of ion abundances with time of reaction for masses, 16, 30, 42 vs. 57
- Infrared spectrometer
  - Double bond shift: 1 butene → 2 butene (900 cm^{-1})
  - Isomerization: *cis*-butene-2 → *trans*-butene-2 (940 cm^{-1})

Originally the determination of addition of deuterium was based on the idea that the butane formed in the initial stages of the reaction should be predominantly butane-d_2 (mass 60). It was thought that butanes of higher mass would result from addition to exchanged olefin, and that butanes of lower mass than 60 would result only from hydrogen returned to the gas phase as a result of exchange. On this basis, the increase in mass 60 during the initial stages of the reaction should have been a reasonable measure of the addition reaction. When it became evident that the processes were not this simple, Weiss and Taylor[247] re-examined the addition and exchange reaction by separating the butanes from the butenes before analysis. The results of these experiments will be discussed later. It is now known, of course, that mass 60 cannot be used to monitor the addition reaction. Light butane is one of the most abundant initial products and all deuterated butanes are obtained directly without proceeding through exchanged butenes. Although this behavior affects some of the calculations from mass spectral data obtained by Dibeler and Taylor, the general results will be summarized here.

Rates and Activation Energies. The results of experiments using 50 mm of reactants at various temperatures are recorded in Table 20 and given graphically in Figure 4. The "rate constants" listed were obtained from the slopes of the first order plots of the data for initial rates; and the activation energies E were from plots of the logarithm of this k against $1/T$.

Addition of Hydrogen. The results listed in Table 20 indicate that the rates and activation energies for addition of hydrogen to *cis*- and *trans*-2-butene were nearly the same. At higher temperatures (135°C) the rates of hydrogen addition to butene-1 and butene-2 were not greatly different, but at lower temperatures, addition to 1-butene occurred more rapidly by a factor of about 1.5. Activation energies were 2.0 ± 0.3 kcal for 1-butene and 3.5 ± 0.7 kcal for 2-butene.

Double-Bond Migration in the Presence of Hydrogen. When butene-1 was admitted to an activated nickel wire in the absence of hydrogen or deuterium, the double-bond did not shift. However, in the presence of hydrogen the double bond in general shifted faster than addition took place. At 60°C double bond migration and addition of hydrogen were approximately the same, but at 135°C, the rate of double bond migration was greater than addition of hydrogen by a factor of 2.5. Twigg[237] found the rate of double-bond migration to be 2.5 times greater than addition of hydrogen at 65°C. Apparently the relative rates are sensitive to the nature of the catalyst surface. The energy of activation for double bond migration

TABLE 20. SUMMARY OF "RATE CONSTANTS" AND ACTIVATION ENERGIES[220]

PROCESS	1-BUTENE			*cis*-2-BUTENE			*trans*-2-BUTENE		
	t	k	E	t	k	E	t	k	E
	°C.	$hr.^{-1}$	kcal.	°C.	$hr.^{-1}$	kcal.	°C.	$hr.^{-1}$	kcal.
Hydrogenation (H_2)	60	1.2		75	0.7		75	0.7	
	80	1.4							
	100	1.6							
	120	1.8		120	1.5		120	1.4	
	135	2.0	2.0 ± 0.3	130	1.9	3.5 ± 0.7	130	1.6	3.5 ± 0.7
Double-bond shift (H_2)	60	1.2							
	80	2.0							
	100	2.8							
	120	3.7							
	135	4.9	5.0 ± 0.5						
Double-bond shift (D_2)	55	0.25							
	83	0.5							
	93	0.7							
	105	0.9							
	130	1.8	7.8 ± 0.8						
Exchange (D_2)	55	0.23							
	83	0.5		75	0.32		75	0.32	
	93	0.6							
	105	0.8		120	1.2		120	1.1	
	130	1.6	7.1 ± 0.7	130	1.5	8.0 ± 1.0	130	1.8	8.0 ± 1.0
Cis-trans isomerization (H_2)				75	3.2		75	2.6	
				120	9		120	7	
				130	9	5.3 ± 1.0	130	9	4.8 ± 1.0
Cis-trans isomerization (D_2)				75	2.8		75	3.1	
				120	7		120	6	
				130	8	5.3 ± 1.0	130	8	4.8 ± 1.0

was higher than that for hydrogenation (5.0 ± 0.5 kcal compared to 2.0 ± 0.3 kcal) even though the rate of double bond migration was greater. This indicates that the rate controlling steps for the two reactions are different.

Double-Bond Migration and Exchange with Deuterium. In the presence of deuterium, addition, double bond migration, and exchange can occur simultaneously during reaction with butene-1. Examination of the data in Table 20 and Figure 4 indicates that the rates of double bond migration and exchange were about the same over the temperature range from 55 to 130°C. The rate of double bond migration was slightly faster, which might result from the presence of hydrogen from the exchange reaction. Hydrogen was found to be more effective than deuterium by a factor of 2.5 to 4.5 in causing the double bond shift. These results are different from those reported by Twigg[237] in which he found that the rate of double bond shift was five to six times greater than the rate of exchange instead of about the same rate. More experiments are needed to determine the reason for

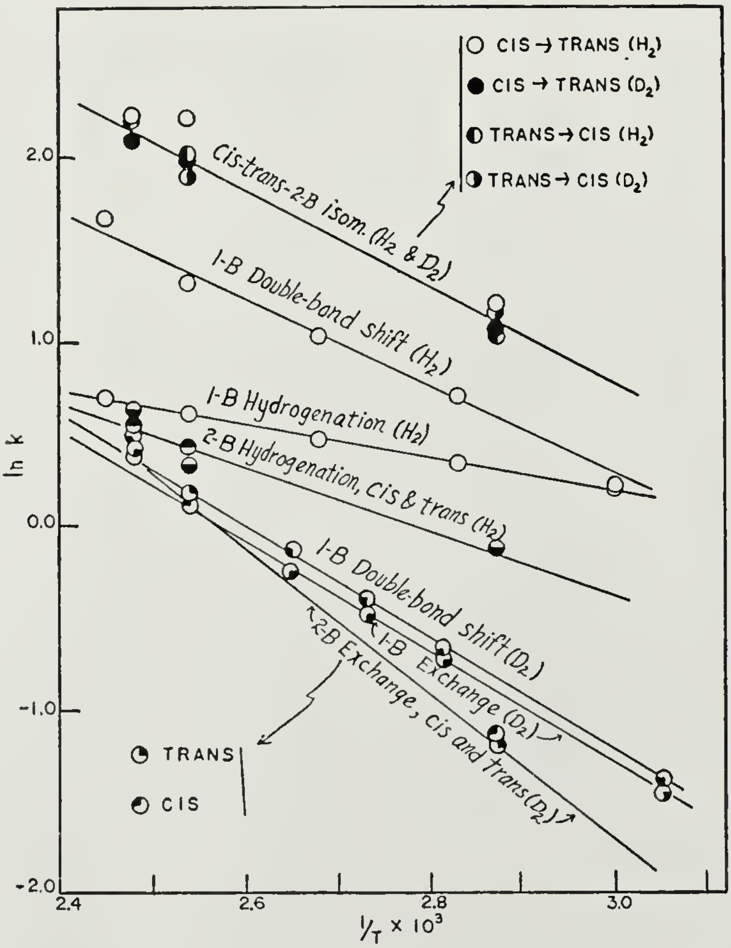


Figure 4. Summary of first-order constants *vs.* $1/T$.[220]

this great difference, but it might be related to the method by which exchange was measured. In his experiments, exchange was measured by the rate of return of hydrogen to the gas phase. The results of Bond and Turkevich[40] with propylene and deuterium on platinum indicated that the rate of return of hydrogen under certain conditions is small (p. 344).

The equivalence in the initial rates of exchange and double bond migration reported here indicates that the process of exchange and double bond shift might be closely related. It would appear that the double bond shifts each time an exchange occurs. Similar results were obtained earlier by Turkevich and Smith[234], for the exchange and double bond shift with phosphoric acid catalysts. They arrived at an equality in these rates from activation energies of reactions involving tritium and a number of acid catalysts.

A comparison of the rates of double-bond shift of butene-1 in the presence of hydrogen and deuterium shows that, at 60°C the double bond migrates about 4.0 times faster and that at 130°C, 2.4 times faster in the presence of hydrogen than in the presence of deuterium. There is, of course, the possibility of trace impurities present in the deuterium but not in the hydrogen causing such an effect. Activation energies are 5.0 ± 0.5 kcal in the presence of hydrogen and 7.1 ± 0.7 kcal in the presence of deuterium. These results indicate that the breaking of a hydrogen or deuterium bond is involved in the rate controlling step of the double bond migration.

Since the initial rate of increase of mass 57 was about the same for 1-butene and 2-butene, the rate of exchange of one hydrogen with one deuterium appeared to be about the same. However, the ratio of mass 58 to 57 and of mass 43 to 42 was considerably larger for the reaction of 2-butene with deuterium as shown in Table 21. There is a significant difference in the distribution of the products from the two reactions, which, when studied in more detail, should lead to further detailed information on the behavior of these two molecules on the surface.

During the initial stages of the exchange of deuterium with 1-butene, it was found that the rate of increase in abundance of ions of mass 16, 30, and 42 was about the same as that of ions of mass 57. A consideration of possible dissociation fragments indicates that this is consistent with the idea that the first deuterium atom goes to the end carbon atom. With the aid of gas chromatography it will be possible to separate 1-butene and 2-butene and determine this more definitely. That is one can determine whether each 1-butene exchanged has in fact, isomerized to 2-butene.

Comparison of the exchange rates for *cis* and *trans*-2-butene shows that they were approximately the same. Since, as will be discussed in the following section, the *cis*-trans isomerization was several times faster than exchange, the observed rate of exchange was essentially that of an equilibrium mixture and therefore little difference would be expected between the rate starting with either the *cis* or the *trans* form of 2-butene.

Cis-Trans Isomerization. Neither *cis*- nor *trans*-2-butene isomerized in 18 hrs at 130°C on the activated nickel wire in the absence of hydrogen or deuterium. However, both *cis*-to-*trans* and *trans*-to-*cis* isomerizations occurred rapidly when the reactor was filled with 50 mm of hydrogen and 50 mm of the 2-butene. No significant difference was observed when deuterium was substituted for hydrogen. It was significant that the presence of hydrogen or deuterium is required for the isomerization yet there is no appreciable difference in the rates. If the breaking of a hydrogen bond were involved in the rate controlling step, a difference in rates would be expected.

Table 21. Portion of Mass Spectral Data for Products of Reaction of 2-Butene and 1-Butene with Deuterium[220]

Mass	10 cm *cis*-2-butene + 10 cm deuterium 75° C			10 cm 1-butene + 10 cm deuterium 83°C			
	Time (min)						
	0	15	30	0	10	20	30
41	540	920	745	735	825	820	850
42	18.5	128	187	24.2	95.2	191	219
43		42.9	77.3		7.0	15.2	15
44		4.7	11.5			0.5	1
56	239	408	336	257	300	283	326
57	11.3	63.2	90.1	11.4	36.7	58.4	90.5
58		20.0	36.4		1.3	5.1	10.0
59		2.2	5.5			0.4	3.3
60			1.2				1.0

In the presence of hydrogen or deuterium, *cis-trans* isomerism is the fastest of the several possible reactions in the system. At 75°C, for example, *cis-trans* isomerization was eight to ten times faster than the exchange with deuterium and four to five times faster than hydrogenation. This shows that different rate controlling steps are operative in all of these reactions. The results also explain why *cis*- and *trans* 2-butene exchange or hydrogenate at about the same rate because an equilibrium mixture is formed rapidly.

Effect of Pressure. A few experiments on the effect of pressure gave the following results for initial rates of reaction. So long as hydrogen was in excess and not above 100 mm, the initial rates of addition and of double bond shift were roughly proportional to the square root of the initial hydrogen pressure and to the square root of the initial 1-butene pressure. Approximately the same pressure dependencies were found for exchange and double bond shift with deuterium and 1-butene. That is, the initial rates of both reactions varied roughly as the square root of the initial deuterium pressure and as the square root of the initial 1-butene pressure as long as deuterium was in excess. These results are in agreement with those obtained by Twigg[237].

At pressures above 100 mm for either hydrogen or butene the dependence on pressure changed. In this pressure range, an increase in hydrogen or deuterium pressure did not change the rate appreciably except at the highest pressures (400 mm) where the rates were decreased when the 1-butene pressure was low. At the higher hydrogen or deuterium pressures (100 mm and above), increases in the 1-butene pressure increased the rate approximately proportionately to the change in the initial 1-butene pressure. However, when the 1-butene pressure was two to four times the pressure of hydrogen or deuterium, even at low total pressures, the reactions were markedly inhibited and not reproducible. This indicates that butene is somewhat more strongly adsorbed than hydrogen and that excess butene can inactivate sites normally effective in the reactions.

Addition of Hydrogen and Deuterium. A portion of the mass spectral data for the products of the reaction of deuterium with 1-butene is given in Table 22. If two deuterium atoms from the same molecule added to the double bond, or even if chemisorbed deuterium atoms added separately, one would expect to obtain a butane of mass 60 ($C_4H_8D_2$). It is apparent from Table 22 that mass 60 did not form in appreciable amounts during the initial stages of the reaction.

From the above behavior, Dibeler and Taylor assumed that most of the deuterium in the initial stages reacted via exchange rather than addition and that the higher masses resulted from successive or multiple exchanges of butene molecules. The hydrogen from the exchange could then add to butene accounting for the decrease in pressure of the system. Without separation of the butenes from the butanes it was not possible to unravel the mass spectral data because electron dissociation patterns of the deuterated molecules were not known. For this reason Weiss and Taylor[247] undertook a more detailed investigation of the butene and butane fractions from the reaction of 1-butene with deuterium.

Distribution of Deuterium in Butane and Butene Fractions. When 10 cm of D_2 and 10 cm of 1-butene were reacted at 90°C on a nickel wire catalyst in a system similar to that used by Dibeler and Taylor, the compositions of the butane and butene fractions obtained are illustrated in Figures 5 and 6. It can be seen from Figure 5 that, in the initial stages of the reaction, one of the most abundant products is butane containing no deuterium. This is followed in abundance by butanes with one, two, three, four, etc., deuterium atoms. The relative abundance of these deuterobutenes is about that expected for a random distribution of deuterium before desorption as butane. These results are similar to those obtained by Turkevich *et al.*[231, 232] for ethylene, Bond and Turkevich[40] for propylene and by Wagner *et al.*[243, 244, 252] for 2-butene, as described in previous sections of this chapter.

Table 22. Portion of Mass Spectral Data for the Exchange of Deuterium with 1-Butene at 55°C[220]

m/e	Time (min.)					
	0	30	60	90	120	150
15	26.3	25.5	27.1	23.8	24.1	24.0
16*	0.4	2.7	6.2	9.7	12.7	10.0
29	120.	153.	171.	148.	137.	140.
30	7.3	25.0	46.1	67.0	68.5	69.5
31		2.0	4.0	5.3	6.7	7.0
32					4.0	4.5
41	758.	780.	802.	725.	671.	588.
42	27.5	137.	234.	319.	335.	325.
43		9.6	21.7	33.7	44.5	73.
44				5.5	14.3	18.
56	280.	286.	305.	296.	254.	200.
57	12.3	47.1	85.1	110.	122.	125.
58		1.5	7.0	12.6	19.0	33.
59			0.5	3.7	7.9	18.
60				0.5	1.7	3.5
61					1.0	1.9

* Values for mass 16 are somewhat uncertain because of background corrections due to water vapor.

It is clear that under the conditions of these experiments, the reaction between $CH_2{=}CH_2CH_2CH_3$ and D_2 does not result in the formation of $CH_2D{-}CHDCH_2CH_3$ alone. Instead all possible deuterobutanes are obtained. For this reason mass 60 cannot be used to monitor the addition of deuterium to a double bond as was at first assumed by Dibeler and Taylor. In fact it is difficult to define what is meant by the rate of addition of deuterium to the double bond of butene, especially when light butane is one of the principal initial products.

The rate of exchange with deuterium on the particular nickel wire catalyst used was about twice the rate of addition as measured by the decrease

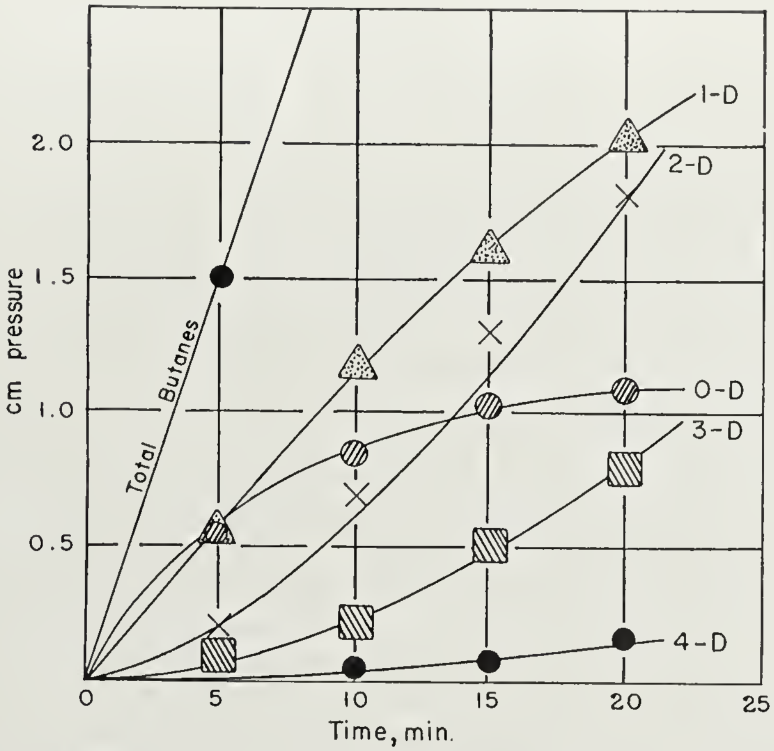


Figure 5. Deuterobutanes formed during the reaction of 10 cm of butene with 10 cm of deuterium at 90°C on a nickel wire catalyst.[220]

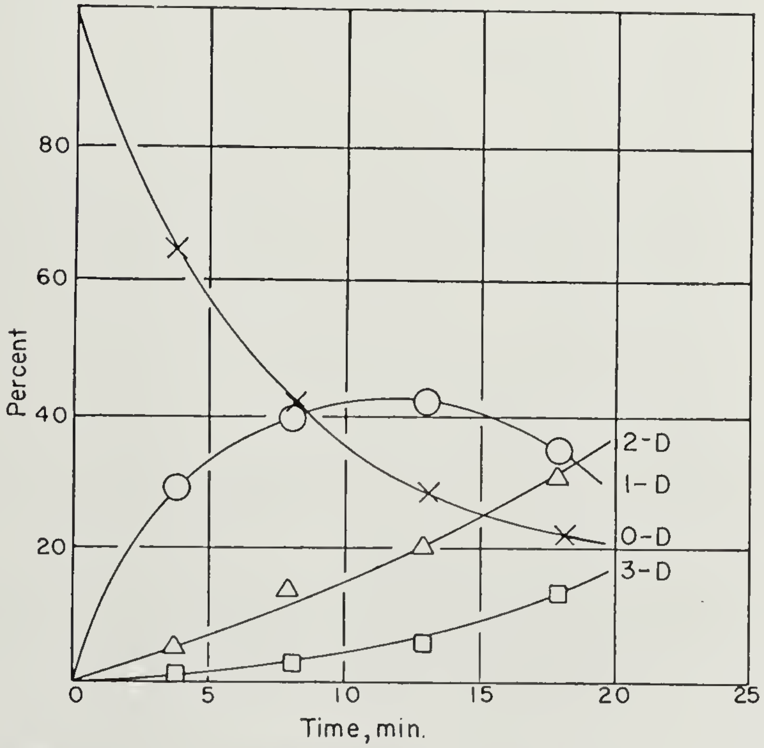


Figure 6. Distribution of deuterobutenes from the reaction of 10 cm of butene with 10 cm of deuterium at 90°C on a nickel wire catalyst.[220]

in pressure of the system. Butenes were recovered from the products by reaction with bromine water followed by regeneration of the butenes with zinc. Figure 6 shows the distribution of the deuterobutenes as a function of reaction time. This distribution indicates that the second deuterium atom enters the butene molecule by exchange of butene-d_1. In other words, the higher deuterated butenes seem to occur as a result of successive single exchanges rather than multiple exchanges during a single adsorption. Contrary to this, the higher deuterated butanes seem to result from multiple exchanges.

Apparently, once a butene molecule is adsorbed on sites appropriate for formation of butane, it is not likely to reevaporate as butene. Instead it remains on the surface long enough to equilibrate with the adsorbed deuterium and hydrogen before it leaves as a butane molecule. Otherwise, butenes with more deuterium atoms in the molecule would be observed. Thus, the exchange and the addition reactions may not be as closely related as sometimes thought, and indeed the two reactions probably occur on different types of sites and by quite different mechanisms.

The relative rates of exchange, return of hydrogen to the gas phase, and redistribution of hydrogen and deuterium among the adsorbed species, will all affect the composition of the products. These relative rates will undoubtedly depend upon the pressures of the reactants, the temperature and particularly on the catalyst.

Summary of Observations to be Explained. Among the experimental observations of Dibeler and Taylor and Weiss and Taylor the following were listed as significant with respect to mechanisms for the reactions. These apply to initial reactions on a nickel wire catalyst in the temperature range 50 to 135°C and at pressures of about 10 cm for each reactant.

(1) Hydrogen or deuterium was required for double bond migration of 1-butene and for *cis-trans* isomerization of the 2-butenes. For reproducible results it was necessary that some hydrogen or deuterium be present in the reaction vessel before the butene was admitted.

(2) The initial rate of double-bond migration in the presence of hydrogen was greater than in the presence of deuterium by 4 times at 60°C and 2.5 times at 130°C. Activation energies were 5.0 kcal in the presence of hydrogen and 7.8 in the presence of deuterium.

(3) The initial rate of double bond migration for 1-butene in the presence of deuterium was approximately the same as the initial rate of exchange. Deuterium seems to appear on the terminal carbon atom next to the double bond.

(4) Both *cis*- and *trans*-2-butene exchanged the first deuterium atom at about the same rate as 1-butene, but the distribution of butanes and

the more highly exchanged butenes were different for 2-butene than for 1-butene.

(5) *Cis*-to-*trans* and *trans*-to-*cis* isomerization occur at about the same rate, but both rates are several times faster than exchange or addition. Even though hydrogen or deuterium was required for the *cis-trans* isomerizations, no marked differences in rates were noted when deuterium was used in the place of hydrogen.

(6) Rates of addition of hydrogen (activation energy 2.0 kcal) and of double bond migration of 1-butene in the presence of hydrogen (activation energy 5.0 kcal) were about the same at 60°C but at 135°C double bond migration was about 2.5 times faster.

(7) The reaction of deuterium with 1-butene or 2-butene did not result in the formation dideuterobutane ($C_4H_8D_2$) alone. Light butane as well as a roughly random mixture of all possible deuterobutanes resulted.

(8) The exchanged butenes were not highly deuterated and followed a different distribution pattern than the deuterobutanes.

(9) The dependence of the initial rates of the reactions on pressure was influenced by the relative pressures of the gases, the total pressure, and the catalyst preparation. With excess hydrogen and with pressures of the order of 50 mm, all of the reactions appeared to have about the same pressure dependencies, i.e., proportional to the square root of initial butene pressure, and to the square root of the hydrogen or deuterium pressure. In one series of reactions the rates appeared to be independent of the butene pressure.

Mechanisms. Items 1 and 2 indicate that hydrogen or deuterium is necessary for double bond migration and that the breaking of a hydrogen or deuterium bond is involved in the rate controlling step. Otherwise there would not have been a factor of from 2.5 to 4.0 in relative rates.

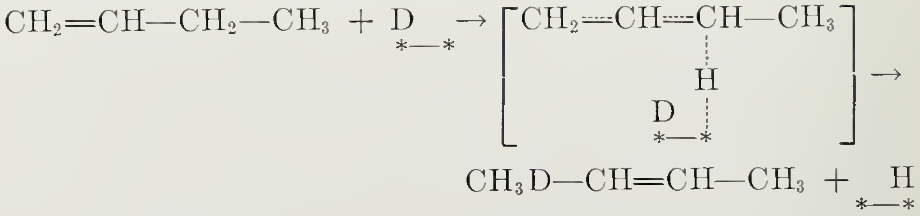
Item 3 indicates that the double bond probably shifts each time exchange occurs unless some accidental circumstances caused the reactions to occur at the same rate over the whole temperature range.

Item 6 indicates that the rate controlling step for hydrogenation is different from that of exchange and double bond migration since both the rates and the activation energies are different. The distribution of deuterated products during reaction with deuterium (items 8 and 9) also indicate little connection between the addition and the exchange reaction.

The low rate of formation of $C_4H_8D_2$ (mass 60) shows that two deuterium atoms do not add simultaneously to the double bond. Also the high initial rate of formation of light butane from the reaction of butene and deuterium shows that a redistribution of hydrogen occurs. Proposed mechanisms for this process have been formulated by Twigg[239], Wagner *et al.*[243, 244, 252] and Turkevich *et al.*[40].

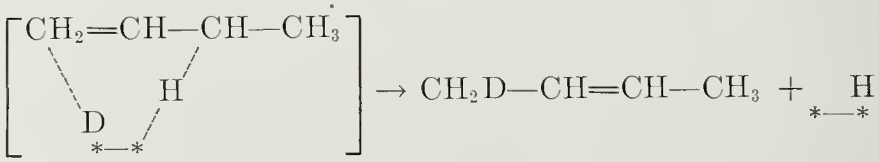
One other type of formulation suggested by Dibeler and Taylor for exchange and double-bond migration was:

(145)



The complex is aided in its formation by allyl radical resonance and the tendency of hydrogen to form a metal-hydrogen bond. As deuterium goes to the first carbon atom, the double bond shifts, giving one exchange for each double bond shift. This is essentially the hydrogen switch mechanism originally proposed by Turkevich and Smith[234]:

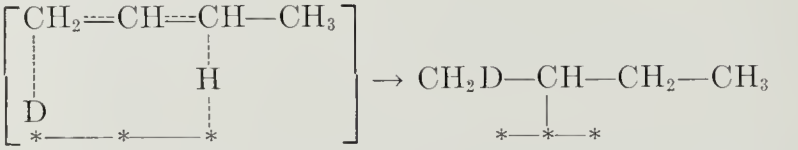
(146)



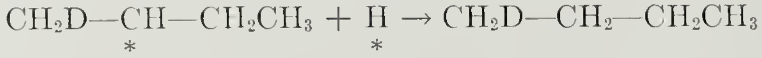
The initial presence of hydrogen or deuterium may be required to reduce the extent of strong two-point adsorption across the double bond and to produce more active isolated nickel sites. Without hydrogen or deuterium, or with excess butene, such adsorption could slow down the reactions. The intermediate postulated above can also allow *cis-trans* isomerization, the presence of hydrogen or deuterium being required to prevent extensive adsorption across the double bond and covering of the surface. If a more complete investigation shows that the pressure dependencies of all the reactions are, in fact, the same, the idea of a common intermediate for the reactions may have more significance.

For the addition reaction, the complex could be assumed to proceed via another path if it were adjacent to a site appropriate for the formation of a chemisorbed alkyl radical:

(147)



(148)



$$\underset{*}{CH_2D—CH}—CH_2CH_3 + \underset{*}{H} \rightarrow CH_2D—CH_2—CH_2CH_3$$

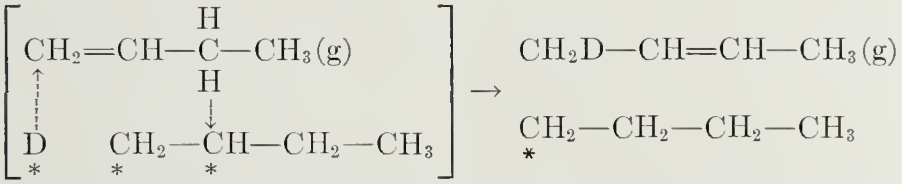
Once adsorbed in this manner the radical has a higher probability of remaining until it reacts with $\underset{*}{H}$ or $\underset{*}{D}$, or with alkyl radical to form butane. The greater the ratio of exchange to addition, the greater will be the concentration of $\underset{*}{\mathrm{H}}$ relative to $\underset{*}{\mathrm{D}}$ on the surface and the greater will be the proportions of light butane. This ratio, as well as the relative rates of some of the other reactions, appear to depend on the catalyst preparation and on temperature and pressure.

Redistribution can occur via alkyl radicals as already proposed by Wagner *et al.*[243, 244, 252] (p. 353). Such reactions as the following can also contribute to the random distribution of deuterium atoms in the butanes:

$$(149)\qquad \mathrm{CH_2D{-}\underset{*}{CH}{-}CH_2CH_3} + {*}{-}{*} \rightarrow \mathrm{\underset{*}{CH_2}{-}\underset{*}{CH}{-}CH_2CH_3} + \underset{*}{\mathrm{D}}$$

$$(150)\qquad \mathrm{\underset{*}{CH_2}{-}\underset{*}{CH}{-}CH_2{-}CH_3} + \underset{*}{\mathrm{H}} \rightarrow \mathrm{CH_3{-}\underset{*}{CH}{-}CH_2{-}CH_3} + {*}{-}{*}$$

It is possible that reactions involving gaseous butene with chemisorbed butene and chemisorbed deuterium or hydrogen could also contribute to exchange and redistribution:

(151) 

$$\left[\begin{matrix} \mathrm{CH_2{=}CH{-}\overset{H}{C}{-}CH_3(g)} \\ \mathrm{\underset{*}{D}\qquad \underset{*}{CH_2}{-}\underset{*}{\overset{H}{C}H}{-}CH_2{-}CH_3} \end{matrix}\right] \rightarrow \begin{matrix} \mathrm{CH_2D{-}CH{=}CH{-}CH_3(g)} \\ \mathrm{\underset{*}{CH_2}{-}CH_2{-}CH_2{-}CH_3} \end{matrix}$$

Not enough detailed experimental data have been obtained on the disappearance and formation of every molecular species over a sufficiently wide range of conditions to attach a number to the relative contribution of each of the many possible reactions suggested by various authors. It does seem clear that more can be learned by following all the simultaneous reactions that occur rather than by focussing attention on any one in particular. With the aid of isotopes and modern analytical methods for identifying molecular species, considerable progress has been made and more can be expected. The problem of obtaining reproducible catalysts has been one of the most difficult problems in comparing different researches. Recently developed techniques of producing metal films in high vacuum will undoubtedly simplify this problem.

THEORETICAL APPROACHES

Application of Theory of Absolute Rates of Reaction. A number of attempts have been made[76, 154, 157, 158, 162] to apply the theory of absolute reaction rates to the addition and exchange reactions of the olefins. The model chosen and the assumptions made with respect to the nature of the reactions are sometimes based on experimental conclusions that apply only to a limited set of conditions. Even here the results may not be established beyond question. From a choice of activation energies and other parameters, rates are calculated and compared with certain experimental values. If approximate agreement is found, the model and assumptions are considered to be correct and a mechanism based on these is inferred. This procedure may place undue weight on certain observed kinetics without sufficient consideration of all of the variables. For these reasons the theoretical approaches do not seem to be decisive, but there is no doubt that they are valuable. Certain mechanisms or models can be ruled out and others can be supported.

In the theoretical treatment by Eyring, Colburn and Zwolinski[76, 174a] the following assumptions were made: (a) In every surface process, the activated complex consists of the reactants and the catalyst. Where the activated state contains the same number and kind of atoms (except for catalyst atoms) of reactants as a homogenous reaction, the difference in energies of activation between the homogenous and heterogenous reaction is the heat of adsorption of the homogenous activated complex on the catalyst surface. (b) The surface reaction is considered to be a homogenous reaction between the gaseous reactants and the atoms of the catalyst. Volume phenomena, such as solution of reactants, and the effect of the reverse reaction are neglected.

A mechanism for the reaction of ethylene and hydrogen (or deuterium) was based on a model of two different gaseous reactants interacting with the surface. The kind and number of atoms in the activated complex will determine the kinetics of the over-all process, and by proper choice of an activated complex, agreement with experimental data may be obtained. They selected the following observations from the literature as the important ones which have to be explained or with which the proposed mechanism must be in agreement.

(1) Ethylene and hydrogen are rapidly adsorbed by metallic surfaces even at very low temperatures. Pumping at room temperature removes 20 per cent of the adsorbed hydrogen.

(2) Heats of adsorption on Ni vary with increased coverage from 30 to 18 kcal for hydrogen; and from 60 to 23 kcal per mole for ethylene, the average value being 41.5 kcal.

(3) The activation energy for hydrogenation is 10.7 kcal on Ni, Rh, Co, Fe, Pd, Pt, W, and Ta.

(4) The reaction rate at low temperatures can be expressed as

$$r \sim p_{\mathrm{H_2}} p^{0}_{\mathrm{C_2H_4}} \tag{28}$$

and at high temperatures as

$$r \sim p_{\mathrm{H_2}} p_{\mathrm{C_2H_4}} \tag{29}$$

(5) The over-all heat of reaction is 32 kcal per mole.

(6) The hydrogenation appears to be molecular.

The authors state that these observations are apparently satisfied only by the following mechanism. Both hydrogen and ethylene are adsorbed but ethylene tends to displace hydrogen because it is much more tightly held. The activated complex is assumed to be an ethane molecule just desorbed from its two positions on the surface. Using their best estimates for the energies of the appropriate processes and for other parameters of the system, they calculate a rate which agrees with the experimental values found by Beeck[18, 19, 28] for unoriented nickel films. The kinetics based on their model are also in agreement with those observed. Because of these agreements they conclude the above must be the reaction mechanism.

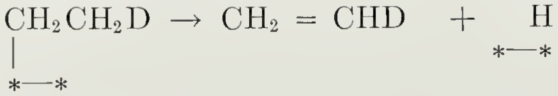
Laidler *et al.*[157, 162] have used a different model in their theoretical treatment of addition and exchange reactions of ethylene. The formulations are essentially those proposed by Wagner, Wilson, Otvos and Stevenson[243, 244, 252]. Ethylene is assumed to be adsorbed on a pair of sites and deuterium is adsorbed by dissociation resulting in deuterium atoms on single sites. Ethyl radicals may be formed by interaction between the adsorbed ethylene and the deuterium atoms. Ethane results from the interaction of an adsorbed ethyl and an adsorbed deuterium atom, or between two ethyl radicals adsorbed on adjacent sites.

In deriving the kinetic laws from absolute rate equations, they assumed that the surface is sparsely covered by all species except ethylene. They conclude that the rate of addition should vary as the deuterium (or hydrogen) pressure by either mode of ethane formation. The dependence of the rate on the ethylene pressure varied in a complex manner, passing through a flat maximum as the ethylene pressure increases. They point out that this maximum would not be predicted from Twigg's[239] mechanism (p. 299) in which hydrogen molecules react with adsorbed ethylene to form adsorbed ethyl radicals and hydrogen atoms. However, they state that the calculations of the absolute rates will not distinguish between the two mechanisms. Comparison of the calculated rates with four experimental investigations[97, 204, 224, 240] gave agreement to within a factor of 10.

Theoretical considerations with respect to exchange leads to even greater difficulty. Twigg and Rideal[240] found experimentally that addition and exchange followed the same pressure dependencies, i.e., proportional to the deuterium pressure and independent of the ethylene pressure. If both reactions occur by similar mechanisms involving adsorbed ethyl radicals as suggested by Twigg, the authors find difficulty with respect to the activation energies of the two reactions. The exchange rate was observed to be only three times that of addition even though the activation energy for exchange is 9 kcal greater. This difference in activation energy would suggest that the exchange should be 10^{-5} times the rate of addition.

The authors suggest that the data could be more readily interpreted if the exchange depended on the square root of the deuterium pressure rather than the first power. If it is assumed that bare sites are nearly always adjacent to ethyl radicals so that a unimolecular molecular reaction results by transfer of H or D to the catalyst,

(152)



$$\underset{\underset{*-*}{|}}{CH_2CH_2D} \rightarrow CH_2 = CHD \quad + \quad \underset{*-*}{H}$$

the difference in activation energies could be accounted for. Since H is in excess over D on the surface, the product is primarily CH_2CHD. The rate equations for this model leads to the result that the activation energy for exchange should be larger than for that for addition by one-half the heat of adsorption of hydrogen, i.e., one-half of 17 kcal[70]. This is about the observed experimental difference. Obviously more precise experimental data are needed on pressure dependencies of exchange and addition.

Each of the theoretical treatments described above found support for a particular model or mechanism, though not the same in both cases. The difficulty comes from incomplete experimental information about the dependence of the rates on pressure, temperature and composition. In particular it is desirable to know more details about products obtained as a function of these variables. This information would add to our knowledge about the nature and concentration of various species on the surface and to an understanding of the conditions under which they react. Some still doubt, for example, that hydrogen atoms are present in any significant quantity during the reaction of hydrogen with ethylene on nickel. Rather complete inhibition of the para-hydrogen conversion and the $H_2—D_2$ exchange reaction is often cited as evidence for very few hydrogen atoms on the surface. Those who do not doubt the presence of hydrogen atoms on the surface may not agree on the method by which they are adsorbed. A similar uncertain state of affairs exist with respect to the formation of the "half-hydrogenated state" in addition and exchange reactions. Thus, it would appear that more detailed experimental investigations are needed to guide the theoretical calculations.

Formulation of Mechanisms. The more recent mass spectrometric investigations have made it clear that addition and exchange reactions are not as simple as they were once thought to be. A number of formulations have been proposed to account for the various reactions, including the redistribution reaction. Some of these have already been discussed (p. 366) in connection with the experimental work of the various authors. Markham, Wall and Laidler[162] did not report any experimental data, but did propose a series of reactions not greatly different from those used by Wagner, Wilson, Otvos and Stevenson[243, 244, 252] to explain the redistribution reaction (p. 356). Bond and Turkevich[40] (p. 347) used a series of reactions based upon the associative type mechanism to explain the redistribution reaction during addition of deuterium to propylene. In a later review article, Bond[32] extends the system of reactions to include redistribution involving adsorbed ethyl radicals. Keii[135, 136] has worked out a reaction scheme to explain the observed distributions on the basis of the "associative mechanism"[121, 125]. He presents arguments against the necessity of assuming a reaction between adsorbed ethyl radicals. Jenkins and Rideal[128] have recently proposed another mechanism and Kemball[141] has critized a number of the proposed mechanisms.

Geometrical and Electronic Considerations. Some of the considerations that have been given to geometrical factors and other parameters of the catalysts have already been discussed in connection with the work of Twigg and Rideal[241] (p. 294), Beeck and Ritchie[26] (p. 308), Sheridan[209] (p. 317), and Kemball[137, 139] (p. 331).

Lattice Spacing. Trapnell[228] has recently reviewed the geometric or lattice spacing factors in catalysis and discussed the influence of the d-band character and the work function of the catalysts. He points out that not all of variations in catalytic activity can be explained by geometric or lattice spacing effects. The activity of metallic catalysts will also depend upon the bonding of the reactants to the surface, either by ionic or covalent bonds. In cases of ionic bonding, the work function may be of significance. However, most gases are bound to metals by covalency. The transition metals, which are among the best catalysts, have incomplete d-bands and this characteristic is also undoubtedly related to catalytic activity.

To determine the variation in catalytic activity of the metal catalysts as a function of lattice spacings or d-band character, it is necessary to measure rates of a reaction which proceeds with an identical mechanism on each catalyst. The rate constant k is given by

$$k = Ae^{-E/RT} \tag{30}$$

Trapnell points out that the true energy of activation E, is not necessarily the correct one when it is obtained by the usual method of plotting log k against $1/T$ at *constant pressure*[187]. It should be done for constant surface coverage of the reactants, and this is not experimentally attainable. In cases where E corresponds to a desorption process, it is given by $E = q - E'$ where q is the heat of adsorption and E' the activation energy of adsorption. The difficulty arises from the fact that q and surface coverage vary with temperature. High activity results when E' and q are small. For rapid chemisorption, where E' is small, q must be small if a reaction controlled by desorption is to be fast. In other cases there is a conflict between low E' and low q. Although some information about the factors causing a variation in activity of different metals can be obtained from experimental values of A and E, Trapnell suggests that one of the best ways to study the specificity is to compare values of k per unit of surface area at fixed temperatures.

The theoretical calculations of Sherman and Eyring[211, 212] for the adsorption of hydrogen on carbon as a function of the C—C distance indicated that the most favorable distance would be 3.5 Å. On graphite, the calculated activation energy for chemisorption on the 2.84 Å spacing of the opposite atoms of the flat hexagon ring was 14 kcal compared to 22 kcal for the experimental value[14, 15]. Agreement is closer for the 2.80 Å spacing of diamond.

Many of the simple gases are chemisorbed on the transition metals without activation, including hydrogen, oxygen carbon monoxide, ammonia, acetylene, and ethylene. When a molecule as a whole is adsorbed at more than one point, the heat of adsorption q may vary with spacing because of strain. This situation was considered in the geometrical considerations by Twigg and Rideal[241] discussed previously (p. 294). The strain for ethylene is less on the 2.47 Å than on the 3.50 Å spacings of nickel. The heat of adsorption on the 2.47 Å spacing is probably higher and consequently the activation energy of desorption would be higher. Thus Trapnell suggests that the 3.50 Å spacing may be the more active one for ethylene reactions. Since the (110) plane of nickel contains both spacings, it should be more active than the 111 plane that contains only the 2.47 Å spacing. This was indeed found by Beeck[18, 28] p. 309) to be the case. Nickel films preferentially oriented to expose (110) planes were about five times more active than the unoriented films.* Also a comparison of the activity of the transition elements showed rhodium with a spacing of 3.75 Å to be the most active, although no consideration was given to the electronic factors. On single crystals of nickel, Cunningham and Gwathmey[57a] have found the rates of hydrogenation of ethylene on the faces to be in the order (321) > (111) > (100), the greatest difference being about tenfold. Decomposition rates of ethylene to form carbon at higher temperatures could not be correlated with hydrogenation rates.

For two-point chemisorption of acetylene Herington[116] calculated an ideal spacing of 3.3 Å for nickel atoms. Chemisorption should, therefore, take place more strongly on the 3.50 Å spacing. Beeck's results[21] for hydrogenation of acetylene indicate that those transition metals with the greater spacings are the more active.

The experimental work of Burk[45] and Balandin[7-13, 255] was among the first to demonstrate the importance of geometric considerations to catalytic reactions. This and other experimental investigations concerned with geometric factors has been reviewed in detail by Trapnell[225, 228] and will

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* Editor's note: Strictly speaking Beeck showed that the oriented films had 110 planes parallel to the glass on which the films were deposited; the actual identity of the faces exposed in the oriented films was uncertain.

not be discussed further (see p. 316) here. It seems clear that both geometric and electronic factors must be considered in understanding the activity of various metal catalysts.

Electronic Factors. In recent years there has been considerable interest in the relation of the d-band character of metals to chemisorption and catalysis[61, 63, 64, 65]. Trapnell[225, 228, 229] reviews the evidence that chemisorption of a number of gases other than oxygen can be correlated with the Pauling d-character[176, 177]. A number of other investigations have been carried out to determine the relation of catalytic activity to d-character.

When Beeck's results[22] (p. 309) for the hydrogenation of ethylene by the transition metals are plotted as log k against a parameter related to the per cent d-character, a smooth curve is obtained. The catalytic activity increases continuously with increasing d-character, or with decreasing heat of chemisorption of hydrogen. Beeck originally correlated the change in activity with lattice spacing, but since d-character controls lattice spacing, the two approaches are not independent. However, the inverse parallelism between heat of chemisorption of hydrogen and catalytic activity suggests that the d-character may be the more fundamental parameter. Variations in the heats of adsorption of hydrogen which dissociated on the surface is not easily ascribed to lattice spacing, although this is possible for a molecule to be adsorbed at two points without dissociation. The heats of chemisorption of hydrogen are more probably related to the availability of atomic d-orbitals. Consequently the above relation between heat of chemisorption of hydrogen and catalytic activity would indicate that electronic factors are of primary significance. Trapnell suggests that the hydrogenation of ethylene proceeds most readily on rhodium because the high d-character of rhodium enables it to chemisorb the reactants weakly and form a highly reactive surface layer rather than because the 3.75 Å spacing is most favorable for a low activation energy.

The study of alloy systems[55, 65, 183, 203] has also shown the importance of electronic factors. In binary systems such as nickel-copper or palladium-gold solutions, the lattice spacing barely changes with composition, but there is a significant change in d-character. Nickel, for example, contains about 0.6 vacancy per atom in the d-band[176, 177]. As copper is added, its outermost s electron fills up these vacancies, until at 60 per cent copper, they are full. Catalytic activity should fall at this point, which in fact it does for the hydrogenation of styrene and decomposition of formic acid or methanol[183]. Similarly with the palladium-gold system, the activity for the para-hydrogen conversion falls sharply above 60 atomic per cent gold[55]. However, Best and Russell[30a] found that no simple relation existed between the composition of nickel-copper alloys and their activity for the hydrogenation of ethylene.

A number of attempts have been made to correlate catalytic activity of metals with their work function, particularly in cases that might involve ionic bonds[65, 138, 246]. In most cases, the results can also be explained by d-character and geometric factors[228]. Correlations with work functions are difficult because during catalysis the surfaces are covered with adsorbed reactants and products which markedly affect the work function.

The present status of the electronic factor in heterogenous catalysis has been reviewed recently by Baker and Jenkins[6a].

Magnetic Studies. Selwood[204a] has reported some important magnetic studies on the nature and mechanism of adsorption of hydrogen and ethylene on nickel catalysts. When hydrogen was admitted to a 7.66 g of a UOP 52.8 per cent nickel-silica catalyst, 68.4 cc of hydrogen ($H/Ni = 0.0886$) was adsorbed at atmospheric pressure and the magnetization decreased 11.3 per cent. At room temperature one-third of the hydrogen could be pumped off and two-thirds of the magnetization was recovered. If nickel has 0.6 unpaired d-band electrons per nickel atom, the adsorption of the hydrogen caused the addition of approximately 0.068 electrons per nickel atom. This effect increases with decrease in particle size because more surface atoms are present. When the effect is measured as a function of temperature, the curves differ depending on particle size and previous heat treatment (sintering) of the sample.

Other measurements indicated that hydrogen is preferentially adsorbed on the smaller nickel particles and indeed the mechanism of the adsorption may be different because the magnetization increased. This may indicate a transfer of electrons from the nickel to the hydrogen, that is, hydride formation. Thus, in addition to obtaining information about the nature of adsorbed hydrogen, the method is a useful one for estimation of particle size and comparison of catalysts including the effect of alloying elements that influence the unpaired electrons in the d-bond.

Similar experiments were reported relative to the effect of adsorbed ethylene on the magnetization and on the nature and extent of adsorption of ethylene. The effect of preadsorbed ethylene on the adsorption of hydrogen was also studied. These results give new information of significance with respect to the mechanism of hydrogenation of ethylene.

Selwood[204b] has reviewed the application of other magnetic studies to problems in catalysis.

ENZYMATIC HYDROGENATIONS

Activation of Moecular Hydrogen by Enzymes. It has been known for some time[110, 213, 214, 215] that enzyme systems activate molecular hydrogen and reduce or hydrogenate a number of substances in the same way that colloidal platinum does. Green and Stickland[110] formulated the reaction as

(153) $$H_2 \rightleftharpoons 2H\cdot \qquad (1)$$

(154) $$H\cdot \rightleftharpoons H^+ + e \qquad (2)$$

Typical reductions that have been studied include those of: fumarate; acetaldehyde; vinyl acetic acid; nitrate; oxygen; ferricyanide; methylene blue and other dyes; carbon dioxide; formic acid; formaldehyde; methanol; sulfate, sulfite and thiosulfate; etc. Others[44, 50, 81, 98, 99, 100] have studied the action of hydrogenase in these enzyme systems on deuterium exchange and on ortho-para conversion as well as the hydrogenation or reduction.

Rittenberg and his co-workers[101, 118, 148, 149, 150, 151] have reviewed previous work and have investigated more completely the mechanism of reductions catalyzed by hydrogenase with the aid of deuterium exchange and ortho-para conversions. In light water (H_2O) it was found that both the exchange reaction

(155) $$D_2 + H_2O \underset{2}{\overset{1}{\rightleftharpoons}} HDO + HD$$

and the para-hydrogen conversion para $H_2 \rightleftharpoons$ ortho H_2 were first order and were equally affected by oxygen and cyanide. Under conditions where the rate was determined by the concentration of the *Proteus Vulgaris* bacteria cells, rather than by diffusion, the rate of conversion ($k = 6.3 \times 10^{-3}$ per min. for 1.88 mg nitrogen/ml) was about three times that of the exchange reaction ($k = 2.4 \times 10^{-3}$ per min. for 1.32 mg nitrogen/ml). However, when the solvent was D_2O rather than H_2O, the para-hydrogen conversion did not occur.

Mechanisms of Hydrogenase Activity. On the basis of their experimental results, Krasna and Rittenberg[151] give the following reasons for a mechanism they propose. Since hydrogenase in D_2O does not catalyze the para- to ortho-hydrogen conversion, they conclude that the first reaction in the mechanism proposed by Green and Stickland does not occur. This reaction should lead to the conversion regardless of whether the solvent is D_2O or H_2O because recombination of atomic hydrogen leads to normal hydrogen. Also the mechanism does not assign a role to the enzyme, *E*. Instead, they suggest the following formulation:

(156) $$H_2 + E \overset{3}{\rightleftharpoons} H{:}E^- + H^+$$

(157) $$H{:}E^- + D^+ \overset{4}{\rightarrow} HD + E$$

$$D_2O + H^+ \overset{5}{\rightleftharpoons} HDO + D^+$$

The back reaction of (3) explains the conversion when H_2O is the solvent. In D_2O where considerable D^+ is potentially present, reaction (4) occurs forming HD and not normal H_2. The H_2 molecules remaining in the gas phase will, therefore, all be $p - H_2$. Since H^+ is in rapid equilibrium with water, the exchange reaction can be explained by the above mechanism.

If H:E does not exchange rapidly with water, the mechanism requires that the conversion rate be twice as fast as the exchange rate. Every time $p - H_2$ reacts with the enzyme in H_2O one molecule is converted. However, when H_2 reacts with the enzyme in D_2O, only one half of a hydrogen molecule will come to equilibrium since HD is formed. The proposed mechanism is consistent in this respect with the experimental results.

They cite the results of Farkas and Schneidmesser[100] on the reduction of fumarate as support for their mechanism:

$$\text{H:E}^- + \text{fumarate} + \text{H}^+ \xrightarrow{6} \text{succinate} + \text{E} \tag{158}$$

The hydrogen rather than deuterium added to the double bond in this reduction of fumarate. The system was H_2O and *B. Coli* with a gas phase consisting of 20 per cent deuterium in hydrogen. These results show that the deuterium activated by the enzyme is not in complete and rapid equilibrium with the water. The addition of hydrogen is consistent with the mechanism since it was postulated that only one of the deuterium atoms activated is rapidly exchangeable with water. The relative rates of reactions (3) and (6) will determine the concentration of deuterium in the product.

From the behavior of hydrogenase in *Proteus Vulgaris*, Hoberman and Rittenberg[118] concluded that the enzyme was a ferrous iron-porphyrin-protein complex for the following reasons: it could be inactivated by CO; the inhibition could be reversed by light; after oxygen inactivation, it could be reactivated with hydrogen, sodium hydrosulfite or glucose; cyanide did not affect the active enzyme but permanently inactivated the oxidized enzyme; it can be oxidized and reduced as well as oxygenated and de-oxygenated. It has also been suggested that the enzyme might be a ferrous iron-sulfhydryl-protein complex.

HOMOGENEOUS HYDROGENATIONS

Cuprous Acetate in Quinoline. Practically all catalytic hydrogenations have involved heterogeneous systems. However, Calvin[47, 48] has found that molecular hydrogen can be activated in homogeneous systems. Cuprous acetate dissolved in quinoline catalyzed the hydrogenation of quinone and the reduction of cupric acetate. The rate of the reaction was found to be proportional to the concentration of hydrogen in solution and somewhat more than proportional to the concentration of cuprous acetate. Quinone had a small depressing effect on the rate. Deuterium reacted only slightly slower than hydrogen and para-hydrogen reacted at the same rate as normal hydrogen. However, during the reduction ortho-para conversion was not observed until the reaction was nearly complete.

The mechanism of the homogeneous catalysis was represented by the following formulations:

(159) $$Cu^I + Q \rightleftharpoons Cu^IQ$$

(160) $$2(Cu^IQ) \rightleftharpoons (Cu^IQ)_2$$

(161) $$(Cu^IQ)_2 + H_2 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} (Cu^IQ)_2H_2$$

(162) $$(Cu^IQ)_2H_2 + 2Su \xrightarrow{k_2} (Cu^IQ)_2 + 2HSu$$

(163) $$(Cu^IQ)_2H_2 \xrightarrow{k_3} 2Cu^0\ 2Q\ 2HAc$$

where Q is quinoline; Cu^I is cuprous acetate; Su is one equivalent of reducible substrate; and HAc is acetic acid. In these reactions $k_2 > k_1' > k_1 > k_3$. The species responsible for the activation of the hydrogen was assumed to be the dimer of cuprous acetate. This was based in part on the fact that the rate increased more than linearly with the cuprous acetate concentration.

Wilmarth and Brash[250, 251] have made the more complete investigation of the para-hydrogen conversion and of the deuterium exchange reaction in quinoline solutions of cuprous acetate. Their results confirmed those of Calvin and were consistent with the assumptions that: (1) the cuprous acetate is involved in a rapid monomer-dimer equilibrium; (2) the dimer is responsible for the activation of hydrogen for the conversion; (3) the concentration of the dimer is always small with respect to the monomer.

Kinetics and Mechanism of the Reduction. Weller and Mills[248] have made a further detailed investigation of the kinetic of the reduction of quinone and cupric ion in quinoline solutions catalyzed by cuprous acetate. They find that the rate can be expressed by $-d(H_2)/dt = kpH_2[Cu_2^I]$ and is independent of the quinone or cupric ion concentration.

With mixtures of hydrogen and deuterium, no appreciable exchange occurred during the homogeneous reduction period. However, in solutions of reduced cupric acetate, which are relatively stable toward further reduction to the metal, the formation of HD was observed. That is, under conditions where H_2 (or D_2) was not being absorbed rapidly by chemical reaction, appreciable exchange occurred. This suggested that the rate determining step was concerned with the activation of deuterium by the cuprous acetate, the activated deuterium being removed rapidly by reaction with quinone or cupric ion before it could return to the gas phase. They suggested that the H_2—D_2 exchange occurred through aniline present as an impurity rather than between the activated H_2 and D_2 molecules.

The mechanism of hydrogenation proposed was similar to that suggested by Calvin[47, 48] except that the rate determining step was assumed to be the reaction of the cuprous ion dimer with hydrogen to form a complex in which hydrogen is dissociated i.e.,

$$(\mathrm{Cu}_2^{\mathrm{I}}) + \mathrm{H}_2 \rightleftharpoons (\mathrm{Cu}_2^{\mathrm{I}})\cdot 2\mathrm{H} \tag{164}$$

This complex was assumed to be capable of reacting rapidly with quinone or cupric ion. The factors they considered to be important in the effectiveness of the dimer were: a structure possessing two sites capable of accommodating the two atoms of hydrogen simultaneously, an electronic structure permitting the formation of strong bonds with hydrogen atoms, and a favorable geometry. Further studies by Wright and Weller[254] have been concerned with the effect of chelation on the copper in these systems. Weller and Mills[248a] have written a rather complete review of the activation of molecular hydrogen in homogeneous systems and Halpern[112a] has reviewed the work in his laboratory relative to the homogeneous activation of molecular hydrogen by Cu^{++}, Ag^{+}, Hg^{++} and MnO_4^-.

DEUTERIUM ADDITION IN THE PREPARATION OF ISOTOPIC TRACERS

Use of Deuterium in Tracer Molecules. Deuterium and tritium, when attached appropriately to molecules, have found considerable use as tracers in biological and kinetic studies. No attempt will be made to review this field but a few examples will be given for illustration. For relatively stable tracer compounds in biological research, deuterium or tritium attached to carbon seem to be the most satisfactory. Deuterium may exchange with water if it is attached to oxygen, nitrogen, sulfur, or carbon atom next to a carbonyl group, a methylene group as in glycine, or other "activated" positions. For uses as a tracer the stability of the hydrogen linkage must be determined. In general hydrogen attached to aliphatic chains or to inactive aromatic rings are rather stable under biological conditions.

Deuterium or tritium can be introduced into molecules by a variety of methods[29, 31, 132, 159, 165, 182], including addition to a double bond, exchange reactions with hydrogen in the molecule, reductions with lithium deuteride, replacement of another element, synthesis in the appropriate deuterated solvent, or by biosynthesis. Of these, only additions to carbon-carbon, carbon-oxygen and carbon-nitrogen double bonds or to triple bonds will be referred to here.

Reduction of Double Bonds with Deuterium. Rittenberg, Ratner and Hoberman[190] catalytically hydrogenated maleic acid with deuterium (D_2) to form succinic acid in the presence of active palladium or platinum and light water (H_2O). The succinate ion formed had three to five times the deuterium concentration of the liquid phase. When the reduction was carried out with light hydrogen (H_2) in heavy water (D_2O), the resulting compound contained practically no deuterium. It is apparent that the hydrogen active in these hydrogenation reactions did not come to equilibrium with the solvent. That is, reduction is more rapid than exchange with water.

Similar results were obtained in the reduction of α-keto glutaric acid in ammoniacal solution. However, it was also found that after reduction for six hours with deuterium gas (D_2) in light water (H_2O) using a palladium catalyst, the α-carbon atom had 26 per cent and the β-carbon atom 56 per cent of the deuterium, as determined by degradation. The unexpected high concentration of deuterium on the β-position indicated that a keto-enol mechanism was not causing equilibration with the normal hydrogen of the light water medium. Processes such as those to be discussed later for acetone (p. 393) may be involved here.

Other Reductions with Deuterium. Other reductions reported by Schoenheimer and Rittenberg[51, 191, 197, 198, 199] with deuterium gas include such preparations as: propionic acid from acrylic acid, butyric acid from crotonic, and caproic acid from sorbic acid, stearic acid from linoleic acid, ornithine from α-pyridone; coprostanone from cholestenone. Similarly, preparations have been made by others including: leucine from isopentenal diethylacetal and valine from the next lower homolog[143]; homocystine and methionine from acetylene[175] etc.

Reduction of Unsaturated Steroids. The reduction of unsaturated steroids with deuterium has been reviewed recently by Fukushima and Gallagher[104] and Eidenoff *et al.*[66]. They used a platinum catalyst in acetic acid-d (CH_3COOD) and found that significantly more than two deuterium atoms per molecule was introduced into the cholestanol obtained from cholesterol. The distribution of these deuterium atoms was determined and a mechanism was suggested to account for the observations.

CATALYTIC HYDROGENATION OF CARBONYL COMPOUNDS

Catalytic Reduction of Acetone. Farkas and Farkas[91] studied the interaction of deuterium with acetone on platinized platinum foil in the temperature range from −42 to 86°C, using thermal conductivity and pressure changes for rate measurements. They found that propane was produced practically quantitatively above 0°C and in 68 per cent yield at −42°C. Very little isopropyl alcohol was produced. Their method of analysis indicated some exchange at 0°C and above but at temperatures below −10°C no exchange was observed.

Exchange with isopropyl alcohol was faster than its reduction to propane. However, propane formation was slower than with acetone. Therefore, isopropyl alcohol could not be an intermediate in the reduction of acetone. Three independent reactions were used to explain the exchange and reduction processes: (1) the direct reduction of carbonyl group to form propane $CH_3CD_2CH_3$; (2) the formation of isopropyl alcohol by the reaction $CH_3COCH_3 + D_2 \rightleftharpoons CH_3CH(OD)CH_3$; (3) the exchange of hydrogens in the methyl groups of acetone. They assumed that the reduction of isopropyl alcohol occurs through acetone via the above equilibrium.

Their measurements and treatment of the data indicated that no exchange occurred with acetone below −10°C. Also isopropyl alcohol was not formed in significant quantities. They, therefore, suggested that $CH_3CD_2CH_3$ could be prepared relatively pure by reduction of acetone with deuterium under these conditions, particularly since propane does not readily exchange with deuterium at −10°C.

Kauder and Taylor[133] attempted to prepare $CH_3CD_2CH_3$ for use in obtaining electron dissociation patterns for mass spectrometer analyses. With a platinized platinum foil at −20°C, about 30 per cent of the acetone had been reduced to propane in 6 minutes. However, when the deuterated propanes were examined with the mass spectrometer, masses up to 52 ($CD_3CD_2CD_3$) were observed. The distribution of the deuterated propanes were about the same at 30 and 70 per cent reduction indicating rapid exchange or redistribution. At 25°C the reduction was almost complete in 9 minutes giving a greater abundance of the more highly deuterated species.

Friedman and Turkevich[103] made a similar but more complete investigation of the interactions of acetone with deuterium on a platinum-charcoal catalyst. In a flow system at −77°C the propane obtained had the following percentage composition: $C_3H_8 = 9.9$; $C_3H_7D = 7.8$, $C_3H_6D_2 = 32.8$; $C_3H_5D_3 = 15.5$; $C_3H_4D_4 = 11.9$; $C_3H_3D_5 = 8.6$, $C_3H_2D_6 = 6.3$; $C_3HD_7 = 4.8$; $C_3D_8 = 2.4$. At 0°C in a static system, a similar distribution with slightly lower percentages of the most highly deuterated products was obtained. Higher ratios of deuterium to acetone gave appreciably greater percentages of the more highly deuterated products.

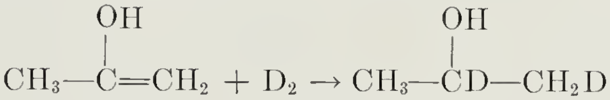
In their experiments they established that no significant exchange occurred between propane and deuterium after circulating a 1:1 mixture over the catalyst for 5 minutes. Also, no exchange occurred between deuterated and undeuterated propanes. Unreacted acetone was shown from its mass spectra to exchange only slowly under the conditions of the reduction. Approximately 5 per cent contained one deuterium and none with two. In agreement with Farkas and Farkas[91] they found that isopropyl alcohol was converted only slowly to propane. However, at room temperature they found that the unreacted isopropyl alcohol exchanged only one hydrogen for deuterium, presumably on the OH group. Exchange reactions with a number of alcohols have been re-investigated by Anderson and Kemball[3].

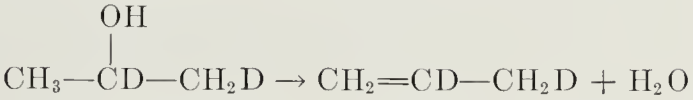
When the reduction of acetone was carried out in the liquid phase at about 2 atmospheres pressure of deuterium on an iron promoted platinum-charcoal catalyst, they obtained predominantly isopropyl alcohol containing only two deuterium atoms, $CH_3CD(OD)CH_3$.

Mechanism of Gas Phase Reduction of Acetone. A mechanism for the reduction of acetone with deuterium involving the enol form was rejected by Farkas and Farkas[91] in favor of direct reduction of the double bond of the $\rangle C{=}O$ group:

(165) $$CH_3C{=}OCH_3 + 2D_2 \rightleftharpoons CH_3CD_2CH_3 + D_2O$$

This was done on the grounds that the slower reducing isopropyl alcohol would be an intermediate in the enol process. Also the enol form would involve exchange which they did not detect. Friedman and Turkevich suggest the following formulation as one that would not involve exchange for the introduction of four deuterium atoms:

(166)

$$CH_3{-}\overset{\overset{OH}{|}}{C}{=}CH_2 + D_2 \rightarrow CH_3{-}\overset{\overset{OH}{|}}{C}D{-}CH_2D$$

(167)

$$CH_3{-}\overset{\overset{OH}{|}}{C}D{-}CH_2D \rightarrow CH_2{=}CD{-}CH_2D + H_2O$$

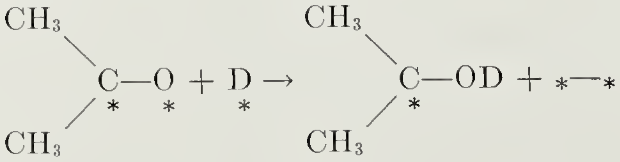
(168) $$CH_2{=}CD{-}CH_2D + D_2 \rightarrow CH_2D{-}CD_2{-}CH_2D.$$

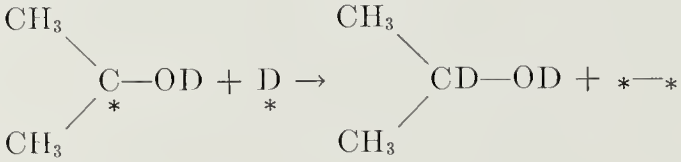
Since a peak occurs in the distribution of deuteropropanes at mass 46 corresponding to $CH_3CD_2CH_3$, they suggest that some of the reduction might occur by direct addition of D_2 to the double bond as suggested by Farkas and Farkas. The fact that the latter authors did not detect exchange was attributed to the relatively insensitive analytical methods.

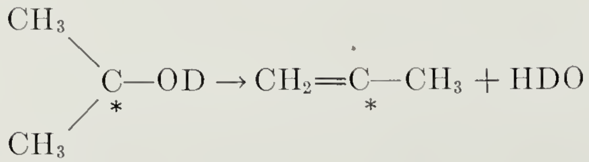
The situation with respect to the interaction of acetone with deuterium appears to be very similar to that with unsaturated hydrocarbons. At low temperatures there was relatively little exchange and return of hydrogen to the gas phase. Yet both highly deuterated and light hydrocarbons were produced. This similarity, and the observation of Friedman and Turkevich[103] that unreacted acetone had not exchanged to form highly deuterated acetones, leads to the following suggestion. Once acetone is adsorbed on sites appropriate for reduction its residence time is long enough to approach equilibrium with the deuterium and hydrogen on the surface. That is, the adsorbed complex undergoes many exchanges with the adsorbed deuterium or equilibrates via redistribution reactions among radicals before leaving the surface as propane. During this process some of the hydrogen atoms of acetone that were replaced by deuterium to form the more highly deuterated propanes appear in the light propanes. The quantity of H returned to the gas phase would be reduced by this process making exchange appear small by thermal conductivity analysis.

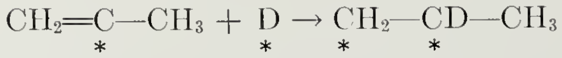
It is possible to formulate the above mechanism in a number of ways. One such might be the following:

(169)  (1)

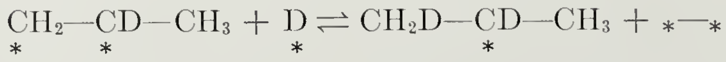
(170)  (2)

(171)  (3)

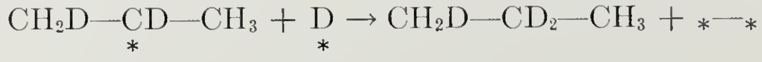
(172)  (4)

(173)  (5)

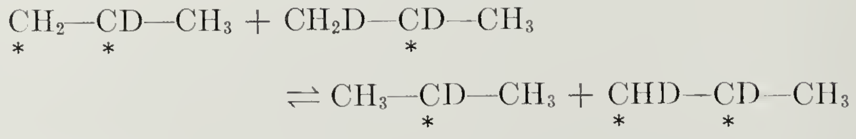
$$CH_2{=}\underset{*}{C}{-}CH_3 + \underset{*}{D} \rightarrow \underset{*}{CH_2}{-}\underset{*}{C}D{-}CH_3 \qquad (5)$$

(174)  (6)

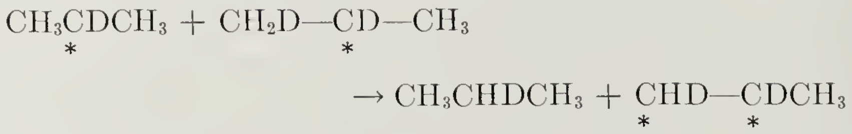
$$\underset{*}{CH_2}{-}\underset{*}{C}D{-}CH_3 + \underset{*}{D} \rightleftharpoons CH_2D{-}\underset{*}{C}D{-}CH_3 + *{-}* \qquad (6)$$

(175)  (7)

$$CH_2D{-}\underset{*}{C}D{-}CH_3 + \underset{*}{D} \rightarrow CH_2D{-}CD_2{-}CH_3 + *{-}* \qquad (7)$$

(176)  (8)

$$\underset{*}{CH_2}{-}\underset{*}{C}D{-}CH_3 + CH_2D{-}\underset{*}{C}D{-}CH_3 \rightleftharpoons CH_3{-}\underset{*}{C}D{-}CH_3 + \underset{*}{C}HD{-}\underset{*}{C}D{-}CH_3 \qquad (8)$$

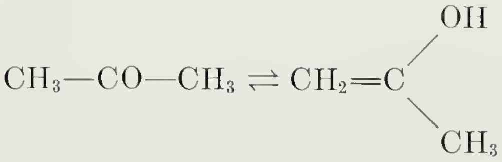
(177)  (9)

$$CH_3\underset{*}{C}DCH_3 + CH_2D{-}\underset{*}{C}D{-}CH_3 \rightarrow CH_3CHDCH_3 + \underset{*}{C}HD{-}\underset{*}{C}DCH_3 \qquad (9)$$

Reaction (3) would be slower than (4) in the gas phase since little isopropyl alcohol is formed. Following reaction (5), redistribution and propane formation are essentially the same as for unsaturated hydrocarbons, reactions (7) and (9) being responsible for final formation of propane.

Another similar series could also be written starting with the enol form of acetone:

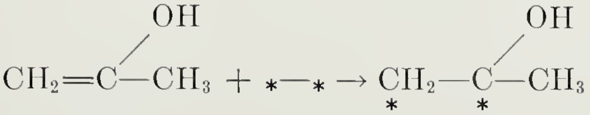
(178)



$$CH_3{-}CO{-}CH_3 \rightleftharpoons CH_2{=}C\begin{array}{l}\diagup OH\\ \diagdown CH_3\end{array}$$

(10)

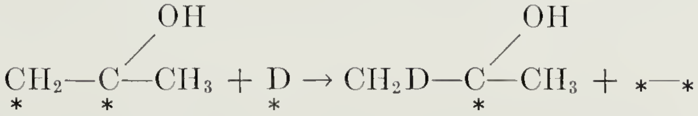
(179)



$$CH_2{=}\overset{OH}{C}{-}CH_3 + *{-}* \rightarrow \underset{*}{CH_2}{-}\underset{*}{\overset{OH}{C}}{-}CH_3$$

(11)

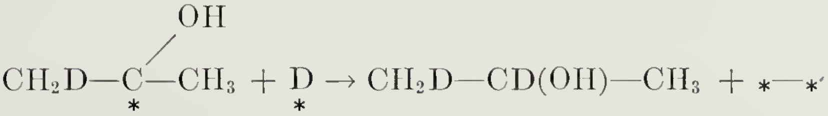
(180)



$$\underset{*}{CH_2}{-}\underset{*}{\overset{OH}{C}}{-}CH_3 + \underset{*}{D} \rightarrow CH_2D{-}\underset{*}{\overset{OH}{C}}{-}CH_3 + *{-}*$$

(12)

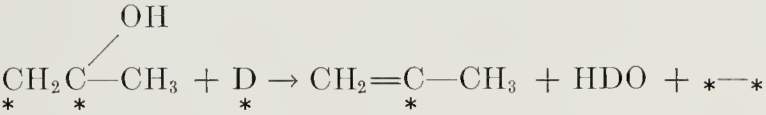
(181)



$$CH_2D{-}\underset{*}{\overset{OH}{C}}{-}CH_3 + \underset{*}{D} \rightarrow CH_2D{-}CD(OH){-}CH_3 + *{-}*'$$

(13)

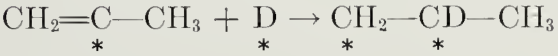
(182)



$$\underset{*}{CH_2}\underset{*}{\overset{OH}{C}}{-}CH_3 + \underset{*}{D} \rightarrow CH_2{=}\underset{*}{C}{-}CH_3 + HDO + *{-}*$$

(14)

(183)



$$CH_2{=}\underset{*}{C}{-}CH_3 + \underset{*}{D} \rightarrow \underset{*}{CH_2}{-}\underset{*}{CD}{-}CH_3$$

(15)

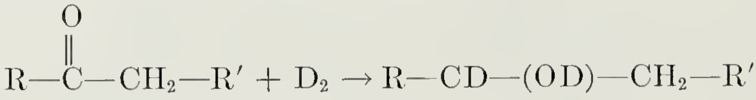
etc., as above.

Although the first series of reactions seem more likely, not enough is known about all of the molecular species to distinguish between these formulations for the gas phase reaction. More detailed examination of the small amounts of isopropyl alcohol produced may indicate whether reactions (2) and (3) or (12) and (13) are the principal ones under a given set of conditions. Such studies have been made on the alcohols resulting from the liquid phase reduction of a number of ketones and aldehydes.

Liquid Phase Reduction of Carbonyl Compounds. Anderson and MacNaughton[4] reduced a number of liquid carbonyl compounds, including acetone, methyl ethyl ketone, diethyl ketone, acetaldehyde, and butyraldehyde with deuterium using Raney nickel, copper chromite, and Adams' platinum catalyst to which some ferric chloride had been added. The presence of iron in platinum catalysts has been shown by Faillebin[77] to favor formation of alcohols rather than hydrocarbons. A mixture of 20 per cent of deuterium and 80 per cent hydrogen was used at 30 to 40 psi at room temperature and at 1000 psi at 150 and 250°C. About 30 to 40 g of the ketone or aldehyde and 0.1 to 0.2 g of platinum oxide catalyst (or 5 to 10 g of Raney nickel, or 3 to 5 g of copper chromite) were used in a hydrogenation unit. After hydrogenation, about 20 g of the middle portion of the liquid from a fractional distillation were examined in the Raman spectrograph for the presence of O—D ($\Delta\nu = 2150$ cm^{-1}) and C—D ($\Delta\nu = 2500$ cm^{-1}) bonds. The products from a chromic acid oxidation of the liquid were also examined for O—D and C—D bonds.

They considered two paths by which the reduction to the alcohol might go: (1) direct addition to the carbonyl group:

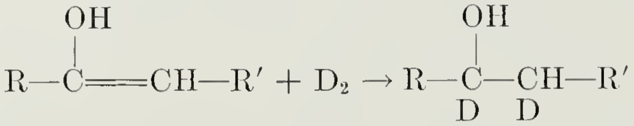
(184)



$$R{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}R' + D_2 \rightarrow R{-}CD{-}(OD){-}CH_2{-}R'$$

and (2) addition of deuterium to the ethylenic linkage of the enol form

(185)



$$R{-}\overset{\overset{OH}{|}}{C}{=\!=}CH{-}R' + D_2 \rightarrow R{-}\underset{D}{\overset{\overset{OH}{|}}{C}}{-}\underset{D}{CH}{-}R'$$

If the reaction proceeds through the keto form, the resulting alcohol should contain both C—D and O—D bonds, and the oxidation product should contain no C—D or O—D bonds. If the reaction proceeds through the enol form, two C—D bonds and no O—H bonds should be observed. The oxidation product in this case had deuterium on the alpha carbon atom. These conclusions are on the assumption that no exchange occurs during oxidation.

Using the above criteria for interpreting their experiments, the authors concluded that keto reduction occurs at room temperatures, while at the higher temperatures (150, 200 and 250°C) enol addition takes place. Exchange during the reductions could, of course, confuse the above interpretations. For example, at the higher temperatures exchange on the carbon atoms of the keto form might give results similar to those expected for the enol mechanism. Not enough information is given on their methods of determining exchange to evaluate this possibility. Mass spectrometric examination of the products would aid in this respect.

The authors did examine the exchange of isopropyl alcohol and *n*-butyl alcohol under the conditions of the reduction. They found no exchange at any temperature up to 250°C in the absence of catalysts although the sensitivity of their method was not stated. Exchange was observed with the O—H group in the presence of platinum at 250°C and in the presence of nickel at 25°C, but no exchange was observed on the carbon. At 250°C nickel and copper chromite gave exchange on both oxygen and carbon, presumably by a dehydrogenation path. The fact that the final product does not exchange with deuterium under the conditions of the reductions, does not exclude the possibility of a lively exchange of the surface complex, as observed in the gas phase reactions of acetone. The extent to which the enol mechanism participates does not seem to be conclusively shown by their analytical methods.

Friedman and Turkevich[103] reduced liquid acetone to isopropyl alcohol at room temperature with 2 atmospheres pressure of deuterium on an iron promoted platinum-charcoal catalyst. The mass spectra of the products indicated that only a small amount of exchange occurred and that the predominant product of the reduction was $CH_3CD(OD)CH_3$. This result confirms the keto mechanism discussed by Anderson and MacNaughton. Mass spectrometric examination of the products at the higher temperatures would be useful in determining the contribution of the enol path.

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CHAPTER 6

THE HYDRODESULFURIZATION OF LIQUID PETROLEUM FRACTIONS

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Introduction

Practically from the beginning of the application of hydrogenation processes to the conversion of petroleum fractions and coal into lighter products, it was recognized that hydrogenation was also effective for the simultaneous removal of oxygen, nitrogen, and sulfur compounds. The procedure was not economical for application to petroleum fractions because of the high cost of hydrogen and because the demand for low sulfur content petroleum products could be met by refining low-sulfur crudes or by alternate desulfurization methods. Recently, the widespread installation of hydroreforming with its tremendous quantities of by-product hydrogen has made commercial hydrodesulfurization operations feasible. The need for such commercial operations has simultaneously become more acute because of an increase in the amount of high-sulfur crudes which are being refined[1, 2, 3] and the increasing demand for low-sulfur middle and heavy distillate fractions which cannot be prepared in a completely satisfactory fashion by other desulfurization methods. Such high-sulfur crudes in the United States include those from some California, Mississippi, Wyoming, and Texas fields which may contain as high as 3.0 per cent sulfur[2, 4]. Many foreign crudes are also rich in sulfur. Those from the Middle East, used extensively in Europe, invariably have high sulfur contents[4, 5, 6]. Oils from tar sands can be very rich in sulfur[7], and those from oil shale are high in sulfur as well as oxygen and nitrogen compounds[8, 9, 10]. When these latter oils come into general use, the problem will be aggravated.

There are many valid reasons for removing sulfur compounds from petroleum fractions. These include (1) reduction or elimination of corrosion during refining, handling or use of most petroleum fractions and products; (2) the production of fractions having an acceptable odor; (3) in the case of gasoline, increasing color stability and resistance to the formation of gum as well as increasing lead susceptibility and octane number; (4) for kerosenes, decreasing smoking and undesirable wick deposits; (5) for gas oils, improving their quality as diesel oils, prevention of gas oil sulfur from appearing in lower boiling products obtained from cracking operations, and improving stability and possibly burning characteristics when they are used as burning oils; and (6) for heavy fuel oils, reduction of sulfur content to a level which will make them suitable for use in steel mill open hearth operations.

Considerable use has been made and is still being made of extraction, chemical processing and nonhydrocatalytic treatment of various petroleum fractions for sulfur removal or conversion of sulfur compounds to less objectionable bodies[11, 12, 13]. However, hydrodesulfurization is the only method generally applicable for the removal of all types of sulfur compounds. Hydrodesulfurization in its simplest sense refers to the removal of sulfur from oils by the reaction of the sulfur compounds with hydrogen in the presence of a hydrogenation catalyst with the resulting formation of one or two hydrocarbon molecules and hydrogen sulfide. This in general may be accomplished in the temperature range of about 600 to 800°F and at pressures of from about 15 to 1000 psig, and usually above 250 psig. Actually this range of conditions is somewhat arbitrary and is that normally employed for pretreating naphthas and for middle distillate hydrodesulfurization. The upper pressure limit is too low to cover all studies; thus, examples of nondestructive hydrodesulfurization at higher pressures (e.g., ca. 3000 psig) are available. Also hydrodesulfurization may be accomplished in hydrocracking or hydroreforming operations at higher temperatures. However, in spite of the varied conditions under which hydrodesulfurization reactions occur, for the present purposes most emphasis has been placed on the relatively mild nonhydrocracking type of operation. The literature through 1955 has been considered together with a few references in 1956.

FUNDAMENTALS

Types of Compounds in Fractions

Sulfur is found in petroleum or its straight-run and cracked fractions mainly as elemental sulfur, hydrogen sulfide, thiols (mercaptans), open-chain sulfides (aliphatic or alkane sulfides and aromatic sulfides—all often designated as thioethers or thialkanes), disulfides (dithialkanes), saturated cyclic (alicyclic) sulfides, and thiophenes. Disulfides may be present as a result of oxidation of thiols, and sulfur may be formed as a result of oxidation of hydrogen sulfide. The presence of elemental sulfur in certain crudes has been proved by Eccleston, Morrison and Smith[14] by careful collection of crude samples and examination by a polarographic method. Depending on whether a whole crude is being considered or a straight-run or cracked product and upon the source from which it was derived, the relative contents of the various compounds will differ. No complete picture in this respect is possible because of lack of published data, but in the following text certain aspects are discussed.

Straight-Run Materials. The varied distribution of sulfur types which may be present in vacuum-distilled straight-run naphthas boiling up to 482°F is demonstrated by the results of type analyses on distillates from seventeen United States and Middle East crude oils described by Hale, Thompson, Barker, Smith, and Ball[15]. The presence of varying amounts of free sulfur, hydrogen sulfide, disulfides, mercaptans, sulfides I (mainly aliphatic and cyclic sulfides), sulfides II (mainly aromatic sulfides and thiophenes), and residual sulfur (unknown type) was shown by the Ball method of analysis[16]. Nine of these crudes were also distilled at atmospheric pressure and significant differences were found in the relative proportions of the various types of sulfur compounds. Specifically, residual sulfur compounds, 28.6 per cent to 80.3 per cent of the sulfur compounds found by vacuum distillation, were more or less converted to sulfides I and II and hydrogen sulfide was evolved. The differences between the vacuum and atmospheric distillates from Wasson and Heidelberg crudes are given in Table 1. Most crudes gave results similar to those obtained with Heidelberg Crude, with the amount of sulfides II being larger in the atmospheric distillate. Regardless of the exact nature of the change, however, these data illustrate the marked effect of fairly minor differences in maximum pot temperature during naphtha preparation.

TABLE 1. PER CENT SULFUR (BASED ON TOTAL SULFUR) PRESENT AS CONSTITUENT INDICATED

	Wasson Crude		Heidelberg Crude	
	Vacuum Distillate (0.857 Wt. % S — Max. Pot Temp. 598°F)	Atmospherc Distillate (0.799 Wt. % S — Max. Pot Temp. 745°F)	Vacuum Distillate (0.523 Wt.% S — Max. Pot Temp. 503°F)	Atmospheric Distillate (0.453 Wt. % S — Max. Pot Temp. 723°F)
Elemental S	0.1	0.5	0.0	0.9
Hydrogen sulfide	0.0	5.1	0.0	4.2
Disulfides	7.4	3.1	0.2	0.4
Thiols	15.3	18.0	0.0	2.4
Sulfides I	11.6	56.2	7.8	8.2
Sulfides II	13.0	6.5	11.7	30.5
Residual S	52.6	10.6	80.3	53.4

A more specific picture of the individual sulfur compounds present in petroleum and its straight-run fractions is available from the results of work which has been done on the isolation and identification of sulfur compounds in various petroleum fractions. Haines, Wenger, Helm and Ball[17], gave an extensive review of the early literature. The results of recent investigations and some of the more important early work can be cited to illustrate the types of sulfur compounds that may be expected in straight-run petroleum fractions as a function of boiling range.

Most complete information is available on Wasson Crude (1.85 per cent S) as the result of API Project 48 work[18]. The various compounds listed in Table 2 have been isolated from the hydrocarbon fractions boiling to 220°C in such a manner as to avoid decomposition reactions and thus to obtain information on compounds indigenous to the crude. Of the forty-three compounds listed, all but three have been positively identified; included are alkane thiols, aliphatic sulfides and alicyclic sulfides boiling up to about 160°C. Examination of these data indicates that secondary thiols are the most abundant type and that their content in the crude should become negligible in fractions above about 12 or 13 carbon atoms. Primary thiols disappear in the 5 to 6 carbon atom range. The content of tertiary thiols is negligible throughout the boiling range studied. In general, the content of aliphatic sulfides (2,4-dimethyl-3-thiapentane and 4-methyl-3-thiahexane excepted) also decreases and alicyclic sulfides appear with increasing molecular weight. Further data were obtained by the examination of the crude topped to 150°C (2.15 per cent S) and deasphaltened. Of the 15 per cent of sulfur compounds present in this 76.1 per cent of the crude, it is indicated that at least 65 per cent of these are thiophenes having two rings (benzothiophenes), three rings (dibenzothiophenes), or four or more rings per molecule and that the remaining compounds include a small amount of simple thiophenes (one ring) but are predominantly sulfides. A more specific generalization excludes consideration of a fraction on which few analytical data were available and is concerned with fractions representing 82.8 per cent of the deasphaltened bottoms. In this portion, sulfur compounds are present to the extent of 11 per cent. Almost 70 per cent of these are thiophenes and the remainder are sulfides. Of the thiophenes, the proportions of those having one, two and three rings are 1, 9 and 9, respectively. The preponderance of complex thiophenes, which are for the most part high-boiling, leads to the conclusion that the higher boiling fractions of Wasson Crude contain a substantial amount of these.

In a general way, the same picture of increase in the cyclic nature of the types of sulfur compounds in petroleum with increase in molecular weight of the fraction is indicated by the results of other investigations on other stocks. Most of these studies were carried out on sulfur bodies recovered from spent treating agents used in refining. In some instances, the sulfur compound or type of compound thus found might not be identical to the parent substance, and selective removal of certain types of sulfur compounds may occur. Also, most of the investigations were carried out on

TABLE 2. SULFUR COMPOUNDS IDENTIFIED IN WASSON, TEXAS, CRUDE OIL AND ESTIMATED WEIGHT PER CENT PRESENT WHENEVER KNOWN

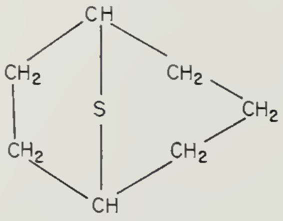
	Boiling Point (°C)	Wt. % in Wasson, Texas, Crude Oil[a]
Methanethiol	5.96	0.00240
Ethanethiol	35.0	.00530
2-Thiapropane	37.31	.00088
2-Propanethiol	52.56	.00199
2-Methyl-2-propanethiol	64.22	.00055
2-Thiabutane	66.65	.00222
1-Propanethiol	67.5	.00041
3-Methyl-2-thiabutane	84.81	.00064
2-Butanethiol	85.15	.00386
2-Methyl-1-propanethiol	88.72	.00003
3-Thiapentane	92.10	.00075
2-Thiapentane	95.52	.00030
1-Butanethiol	98.4	Trace
2-Methyl-2-butanethiol	99.0	.00064
3,3-Dimethyl-2-thiabutane	99.0	
2-Methyl-3-thiapentane	107.4	
3-Methyl-2-butanethiol	109.8	
2-Pentanethiol	112.9	.0014
3-Pentanethiol	113.9	.00057
4-Methyl-2-pentanethiol		
3-Methyl-3-pentanethiol		
3-Thiahexane	118.50	.00012
2,4-Dimethyl-3-thiapentane	120.02	.00053
2,2-Dimethyl-3-thiapentane	120.41	.000058
Thiacyclopentane	121.12	.000077
2-Thiahexane	123.2	.000077
2-Methyl-3-thiahexane	132.05	.000078
Cyclopentanethiol	132.2	
2-Methylthiacyclopentane	133.23	.0023
4-Methyl-3-thiahexane	133.65	.00050
3-Methylthiacyclopentane	138.67	.00046
2-Hexanethiol	138.9	.0028
Thiacyclohexane	141.75	.00032
trans-2,5-Dimethylthiacyclopentane	142.0	.0025
cis-2,5-Dimethylthiacyclopentane	142.28	.0024
3-Thiaheptane	144.24	.000078
2-Methylthiacyclohexane	153.04	.0029
3-Methylthiacyclohexane	158.04	.000024
4-Methylthiacyclohexane	158.64	.000048
Cyclohexanethiol	158.8	.0012

Tentatively identified: 3-Hexanethiol, cis-2-Methylcyclopentanethiol, 2-Octanethiol.

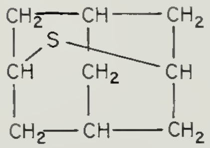
[a] These are minimum values. For the thiols and sulfides boiling below 100°C and for thiols boiling above 100°C the values should be 90-95 per cent correct. The values reported for cyclic and chain sulfides boiling above 111°C may be low by 50 per cent because of processing losses.

products prepared by ordinary distillation. As previously indicated, this method of preparation would effect an alteration of some of the sulfur compounds. Atmospheric distillation also permits reaction between any free sulfur present and a wide variety of hydrocarbons and other substances in the crude to form hydrogen sulfide and perhaps other sulfur bodies. Coleman, Thompson, Rall and Smith[19] have found that this latter reaction begins at 200 to 300°F and is rapid at 400°F. However, studies on stocks subjected to conventional atmospheric distillation are desirable because it is such stocks that are processed by hydrodesulfurization.

Birch[20] reviewed the literature concerning the isolation of sulfur compounds from spent treating agents used to refine light Iranian distillates. Various alkane thiols and sulfides, thiacyclopentane and its 2- and 3-methyl derivatives and thiacyclohexane have been identified. Thompson, Coleman, Mikkelsen, Yee, Ward and Rall[21] identified thiophene, 2-methylthiophene and possibly 3-methylthiophene as indigenous in the 100 to 232°F boiling range material in Wilmington California Crude. Birch and co-workers[20, 22] examined the neutral oil from an acid sludge formed by the treatment of 284 to 482°F kerosene boiling range fractions derived from Persian Crude (mainly Agha Jari). Tri- and tetra-substituted derivatives of thiophene were found as well as a small amount of alkane sulfides and a large amount of mono- and bicyclic sulfides. The monocyclic sulfides were all derivatives of thiacyclopentane or thiacyclohexane. The bicyclic sulfides included 8-thiabicyclo (3,2,1)-octane (A) and *cis*- and *trans*-1-thiahydrindane. Thia-adamantane (B) was isolated and indications were obtained that other polycyclic sulfides were present.

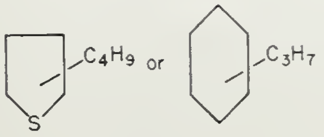


(A)

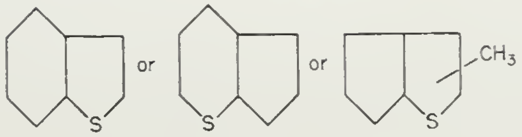


(B)

Emmott[23] examined sulfur dioxide extracts from Texas, Iraq and Kuwait kerosenes. It was indicated that alkyl substituted cyclic sulfides were principal constituents of the Kuwait extract which was studied most completely. Evidence was also found for the presence of bicyclic sulfides. Richter, Williams and Meisel isolated benzothiophene from a distillate fraction from Santa Maria Valley Crude[24]. Brown and Meyerson[25] concluded that the sulfuric acid extract obtained from a 329 to 536°F high-sulfur virgin distillate of West Texas origin contained mono-, bi- and tricyclic sulfides possibly of the types indicated below (C, D and E).



(C)



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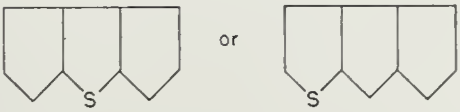

(E)

Hoog, Reman, and Smithuysen[26] studied the total sulfur compounds in several gas oils. Evidence was found for the presence of alkane thiols, alkane sulfides, complex alicyclic sulfides such as the completely hydrogenated dibenzothiophene type, simple thiophenes, benzothiophenes and dibenzothiophenes. In several Middle East gas oils and one of Venezuelan origin, benzothiophenes were found to be the most abundant sulfur type (40 to 60 per cent of the sulfur compounds), dibenzothiophenes were present to a somewhat less extent (20 to 40 per cent), and aliphatic and alicyclic sulfides were the only other major types (20 to 25 per cent). Simple thiophenes were shown to be a minor constituent in one of the Middle East oils. A Texas gas oil in contrast contained mercaptans (10 per cent), only aliphatic sulfides (19 per cent), and somewhat more dibenzothiophenes (70 per cent). Evidence was also obtained for the presence of small amounts of benzothiophenes.

McCoy and Weiss[27] have made group analyses (Table 3) of asphalt and straight-run long and short residues, all of undisclosed origin, by a new method. The sulfur in both of the straight-run residues was about 50 per cent nonthiophenic and 50 per cent thiophenic. The nonthiophenic sulfur was comprised almost exclusively of sulfide (aliphatic and alicyclic) sulfur with but small proportions of thiol and disulfide sulfur. Elemental sulfur and hydrogen sulfide were absent. Only 10 per cent of the sulfur in the asphalt, which would be of higher molecular weight, was nonthiophenic. This new method of McCoy and Weiss, which involves distinguishing between nonthiophenic and thiophenic sulfur compounds by decomposing the former to hydrogen sulfide and presumably hydrocarbons over alumina at 450°C, is applicable to any boiling range fraction. According to their classification, the nonthiophenic compounds include elemental sulfur, aliphatic and alicyclic sulfur compounds in which the sulfur is linked to nonaromatic carbon atoms (e.g., alkane thiols and sulfides, cyclic sulfides, and alkane disulfides), and aromatic mercaptan percursors. The latter types of compounds are those, such as phenyl decyl sulfide and diphenyl disulfide, in which the sulfur atom is linked to one aromatic ring. Thiophenic sulfur compounds include simple and complex thiophenes as well as compounds, such as diphenyl sulfide, in which the sulfur is linked to two aromatic rings. With respect to aromatic mercaptan precursors, McCoy and Weiss state that they are uncommon in petroleum products.

Table 3. Typical Results Obtained for Group Sulfur Analyses[a]

Material	Sulfur, Wt. %						Nonthiophenic Sulfur, % of Total Sulfur	Aromatic Mercaptan Precursor Sulfur, Wt. %
	Mercaptan	Disulfide	Sulfide	Nonthiophenic	Thiophenic	Total		
Commercial gasoline	<0.001	0.007	0.01	0.02	0.09	0.11	18	None detected
			0.01	0.02	0.09		18	
Catalytically cracked gasoline	0.003	0.001	0.014	0.018	1.18	1.20	2	None detected
Thermally cracked gasoline	0.12	0.03	0.39	0.54	1.52	2.06	26	0.018
Jet fuel	<0.001	<0.002	0.072	0.072	0.13	0.20	36	None detected
Catalytic gas oil	<0.001	<0.001	0.002	0.002	0.10	0.10	2	None detected
California lubricating oil	0.0025	<0.001	0.016	0.18	0.10	0.28	64	None detected
			0.017	0.19	0.09		68	
Mid-Continent lubricating oil	0.025	0.012	0.050	0.087	0.053	0.14	62	Approx. 0.003–0.004
			0.052	0.089	0.051		64	
Shale oil	—	0.04[b]	0.18	0.22	0.48	0.70	31	None detected
Thermal distillate	0.004	0.005	0.47	0.48	0.85	1.33	36	Approx. 0.01–0.02
Thermal distillate	—	—	—	0.78	1.62	2.40	32	None detected
				0.80	1.60		33	
Straight-run short residue	0.01	0.01	1.0	1.0	1.1	2.08	49	None detected
Asphalt	—	—	—	0.16	1.42	1.58	10	None detected
Straight-run long residue	0.006	0.007	0.88	0.89	0.81	1.70	52	None detected
			0.89	0.90	0.80		53	

[a] No elemental sulfur or hydrogen sulfide found in these samples.

[b] Sum of the mercaptan and disulfide sulfur.

Cracked Fractions. Knowledge of the individual sulfur compounds present in cracked petroleum products is even less extensive than for straight-run petroleum fractions. In distillation, as has been previously described, or in cracking operations, changes in sulfur compounds are known to occur; thus, the actual compounds in cracked fractions may be largely synthetic. Actually it is difficult to do more than characterize them according to type and to summarize some generalities with respect to comparison of the nature of the compounds present in straight-run and cracked products. Many of the characterizations have been made by the Ball type analysis[16] which is only applicable to light distillates of the gasoline boiling range. The new type analysis of McCoy and Weiss[27], mentioned above, has been used to analyze gasolines and heavier fractions and is a valuable addition to the Ball technique.

As is also true in the case of straight-run distillates, most information is available on cracked fractions of the gasoline boiling range and frequent comparisons have been made of such straight-run and cracked fractions. It was mentioned and illustrated above that Hale, Thompson, Barker, Smith and Ball[15] noted substantial differences in sulfur compound distribution in 482°F end point naphthas from various crudes, depending upon whether they were obtained by atmospheric or vacuum distillation. Ball[16] has reported the distribution of types of sulfur compounds in Oregon Basin straight-run gasoline and pressure distillate. The data are shown in Table 4. These results demonstrate that the quantity of sulfur compounds in thermal distillates may be many times as great as in the straight-run distillate and show, as has been observed in many instances, that the sulfur content in cracked gasolines is more highly thiophenic. Another general observation which has been made[28] is that the thiol content of gasolines produced by cracking higher molecular weight fractions is made up of a greater proportion of lower molecular weight compounds than is the case for straight-run distillates. Some specific compounds and types of compounds which have been identified in thermal gasolines are given in Table 5.

Table 4. Sulfur Compounds in Untreated Gasolines
Percentage of Sulfur in Gasoline

Sulfur Type	Straight-run Oregon Basin	Cracked Oregon Basin
Free	0.013	0.000
Hydrogen sulfide	0.000	0.000
Mercaptan	0.003	0.025
Disulfide	0.024	0.004
Sulfides I	0.159	0.008
Sulfides II	0.000	0.416
Residual	0.018	0.727
Total	0.217	1.180

There is very little information on sulfur compounds in catalytic gasolines. These compounds are entirely synthetic and thiols are present in very small proportions[29]. In general, the proportion of aliphatic and alicyclic sulfur compounds is low and the proportion of thiophenic compounds very high. This would be expected because of the instability of aliphatic and alicyclic compounds over catalysts at high temperatures such as those employed in catalytic cracking. A type analysis for a catalytically cracked gasoline is given in Table 3.

Practically nothing has been established concerning the sulfur compounds present in cracked products boiling above the gasoline range; however, some information is available on catalytic gas oils. It would be expected that the sulfur compounds in these would be highly thiophenic. That this is true in the case of a low sulfur content stock is evident from the data of McCoy and Weiss given in Table 3. It is further evident from the results of Hoog, Reman and Smithuysen[26] who found that a catalytic Middle East gas oil (*ca.* 2.5 per cent S) contained almost exclusively benzothiophenes. On the other hand, straight-run Middle East gas oils contained appreciable quantities of alicyclic and/or aliphatic sulfides.

Table 5. Some Sulfur Compounds in Thermally Cracked Gasolines

Compound	References
Thiols	
1. Methanethiol	1
2. Ethanethiol	1
3. Unidentified propane through pentanethiols	1
4. Benzenethiol	2, 3
5. 2-Methyl-1-benzenethiol	3
6. 4-Methyl-1-benzenethiol	3
7. Hexane and heavier thiols	1
8. Benzenethiols	1
Sulfides	
1. 2-Thiapropane	4
2. 3-Thiapentane	4
Thiophenes	
1. Thiophene	5
2. 2-Methylthiophene	5
3. 3-Methylthiophene	5
4. 2-Ethylthiophene	5
5. 2,3-Dimethylthiophene	5
6. 3,4-Dimethylthiophene	5

References for Table 5

1. Happel, J., Cauley, S. P., and Kelly, H. S., *Petroleum Refiner*, **21**, 406 (1942).
2. Windle, G. S., *Petroleum Refiner*, **23**, 41 (1944).
3. Henderson, L. M., Ayers, G. W., Jr., and Ridgeway, C. M., *Oil Gas J.*, **38**, No. 46, 114 (1940).
4. Kan, T., *C. A.*, **21**, 1344; *J. Soc. Chem. Ind. (Japan)*, **30**, 129 (1927).
5. McKittrick, D. S., *Ind. Eng. Chem.*, **21**, 585 (1929).

Miscellaneous Products. McCoy and Weiss[27] (Table 3) have given type analyses of several products not referred to above. Of particular interest among these are shale oil and lubricating oils. It is apparent that the sulfur compounds present in shale oil produced by the high temperature retorting of oil shale resemble the sulfur compounds in cracked petroleum products. Further indication of this is pointed up by a detailed naphtha analysis by Kinney, Smith and Ball[30] which showed that this fraction from Rifle, Colorado, shale oil contains about 80 per cent of its sulfur in the form of thiophenes, including thiophene itself, various mono-, di- and trialkylated thiophenes, and 2,3-benzothiophene. The McCoy and Weiss data (Table 3) show that the sulfur compounds in both California and Mid-Continent lubricating oils were about 65 per cent nonthiophenic.

Thermodynamics of Hydrodesulfurization

The work of the API Project 48 on thermodynamic properties of sulfur compounds is proceeding at a rapid pace, and any discussion of this subject is constantly in need of revision to include new data. At the time of consideration of this subject, reasonably complete data were available from API Project 48 and other work (see list of references for Tables 6–9) for elemental sulfur, hydrogen sulfide, six thiols, four alkane sulfides, four cyclic sulfides, two disulfides, and three thiophenes. Using S_2 (gas) as the standard state, the heats of formation, free energies of formation, and logarithms of the equilibrium constants of formation for the various sulfur compounds were derived or taken from the references and are given in Tables 6, 7, and 8, respectively. Calculated thermodynamic properties for sulfur and hydrogen sulfide are given in Table 9.

The above data and those of Rossini, Pitzer, Arnett, Braun and Pimentel[31] for hydrocarbons were used to calculate the equilibrium constants for the following typical desulfurization or partial desulfurization reactions:

(1) Hydrogenation of various type compounds to yield saturated hydrocarbons and hydrogen sulfide.

(2) Decomposition of various type compounds to yield unsaturated hydrocarbons and hydrogen sulfide.

(3) Splitting of alkane sulfides to yield thiols and olefins.

(4) Condensation of thiols to yield alkane sulfides and hydrogen sulfide.

(5) Hydrogenation of disulfides to yield thiols.

The logarithms of the equilibrium constants for these reactions at several temperatures are summarized in Table 10. Plots of $\log_{10}K_{eq}$ versus $1/T$ for typical examples involving various sulfur compound types for the first two of the above reactions are shown by Figures 1 and 2. For each reaction illustrated other members of the same compound type will, in general, yield similar data. For example, the equilibrium constants for the reductions of

TABLE 6. HEAT OF FORMATION FOR THE IDEAL GAS STATE

$C\ (\text{graphite}) + H_2\ (\text{gas}) + S_2\ (\text{gas}) \rightarrow \text{Sulfur Compound (gas)}$

Compound	Kcal/Mole at									
	0	298.16	300	400	500	600	700	800	900	1000°K
Methanethiol	−16.65	−19.12	−19.13	−19.87	−20.48	−21.00	−21.43	−21.90	−22.02	−22.19
Ethanethiol	−21.09	−25.12	−25.14	−26.19	−27.07	−27.79	−28.34	−28.90	−29.07	−29.26
1-Propanethiol		−31.46								
2-Propanethiol	−27.95	−33.46	−33.49	−34.83	−35.92	−36.77	−37.40	−37.85	−38.15	−38.28
2-Methyl-2-propanethiol	−34.77	−41.79	−41.82	−43.42	−44.66	−45.59	−46.23	−46.67	−46.90	−46.94
1-Pentanethiol		−41.71								
2-Thiapropane	−19.61	−23.52	−23.54	−24.65	−25.62	−26.42	−27.05	−27.71	−27.95	−28.20
2-Thiabutane	−24.15	−29.49	−29.52	−30.93	−32.06	−33.01	−33.75	−34.44	−34.70	−34.92
3-Thiapentane	−29.1	−35.8	−35.9	−37.6	−39.0	−40.2	−41.1	−41.7	−42.2	−42.5
3-Methyl-2-thiabutane	−30.06	−36.83	−36.86	−38.51	−39.84	−40.88	−41.64	−42.15	−42.43	−42.48
Thiacyclopropane	+6.82	+3.93	+3.92	+3.11	+2.48	+1.98	+1.59	+1.31	+1.10	+0.98
Thiacyclobutane	+3.91	−0.62	−0.65	−1.94	−2.98	−3.77	−4.37	−4.80	−5.07	−5.21
Thiacyclopentane	−17.3	−23.5	−23.5	−25.1	−26.4	−27.4	−28.1	−28.6	−29.1	−29.4
Thiacyclohexane	−22.35	−30.38	−30.43	−32.45	−33.91	−34.85	−35.35	−35.47	−35.28	−34.78
2,3-Dithiabutane	−18.62	−22.6	−22.63	−23.61	−24.42	−25.03	−25.50	−26.10	−26.01	−−26.07
3,4-Dithiahexane	−29.02	−35.40	−35.43	−36.92	−38.11	−39.00	−39.93	−40.46	−40.47	−40.54
Thiophene	+15.02	+12.07	+12.06	+11.31	+10.77	+10.36	+10.07	+9.87	+9.76	+9.74
3-Methylthiophene	+8.81	+4.54	+4.52	+3.42	+2.54	+1.85	+1.32	+0.91	+0.63	+0.46
2-Methylthiophene	+8.93	+4.74	+4.72	+3.62	+2.75	+2.08	+1.58	+1.22	+0.99	+0.88

Table 7. Free Energy of Formation for the Ideal Gas State

$C\ (graphite) + H_2\ (gas) + S_2\ (gas) \rightarrow$ Sulfur Compound (gas)

Compound	Kcal/Mole at									
	0	298.16	300	400	500	600	700	800	900	1000°K
Methanethiol	−16.65	−10.13	−10.09	−6.97	−3.67	−0.26	+3.23	+6.78	+10.35	+13.97
Ethanethiol	−21.09	−9.36	−9.27	−3.81	+1.89	+7.74	+13.71	+19.75	+25.84	+31.95
1-Propanethiol					+7.41	+15.50				
2-Propanethiol	−27.95	−10.00	−9.86	−1.77	+6.63	+15.21	+23.93	+32.73	+41.55	+50.44
2-Methyl-2-propanethiol	−34.77	−9.60	−9.40	+1.65	+13.08	+24.71	+36.49	+48.32	+60.32	+72.15
1-Pentanethiol		−5.29								
2-Thiapropane	−19.61	−7.03	−6.92	−1.20	+4.76	+10.90	+17.19	+23.52	+29.95	+36.40
2-Thiabutane	−24.15	−6.66	−6.52	+1.17	+9.57	+17.98	+26.54	+35.19	+43.90	+52.67
3-Thiapentane	−29.1	−5.8	−5.6	+4.8	+15.5	+26.6	+37.7	+49.0	+60.4	+71.8
3-Methyl-2-thiabutane	−30.06	−6.16	−5.96	+4.60	+15.54	+26.70	+38.03	+49.44	+60.92	+72.42
Thiacyclopropane	+6.82	+13.31	+13.37	+16.64	+20.09	+23.66	+27.31	+30.99	+34.72	+38.46
Thiacyclobutane	+3.91	+16.32	+16.43	+22.32	+28.51	+34.89	+41.39	+47.95	+54.56	+61.20
Thiacyclopentane	−17.3	+1.4	+1.6	+10.2	+19.2	+28.4	+37.8	+47.2	+56.7	+66.3
Thiacyclohexane	−22.35	+3.27	+3.47	+15.09	+27.16	+39.47	+51.90	+64.37	+76.84	+89.28
2,3-Dithiabutane	−18.62	−1.63	−1.49	+5.70	+13.11	+20.69	+28.36	+36.07	+43.82	+51.58
3,4-Dithiahexane	−29.02	−0.51	−0.30	+11.65	+23.94	+36.44	+49.09	+61.83	+74.55	+87.32
Thiophene	+15.02	+20.56	+20.62	+23.58	+26.72	+29.95	+33.24	+36.56	+39.90	+43.26
3-Methylthiophene	+8.81	+19.72	+19.81	+25.08	+30.60	+36.28	+42.09	+47.91	+53.81	+59.73
2-Methylthiophene	+8.93	+19.97	+20.06	+25.35	+30.86	+36.58	+42.37	+48.23	+54.11	+60.03

TABLE 8. LOGARITHM OF THE EQUILIBRIUM CONSTANT OF FORMATION FOR THE IDEAL GAS STATE

$C\ (\text{graphite}) + H_2\ (\text{gas}) + S_2\ (\text{gas}) \rightarrow \text{Sulfur Compound (gas)}$

Compound	$\log_{10} K_f$ at								
	298.16	300	400	500	600	700	800	900	1000°K
Methanethiol	+7.43	+7.35	+3.80	+1.60	+0.09	−1.01	−1.85	−2.51	−3.05
Ethanethiol	+6.86	+6.75	+2.08	−0.83	−2.82	−4.28	−5.39	−6.27	−6.98
1-Propanethiol				−3.24	−5.65				
2-Propanethiol	+7.33	+7.18	+0.97	−2.90	−5.54	−7.47	−8.94	−10.09	−11.02
2-Methyl-2-propanethiol	+7.04	+6.85	−0.90	−5.72	−9.00	−11.39	−13.20	−14.63	−15.77
1-Pentanethiol	+3.88								
2-Thiapropane	+5.15	+5.04	+0.66	−2.08	−3.97	−5.37	−6.42	−7.27	−7.95
2-Thiabutane	+4.88	+4.75	−0.64	−4.18	−6.55	−8.29	−9.61	−10.66	−11.51
3-Thiapentane	+4.25	+4.08	−2.62	−6.79	−9.69	−11.77	−13.39	−14.67	−15.70
3-Methyl-2-thiabutane	+4.52	+4.34	−2.51	−6.79	−9.73	−11.87	−13.51	−14.79	−15.83
Thiacyclopropane	−9.76	−9.74	−9.09	−8.78	−8.62	−8.53	−8.47	−8.43	−8.41
Thiacyclobutane	−11.96	−11.97	−12.20	−12.46	−12.71	−12.92	−13.10	−13.25	−13.27
Thiacyclopentane	−1.05	−1.16	−5.58	−8.40	−10.35	−11.80	−12.90	−13.78	−14.48
Thiacyclohexane	−2.40	−2.53	−8.24	−11.87	−14.38	−16.20	−17.58	−18.66	−19.51
2,3-Dithiabutane	+1.19	+1.09	−3.11	−5.73	−7.54	−8.85	−9.85	−10.64	−11.27
3,4-Dithiahexane	+0.37	+0.22	−6.37	−10.46	−13.27	−15.33	−16.89	−18.10	−19.08
Thiophene	−15.07	−15.02	−12.89	−11.68	−10.91	−10.38	−9.99	−9.69	−9.45
3-Methylthiophene	−14.45	−14.43	−13.70	−13.38	−13.21	−13.14	−13.09	−13.07	−13.06
2-Methylthiophene	−14.63	−14.61	−13.85	−13.49	−13.32	−13.22	−13.18	−13.14	−13.12

Table 9. Thermodynamic Functions for Sulfur and Hydrogen Sulfide

	Temperature,°K									
	0	298.16	300	400	500	600	700	800	900	1000
½S_2 (gas) → S (crystalline)[a]										
Heat for formation, Kcal/mole	−15.40	−15.42	−15.41	−14.84	−14.49	−14.11	−13.66			
Free energy of formation, Kcal/mole	−15.40	−9.56	−9.54	−7.60	−5.83	−4.15	−2.51			
$\log_{10}$ of the equilibrium constant of formation		+7.01	+6.95	+4.15	+2.55	+1.51	+0.78			
½S_2 (gas) + H_2 (gas) → H_2S (gas)										
Heat of formation, Kcal/mole	−19.53	−20.24	−20.24	−20.50	−20.74	−20.95	−21.13	−21.27	−21.38	−21.45
Free energy of formation, Kcal/mole	−19.53	−17.47	−17.45	−16.48	−15.44	−14.36	−13.25	−12.11	−10.97	−9.80
$\log_{10}$ of the equilibrium constant of formation		+12.81	+12.71	+9.00	+6.75	+5.23	+4.14	+3.31	+2.66	+2.14

[a] 0 to 368.6°K = Rhombic.
368.6 to 392°K = Monoclinic.
392 to 718°K = L_λ .

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TABLE 10. LOGARITHMS OF EQUILIBRIUM CONSTANTS FOR REACTIONS OF SULFUR COMPOUNDS

Reaction	Log$_{10}$ Keq at			
	298.16	500	700	900°K
Sulfur Compound + H_2 → Saturated Hydrocarbon + H_2S				
Methanethiol → Methane	+14.28	+8.37	+6.10	+4.69
Ethanethiol → Ethane	+11.70	+7.06	+5.01	+3.84
2-Propanethiol → Propane	+9.59	+6.05	+4.45	+3.52
2-Methyl-2-propanethiol → Isobutane	+9.43	+6.18	+4.68	+3.81
1-Pentanethiol → *n*-Pentane	+10.39			
2-Thiapropane → Methane	+25.45	+15.68	+11.41	+8.96
2-Thiabutane → Methane + Ethane	+22.58	+13.85	+9.97	+7.74
3-Thiapentane → Ethane	+20.08	+12.52	+9.11	+7.13
3-Methyl-2-thiabutane → Methane + Propane	+21.30	+13.37	+9.80	+7.72
Thiacyclopropane → Ethane	+28.32	+15.02	+9.26	+5.99
Thiacyclobutane → Propane	+28.88	+15.61	+9.90	+6.67
Thiacyclopentane → *n*-Butane	+16.83	+8.79	+5.26	+3.24
Thiacyclohexane → *n*-Pentane	+16.67	+9.22	+5.92	+3.97
2,3-Dithiabutane → Methane	+42.21	+26.08	+19.03	+14.97
3,4-Dithiahexane → Ethane	+36.75	+22.94	+16.79	+13.23
Thiophene → *n*-Butane	+30.89	+12.07	+3.85	−0.85
3-Methylthiophene → 2-Methylbutane	+29.85	+11.27	+3.17	−1.43
2-Methylthiophene → *n*-Pentane	+28.91	+10.84	+2.94	−1.55
Sulfur Compound → Unsaturated Hydrocarbon + H_2S				
Ethanethiol → Ethylene	−5.98	−0.83	+1.34	+2.53
1-Propanethiol → Propylene		+0.18		
2-Propanethiol → Propylene	−5.51	−0.16	+2.06	+3.26
1-Pentanethiol → 1-Pentene	−4.97			
2-Methyl-2-propanethiol → Isobutylene	−4.40	+0.76	+2.89	+4.04
3-Thiapentane → Ethylene	−15.30	−3.28	+1.75	+4.53
Thiacyclopropane → Acetylene	−14.09	−5.10	−1.22	+0.92
Thiacyclobutane → Allene	−10.68	−2.79	+0.61	+2.50
Thiacyclobutane → Propyne	−10.63	−4.73	−2.23	−0.88
Thiacyclopentane → 1,3-Butadiene	−12.53	−3.67	+0.14	+2.26
Thiacyclopentane → 1-Butyne	−21.54	−8.79	−3.35	−0.35
Thiacyclohexane → 1,4-Pentadiene	−14.60	−4.04	+0.46	+2.91
Thiacyclohexane → 1-Pentyne	−21.56	−8.23	−2.57	+0.49
3,4-Dithiahexane → Ethylene + Acetylene	−23.33	−5.08	+2.64	+6.85
Open-Chain Sulfide → Thiol + Olefin				
2-Thiabutane → Methanethiol + Ethylene	−9.38	−2.63	+0.20	+1.75
3-Thiapentane → Ethanethiol + Ethylene	−9.32	−2.45	+0.41	+2.00
3-Methyl-2-thiabutane → Methanethiol + Propylene	−8.08	−1.42	+1.31	+2.79

TABLE 10—*Continued*

Reaction	$\log_{10} K_{eq}$ at			
	298.16	500	700	900°K
Thiol → Open-Chain Sulfide + H_2S				
Methanethiol → 2-Thiapropane	+3.10	+1.47	+0.79	+0.41
Methanethiol + Ethanethiol → 2-Thiabutane	+3.40	+1.80	+1.14	+0.78
Ethanethiol → 3-Thiapentane	+3.34	+1.70	+0.93	+0.53
Methanethiol + 2-Propanethiol → 3-Methyl-2-thiabutane	+2.57	+1.26	+0.75	+0.47
Open-Chain Disulfide + H_2 → Thiol				
2,3-Dithiabutane → Methanethiol	+13.67	+8.93	+6.83	+5.62
3,4-Dithiahexane → Ethanethiol	+13.35	+8.80	+6.77	+5.56

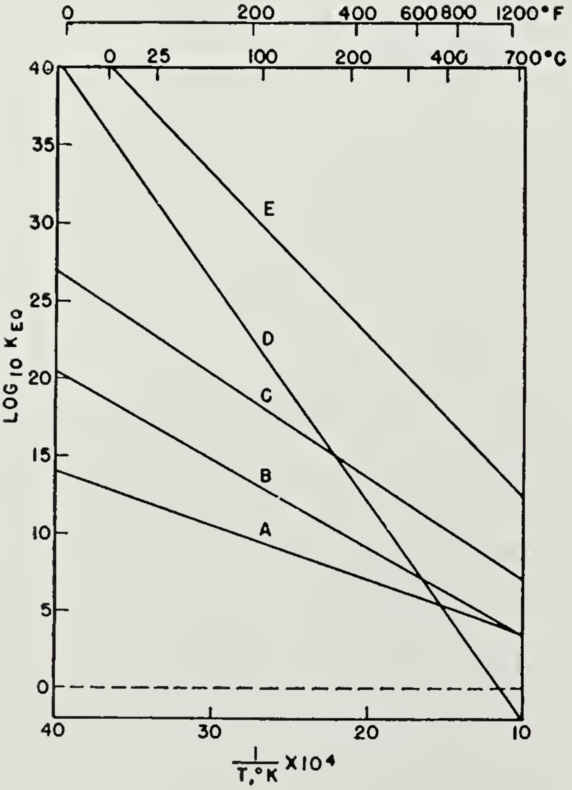


Figure 1. Reduction of sulfur-containing compounds with hydrogen to saturated hydrocarbon and hydrogen sulfide. Curve A, ethanethiol to ethane; Curve B, thiacyclohexane to n-pentane; Curve C, 2-thiabutane to methane plus ethane; Curve D, thiophene to n-butane; and Curve E, 3,4-dithiahexane to ethane.

ethanethiol and 2-propanethiol to ethane and propane, respectively, are close to each other at all temperatures.

Examination of the data in Table 10 and Figure 1 shows that the logarithms of the equilibrium constants for the reduction of sulfur compounds to saturated hydrocarbons are almost all highly positive over the temperature range considered (298–900°K or 25–627°C). Thus, in almost every case the equilibrium reaction can proceed virtually to completion if hydrogen is present in the stoichiometric quantity. The logarithm of the equilibrium constant decreases with increasing temperature for each reaction but is still highly positive at 700°K (427°C or 800°F), about the maximum temperature generally used for purely nondestructive hydrodesulfurization.

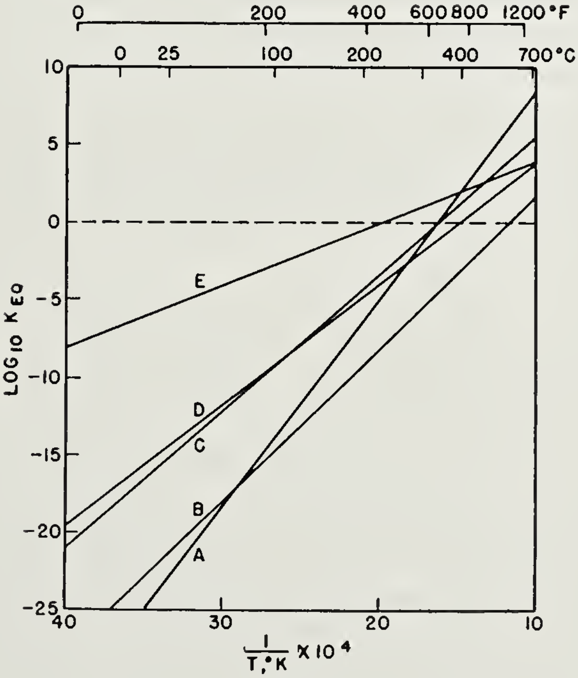
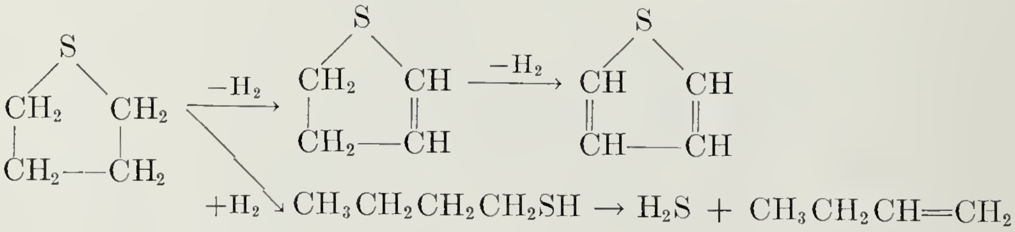


Figure 2. Decomposition of sulfur compounds to unsaturated hydrocarbons and hydrogen sulfide. Curve A, 3,4-dithiahexane to ethylene plus acetylene; Curve B, thiacyclohexane to 1-pentyne; Curve C, 3-thiapentane to ethylene; Curve D, thiacyclohexane to 1,4-pentadiene; and Curve E, 2-propanethiol to propylene.

It appears, in general, from Figure 2 and Table 10 that the decomposition of sulfur compounds to yield unsaturated hydrocarbons and hydrogen sulfide is not favored below about 608°K (325°C) and not until about 900°K (627°C) can decomposition of all aliphatic and alicyclic sulfur types approach completion. However, substantial decomposition of thiols which are the least stable of the compound types can occur at 573°K (300°C) and lower. Also if the decompositions of thiacyclopropane and thiacyclobutane are excluded from consideration as well as the reactions of thiacyclopentane and thiacyclohexane to yield derivatives of acetylene, substantially complete decomposition of all saturated types is favored at 700°K (427°C) or lower.

Thiacyclopropane, thiacyclobutane and their alkylated derivatives are apparently absent in petroleum; thus, their exclusion is reasonable for the present purposes. A comparison of curves B and D (Figure 2) shows that cyclic sulfides, such as thiacyclohexane, are favored to decompose to the diene rather than the acetylenic compound. It may be, however, that neither reaction predominates. Girelli, Helm, Thompson, Meyer and Ball[32] have obtained evidence that thiacyclopentane decomposes at 550°C to hydrogen sulfide and butylene along with thiophene as end products. They postulate the following sequence of reactions as reasonable in depicting the course of the decomposition. Hydrogen required for the opening of the ring to form butanethiol which subsequently decomposes to butylene and hydrogen sulfide is thought to be supplied by dehydrogenation reactions to form thiacyclopentene and thiophene. Amounts of sulfides II (probably thiophene) representing up to 25.2 per cent of the sulfur in the charge were found in products. On the other hand, McCoy and Weiss[27] have reported the recovery of 90 to 94 per cent of the sulfur in thiacyclopentane as hydrogen sulfide upon treating a white oil solution of the sulfur compound over alumina at 450°C.



Actually, the decomposition of disulfides to yield olefins and acetylenes according to Figure 2 and Table 10 is unlikely. Faragher, Morrell, and Comay[33] found hydrogen sulfide, sulfur, sulfides (probably the corresponding compounds) and the expected mercaptans among the products of decomposition of aliphatic disulfides. This indicates that the mechanism could include formation of sulfur and the corresponding sulfide with subsequent decomposition of the sulfide ultimately to unsaturated hydrocarbon and hydrogen sulfide as is thermodynamically possible. Disproportionation of disulfides to sulfides and trisulfides is also possible as has been indicated in the case of diaryldisulfides[34, 35]. With dimethyldisulfide the decomposition proceeds possibly through a free radical mechanism to yield methanethiol, polymerized thioformaldehyde, hydrogen sulfide, ethylene and alkylpolysulfides as major reaction products[36]. Methane, ethane and hydrogen have also been indicated as possible products[37], and there is evidence that a free radical process is not involved at high temperatures and short contact times[37].

Likewise, the decomposition of thiols and sulfides may not be simple, and, in some instances, free radical processes may be involved. This is thought to be the case with 2-methyl-2-propanethiol, which does give the expected hydrogen sulfide and isobutylene but also elemental sulfur, residual sulfur compounds and isobutane[38]. The decompositions of benzyl mercaptan, methanethiol, and, at high temperatures, ethanethiol are all free radical processes[39]. On the other hand, 1-pentanethiol[40] and, at low temperatures, ethanethiol[39] undergo molecular transformations. Free radical mechanisms are involved in the decompositions of methyl benzyl sulfide and dimethyl sulfide[37].

The above discussion emphasizes that some of the thermal decomposition reactions which have been given in Table 10 may not occur and that, in other instances, they may give only a partial picture of the complete reaction. Certainly, formation of hydrogen sulfide from aliphatic and alicycle sulfur types appears to be a typical reaction. Thus, as previously indicated, McCoy and Weiss[27] have observed that aliphatic and alicyclic sulfur types in white oil undergo substantially complete decomposition over alumina at 450°C to yield hydrogen sulfide. Likewise, Hammar[41] presents evidence indicating that carbon disulfide, aliphatic mercaptans and alicyclic sulfides are extensively decomposed to form hydrogen sulfide when treated at 400°C in a slow stream of hydrogen over alumina. Alumina has only weak hydrogenation activity; thus, the reactions were at least partially of thermal nature. In both investigations thiophene or thiophenes were observed to be stable at even more severe conditions.

The data which have been presented above relative to hydrogenation of the sulfur compounds to saturated hydrocarbons are relevant to the problem of hydrodesulfurization. The data for decompositions pertain to desulfurization over a solid catalyst in the absence of hydrogen or in the presence of hydrogen if the catalyst has negligible hydrogenation activity. This latter type of desulfurization is considered only incidentally in this chapter, but the data are interesting in that they indicate the possibility, in some instances, for decomposition of the sulfur-containing molecules to unsaturated hydrocarbons and hydrogen sulfide as a possible first step in the hydrodesulfurization reaction.

The other classes of reactions which have been considered may also bear on the mechanism of hydrodesulfurization. The splitting of the alkane sulfides to yield thiols and olefins is not favored at temperatures much below 700°K (427°C). The condensation of thiols to yield alkane sulfides and hydrogen sulfide is possible over the entire temperature range considered. This is also true for the hydrogenation of alkane disulfides to yield thiols.

The equilibrium constants for these latter two types of reactions decrease with increasing temperature.

Hydrodesulfurization and accompanying hydrogenation reactions which occur during processing of petroleum fractions are exothermic. Table 11 gives examples of the magnitude of the heat evolution at 700°K (427°C or 800°F) for the reactions of some specific compounds.

Hydrodesulfurization Reactions

Under usual commercial hydrodesulfurization conditions which involve the use of elevated temperatures and pressures, fairly high hydrogen to hydrocarbon ratios and generally a mild hydrogenation catalyst, the various major types of sulfur compounds undergo the reactions shown in Table 12. Thiols, open-chain and cyclic sulfides, disulfides and simple thiophenes are converted to saturated and/or aromatic hydrocarbons, depending upon the particular sulfur compound involved. Benzothiophenes are converted to alkyl aromatics and dibenzothiophenes probably partially to biphenyls. Thus, the major reactions which occur appear to involve simple carbon-sulfur bond rupture and saturation of the free valencies and of olefinic double bonds. In general, aromatic rings are not saturated, even though their hydrogenation may be thermodynamically favored, because of the specific inactivity of the catalysts employed. As described below, however, and as indicated by products given in Table 12, partial ring saturation may precede carbon-sulfur bond rupture in the case of dibenzothiophenes.

Table 11. Heats of Hydrogenation Reactions

Reaction	$\Delta H°_{700°K}$, Kcal/mole
$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$ (Ethanethiol)	−16.77
$C_2H_5SC_2H_5 + 2H_2 \rightarrow 2C_2H_6 + H_2S$ (3-Thiapentane)	−27.99
$C_4H_8S + 2H_2 \rightarrow n\text{-}C_4H_{10} + H_2S$ (Thiacyclopentane)	−28.73
$C_4H_4S + 4H_2 \rightarrow n\text{-}C_4H_{10} + H_2S$ (Thiophene)	−66.98
$CH_3C_4H_3S + 4H_2 \rightarrow C_5H_{12} + H_2S$ (3-Methyl- thiophene) (2-Methyl- butane)	−65.79
$C_6H_{12} + H_2 \rightarrow n\text{-}C_6H_{14}$ (Hexene-1)	−31.10

In support of the above general picture of the hydrogenation of sulfur compounds at commercial hydrodesulfurization conditions, it has been observed generally that fractions containing all sulfur types may be ade-

Table 12. Reactions of Sulfur Compounds under Hydrodesulfurization Conditions[a]

I. Thiols

$$RSH + H_2 \rightarrow RH + H_2S$$

II. Disulfides

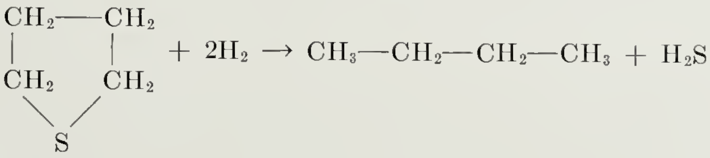
$$RSSR + 3H_2 \rightarrow 2RH + 2H_2S$$

III. Sulfides

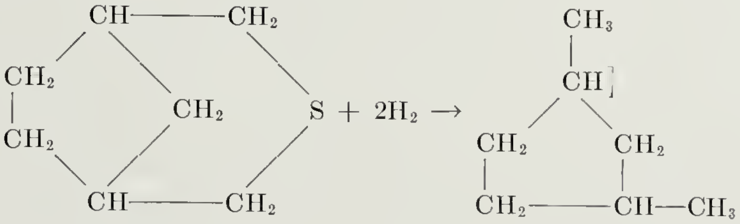
A. Open-Chain

$$R{-}S{-}R' + 2H_2 \rightarrow RH + R'H + H_2S$$

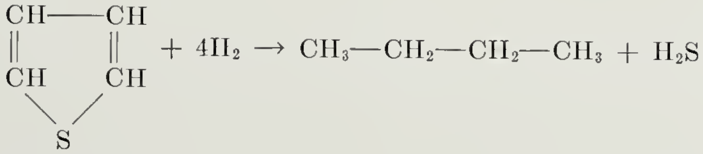
B. Cyclic



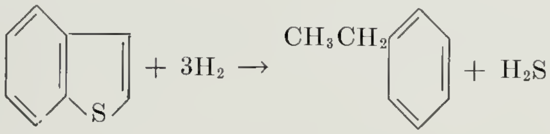
C. Bicyclic



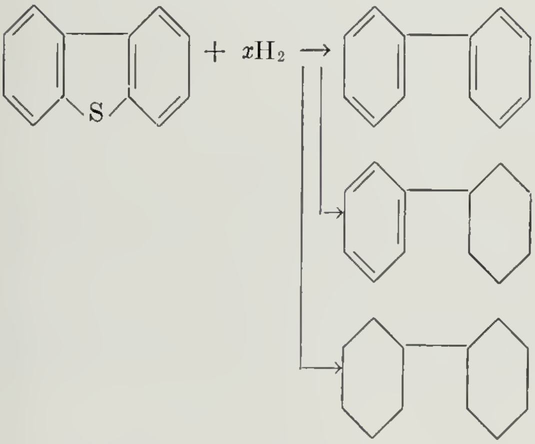
IV. Thiophenes



V. Benzothiophenes



VI. Dibenzothiophencs



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[a] R equals alkyl or aryl

quately desulfurized. In addition, studies have been made of the hydrogenation of pure sulfur compounds. Some of these latter studies are described below. Only a portion of the data have been obtained under commercial hydrodesulfurization conditions. However, information on the hydrogenation under other circumstances is probably significant and has been included.

Carbonyl Sulfide and Carbon Disulfide. These substances are probably never present in liquid petroleum fractions; thus, their reactions are not considered together with those of the major types in Table 12. However, the elimination of carbonyl sulfide and carbon disulfide from certain gases, particularly coal gas, is an important application of hydrodesulfurization. Carbonyl sulfide and carbon disulfide are both completely desulfurized in the presence of hydrogen and a catalyst at high temperatures and pressures. In the case of carbon disulfide methane is the end product[42]. The intermediate formation of methanethiol[43, 44] has been reported.

Thiols. Cope and Farkas[45] have shown that 1-heptanethiol and cyclohexanethiol can be converted to the hydrocarbons at 260°C in the presence of molybdenum trisulfide and hydrogen at 1800 to 3100 psi partial pressure. Molybdenum trisulfide, cobalt sulfide and an alumina supported cobalt molybdate type catalyst were found to be effective under these conditions for the hydrogenation of 1-octanethiol to octane. These catalysts and ruthenium, nickel sulfide, vanadium pentasulfide, ammonium thiomolybdate and ammonium thiotungstate were effective for the conversion of a mixture of *tert*-octanethiols to branched chain octanes. Cawley and Hall[46] have found that a 9.4 per cent solution of benzenethiol in pure cyclohexane was completely desulfurized upon passage over molybdenum disulfide. Reaction conditions were 200°C, 20 atmospheres pressure, 0.5 volume space velocity* and a high partial pressure of hydrogen. At 200 atmospheres pressure, desulfurization of a 9.6 per cent solution of the thiol in a light petroleum fraction was substantially complete at 150°C. Benzene was the hydrocarbon product, showing that desulfurization occurs more readily than hydrogenation of the benzene ring. Komarewsky and Knaggs[47], in atmospheric pressure runs at 400°C, observed that 1-butanethiol reacted with hydrogen over vanadium trioxide catalyst to give a mixture of 80.1 per cent butane and 19.9 per cent butene. It was considered that the reaction proceeded by the splitting out of hydrogen sulfide yielding butene which subsequently became hydrogenated to butane. On the other hand, Cope and Farkas[45] present evidence that hydrodesulfurization of thiols may occur by direct hydrogenolysis of carbon-sulfur bonds. Hoog[48] has

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* Volumes of liquid oil/volume of catalyst/hour—also referred to as LHSV (liquid hourly space velocity).

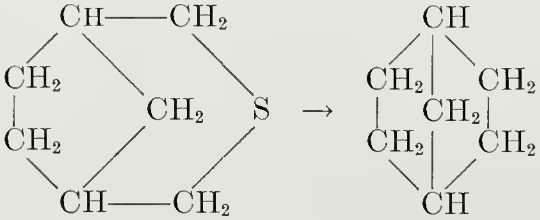
shown that a solution (1.4 per cent S) of 1-octadecanethiol in sulfur-free paraffinic oil was completely desulfurized presumably to yield octadecane upon passage over a supported cobalt molybdate type catalyst at 375°C, 50 atmospheres pressure, about 4 volume space velocity and a hydrogen to oil ratio of about 1000 standard cubic meters per ton. Broadbent, Slaugh and Jarvis[49] found that benzenethiol dissolved in ethanol was 60 to 65 per cent converted to benzene and 35 to 40 per cent to cyclohexane upon hydrogenation over rhenium heptasulfide at 300°C and 3600 psi average total reaction pressure.

Disulfides. It is well-known that disulfides are easily reduced to thiols; thus, it has been observed that this reaction can occur in the case of diphenyl disulfide on contact with an aluminum silicate catalyst[50]. Consequently, the above information on the reactions of thiols is pertinent to the hydrogenation of disulfides. In one study, actually dealing with disulfide hydrogenation, Hoog[48] found that di-*n*-octyl disulfide was hydrogenated to *n*-octane when a solution (1.4 per cent S) of this disulfide in a sulfur-free paraffin oil was passed over a supported cobalt molybdate type catalyst under the conditions given above for 1-octadecanethiol hydrogenation.

Open-Chain Sulfides. Hoog[48] has also studied the hydrodesulfurization of solutions obtained by adding benzyl *n*-octyl sulfide and phenyl *n*-decyl sulfide individually to a paraffin oil under the conditions used for the hydrogenation of 1-octadecanethiol. Virtually complete desulfurization was effected with the formation of the expected hydrocarbons and with negligible saturation of the benzene ring. Cope and Farkas[45] found that diheptyl sulfide could be hydrogenated to heptane at 260°C and high hydrogen partial pressure in the presence of molybdenum trisulfide or cobalt sulfide catalyst. An alumina supported cobalt molybdate type catalyst and a ruthenium catalyst were found to be ineffective for hydrogenation of the sulfide at this temperature.

Cyclic Sulfides. There appear to be no studies of the hydrogenation of cyclic sulfides at high pressures; however, as mentioned below it is possible that thiacyclopentane (tetrahydrothiophene) is an intermediate in the formation of butane from thiophene in pressure hydrogenation over molybdenum sulfide. At atmospheric pressure, Griffith, Marsh and Newling[51] observed that thiacyclopentane was hydrodesulfurized presumably to butane over molybdenum disulfide at 175 to 200°C and over nickel subsulfide at 200 to 400°C. Birch and Dean[52] have shown that *n*-pentane and a small amount of cyclopentane were formed when thiacyclohexane was desulfurized with Raney nickel in a special type of hydrodesulfurization, described more fully below, in which the surface bound hydrogen on the Raney nickel enters into reactions. 6-Thia-(1,2,3) bicyclo-octane yields

1,3-dimethylcyclopentane (reaction IIIC, Table 12) as the main product and a small amount of 1,2,2-bicycloheptane,



Simple Thiophenes. The hydrogenation of thiophene itself has received a great deal of attention. Hendricks, Huffman, Parker and Stirton[53] have studied the hydrogenation of thiophene and 2-methylthiophene over a cobalt molybdate-alumina catalyst presumably at commercial hydrodesulfurization conditions. Products from thiophene were normal and isobutane. Normal and isopentane were produced from the 2-methylthiophene. The isoparaffins were produced in concentrations of from about 35 to 60 per cent of the isomerization equilibrium amounts. Moldavski and Prokoptschuk[54] noticed that thiophene in solution in benzene formed butane when reacted with hydrogen under pressure at 350°C using molybdenum sulfide as catalyst. It was stated that thiacyclopentane and butyl mercaptan were formed as intermediates. Cawley and Hall[46] obtained evidence that thiophene hydrogenated over molybdenum disulfide in this manner by analysis of the reaction product obtained upon treating an 8 per cent solution of thiophene in cyclohexane over this catalyst at 200°C, 0.5 volume space velocity and 200 atmospheres pressure using a high hydrogen partial pressure. In this connection, Broadbent, Slaugh and Jarvis[49] have shown that it is possible to hydrogenate thiophene to thiacyclopentane over rhenium heptasulfide at 230 to 260°C and a total average reaction pressure of 2000 psi. Moldavski and Kumari[55] compared several sulfide catalysts for the hydrogenation of thiophene to yield butane at 210 to 270°C and 30 atmospheres pressure. Molybdenum disulfide was found most active, with cobalt sulfide also showing considerable activity. Nickel sulfide, manganese sulfide and cadmium sulfide all had about equal and lower activity. The formation of mercaptans was not observed in most cases but intermediate thiacyclopentane was found with all catalysts except cadmium sulfide.

Elgin[56] has reported on the atmospheric pressure hydrogenation of thiophene dissolved in naphtha using reduced nickel-kieselguhr catalyst both initially sulfur free and after it had been brought to steady state, and Taylor[57] has described the atmospheric pressure hydrogenation of thiophene dissolved in benzene using (a) molybdenum sulfide, (b) molybdenum oxide, and (c) a mixture of molybdenum sulfide and cobalt oxide as catalysts. However, these investigators do not reveal the nature of the reaction products. Komarewsky and Knaggs[47] used vanadium trioxide as the catalyst in a study of the atmospheric pressure hydrogenation of thiophene at 400°C. No presaturation of the sulfur compound was reported. The main products were hydrogen sulfide, butene and butane. Evidence was presented to indicate that the hydrogenation proceeded stepwise to form butane through the formation of 1-butadienethiol, butadiene and butene intermediates.

Griffith, Marsh and Newling[51] likewise studied the atmospheric pressure hydrogenation of thiophene. Molybdenum dioxide-molybdenum disulfide at 200 to 300°C, molybdenum disulfide at 175 to 200°C and nickel subsulfide at 200 to 500°C were used as catalysts. The molybdenum disulfide catalyst was most active and the nickel subsulfide the least active. Analysis of products obtained using the nickel subsulfide and the molybdenum dioxide-molybdenum disulfide catalysts did not show the presence of thiacyclopentane and mercaptan intermediates. The hydrocarbon product was approximately 60 per cent butene and 40 per cent butane.

Griffith, Marsh and Newling[51] proposed mechanisms for the hydrogenation of thiophene over the catalysts which they employed. These mechanisms naturally do not provide for the formation of thiacyclopentane as its formation was not observed. It was thought that the reaction proceeded over molybdenum sulfide catalyst according to the following sequence:

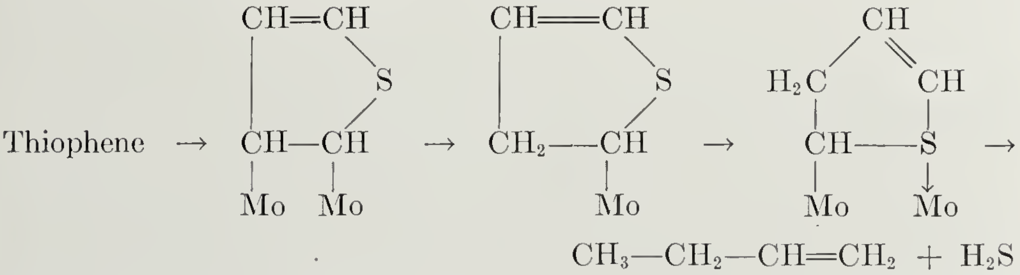
"1. Two-point adsorption of thiophene on a pair of adjacent Mo atoms in an exposed plane of the MoS_2 layer lattice.

2. Conversion to the half-hydrogenated state by reaction with a hydrogen atom adsorbed on an adjacent Mo atom.

3. Rupture of the carbon-sulfur bond by reaction of more hydrogen atoms with the half-hydrogenated molecule in which the sulfur atom has become linked to a molybdenum atom.

4. Conversion of the adsorbed molecule to butane or butene by continued reaction with further hydrogen atoms."

The following scheme represents these steps:



In the case of the hydrogenation over nickel subsulfide, Griffith, Marsh, and Newling proposed[51] that the solid did not act as a true catalyst. In the streaming system and low partial pressures of thiophene which were employed, it was thought that the solid was partially reduced to nickel and that the hetero-atom of thiophene actually reacted with this nickel. The nickel sulfide thus formed was thought to undergo subsequent reduction in "due course". The formation of thiacyclopentane in the work reported by Moldavski and Kumari[55] is explained by Griffith and co-workers[51] by assuming that, in the closed vessel which was employed, nickel sulfide might have survived partly unchanged in the presence of hydrogen and hydrogen sulfide. It is thought that under high pressure, nickel sulfide could catalyze the formation of thiacyclopentane by two-point adsorption of thiophene on suitably spaced nickel atoms in one of the planes that contain only nickel atoms.

Komarewsky and Knaggs[47] favor the idea that the atmospheric pressure hydrodesulfurization of thiophene over vanadium trioxide involves two-point adsorption of the carbon and sulfur linkage on vanadium atoms followed by cleavage of the carbon-sulfur bond as the first step in the reaction.

Benzothiophenes. Hoog, Reman and Smithuysen[26] have obtained evidence for the formation of alkylbenzenes from benzothiophenes present in Middle East catalytic gas oil as a result of its hydrogenation over a cobalt molybdate-alumina type catalyst at 375°C, 50 atmospheres pressure and about 2.6 volume space velocity. Cawley[58] in discussion of this work proposed that the hydrogenation of benzothiophenes most likely occurred in three steps:

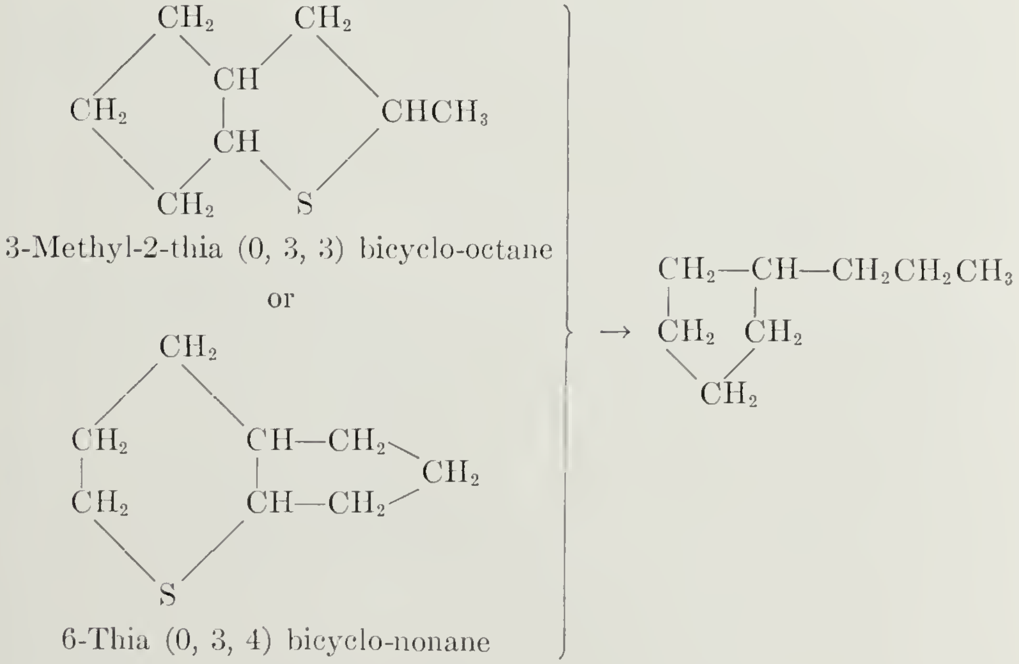
(1) Saturation of the double bond in the thiophene ring.
(2) Opening of the ring.
(3) Elimination of sulfur from the mercaptans.

The hydrogen consumed during treatment of the cracked stock corresponded closely to that required by this sequence.

Dibenzothiophenes. Hoog[48] studied the hydrodesulfurization of a blend (1.4 per cent S) of dibenzothiophene in a sulfur-free paraffin oil under conditions similar to those employed for the above catalytic gas oil. Sixty-five per cent of the reaction products from the sulfur compound consisted of a mixture of cyclohexylbenzene and bicyclohexyl. Thus, this reaction may have proceeded partially by hydrogenation of one to two of the benzene rings followed by carbon-sulfur bond rupture and sulfur removal.

Raney Nickel Desulfurizations. As mentioned above, a special case of hydrodesulfurization involves the use of Raney nickel with its occluded hydrogen. The reaction may be accomplished by heating the sulfur compound in ethanol or other solvent under reflux in the presence of Raney nickel. A large amount of catalyst is employed as it enters into reaction with sulfur and loses hydrogen to become unavailable for effecting further reaction.

There has been considerable interest[59, 60] in this method which was first discovered by Bougault, Cattelain and Chabrier[61]. It has been shown to be applicable to the desulfurization of various sulfur compounds including carbon disulfide[62], thiols[62], sulfides[63], cyclic sulfides[52] and thiophenes[64, 65]. As is mild hydrodesulfurization generally, this specific procedure of desulfurization is useful for structure determination. Thus, for example, it is possible to distinguish between simple aliphatic thiols and sulfides by examination of the hydrocarbon reaction products. Thiols will yield a single hydrocarbon according to reaction I in Table 12, and alkane sulfides will yield two hydrocarbons according to reaction IIIA. Unfortunately, the method gives no information as to the position of the sulfur atom on the carbon chain in the case of thiol desulfurization. With cyclic sulfides alternate structures may yield the same hydrocarbon[20] as illustrated below, thus limiting the usefulness of the procedure.



3-Methyl-2-thia (0, 3, 3) bicyclo-octane

or

6-Thia (0, 3, 4) bicyclo-nonane

Also, in the case of cyclic sulfides there exists some possibility of the formation of cyclic hydrocarbons. This aspect has already been discussed under reactions of these types of sulfur compounds.

At the present, the mechanism of desulfurization over Raney nickel most generally accepted and supported by a mass of evidence is a free radical mechanism involving, as a first step, the chemisorption of the sulfur compound on the catalyst surface through unshared sulfur electrons. The carbon-sulfur bond is thus weakened and a free radical is detached. The hydrogen present on the catalyst surface then reduces the radical to the corresponding hydrocarbon. A simplified mechanism is roughly schematized as follows:

$$\mathrm{R{-}S{-}R + Ni \rightarrow R^{\cdot} + RS{-}Ni}$$

$$\mathrm{R^{\cdot} + H\ (surface\ bound) \rightarrow RH}$$

When there is no hydrogen available, such radicals may react in other ways. They may combine with one another,

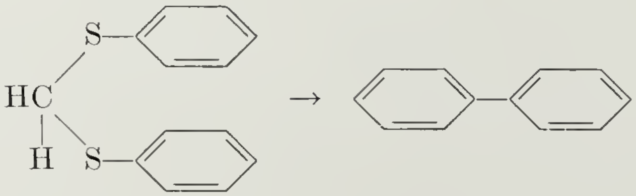
$$\mathrm{R^{\cdot} + R^{\cdot} \rightarrow R{-}R},$$

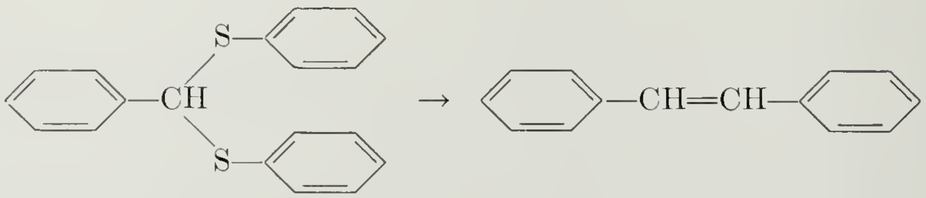
or they may form olefins.

$$\mathrm{RCH_2CH_2^{\cdot} \rightarrow RCH{=}CH_2 + H^{\cdot}}$$

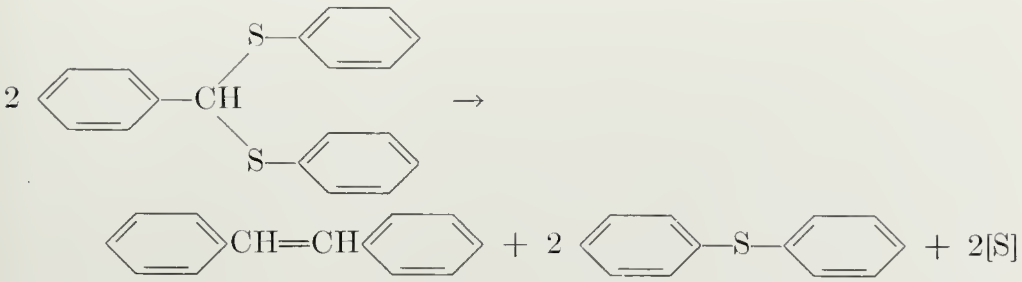
The work of Mozingo, Wolf, Harris and Folkers[63] may be cited in support of the mechanism represented by the first two equations. These investigators found that, when hydrogen rich Raney nickel was used for the desulfurization of sulfur compounds, carbon-sulfur bond rupture was accompanied by carbon-hydrogen bond formation. Thus, diphenyl sulfide gave benzene and dibenzyl sulfide gave toluene.

Relative to some specific results which may be obtained with hydrogen deficient Raney nickel (heated to 100°C *in vacuo*), Hauptmann and Wladislaw[66] found that formaldehyde diphenyl mercaptal gave biphenyl and benzaldehyde diphenyl mercaptal gave stilbene.



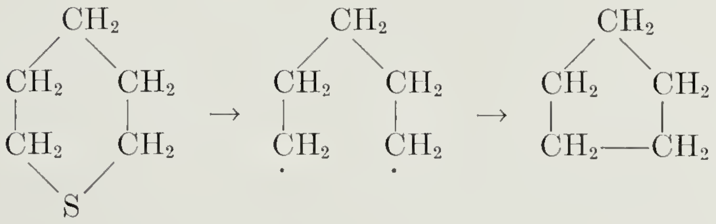


When a hydrogen-free Raney nickel (heated to 200°C in vacuo) was used, formaldehyde diphenyl mercaptal gave diphenyl sulfide. Benzaldehyde diphenyl mercaptal gave stilbene in increased yields as well as an excellent yield of diphenyl sulfide.



In consideration of this latter reaction, Hauptmann and Wladislaw[66] conclude that two types of radicals are formed: (1) benzylidene radicals which combine forming stilbene; (2) arylmercapto radicals which form the sulfide.

The work mentioned above of Birch and Dean[52] which showed the formation of a small amount of cyclopentane during Raney nickel desulfurization of thiacyclohexane was extended to study of the effect of employing hydrogen deficient Raney nickel. No increase in yield of cyclopentane, which was thought to form from the biradical, was observed.



A considerable increase in the formation of pentene was observed, however.

Further information on the mechanisms of Raney nickel desulfurizations is presented by Bonner[67, 68] who showed that sulfides and sulfoxides desulfurize by a different mechanism than sulfones. In the desulfurization of sulfides and sulfoxides, unshared electrons are available on the sulfur atom permitting chemisorption of the sulfur atom on the nickel, weakening of the carbon-sulfur bond, radical formation and subsequent reaction. This mechanism is supported by Bonner's evidence which shows that in the desulfurization of sulfides and sulfoxides, containing an asymmetric center adjacent to the sulfur atom, racemization occurs, indicating the formation of optically unstable free radicals. This behavior is in contrast to that observed in the desulfurization of sulfones where the sulfur atom contains no unshared electron pairs. In this case, racemization does not accompany desulfurization, thus indicating that free radicals are probably not involved. Bonner[68] suggests a mechanism which involves adsorption on the catalyst through the oxygen atoms of the sulfone, followed by an attack of adsorbed hydrogen on the carbon-sulfur bond with the formation of an optically active reduction product.

Kinetics

The expected relative rates at which various petroleum fractions should hydrodesulfurize has received some attention mostly through qualitative studies on pure compounds and on petroleum fractions. In general, while all types of sulfur compounds are effectively removed by hydrogenation as would be predicted on the basis of the above discussion of the thermodynamics of hydrodesulfurization, it appears that nonthiophenic sulfur compounds are removed at a more rapid rate than those of a thiophenic nature. It also appears that the rate of hydrodesulfurization decreases with increasing molecular weight of the fraction being processed or in other words with increasing molecular weight of the sulfur compounds being removed. On the basis of both of these considerations, it would be expected that sulfur removal from a light straight-run fraction such as a naphtha could be accomplished more easily than sulfur removal from a stock such as a gas oil, the sulfur content of which would be more thiophenic and in higher molecular weight compounds than characteristic of a naphtha. This has actually been observed to be the case and milder conditions may be employed in the case of such a naphtha. However, much remains to be determined about the relative rates of hydrogenation of specific sulfur types particularly as regards the effect of molecular weight and the effect of structure at the same molecular weight.

Pure Compound Work. Actually, very little has been established concerning the relative rates of the hydrogenation of pure sulfur compounds. Griffith and co-workers[44, 69, 70] have studied the atmospheric hydrogenation of carbonyl sulfide, carbon disulfide and methanethiol over nickel subsulfide catalyst. The former two constituents as well as thiophene comprise the major sulfur compounds in coal and town gas[71]. Carbon disulfide was hydrogenated over the temperature range 100 to 250°C; the concentration of sulfur compound in hydrogen was varied between 8.0 and 48.5 mg/cu ft[70]. At the lowest concentrations in hydrogen employed, the reaction with respect to carbon disulfide approached first order. As the concentration of sulfur compound was increased, its decomposition became less than would be predicted for a first order reaction, and, at the intermediate concentrations employed, passed through an apparent zero order stage. At higher concentrations, the rate of carbon disulfide decomposition became inversely proportional to its concentration, and, at the highest concentration studied, the retardation was quite pronounced[70]. Methanethiol was observed as an intermediate and probably the primary hydrogenation product[70]. In the primary reaction, it was considered[70] that adsorption of both carbon disulfide and hydrogen takes place but that the adsorption of carbon disulfide is so much more pronounced that it can easily lead to complete catalyst surface coverage with the consequent reaction rate retardation. The hydrogenation of carbonyl sulfide in excess of hydrogen was found[44] to be first order with respect to sulfur compound between about 150 and 200°C, but there is retardation at lower temperatures. It was suggested[44] that the reaction occurred by collision of carbonyl sulfide with adsorbed hydrogen on the catalyst. Carbonyl sulfide and carbon disulfide were found to react about equally readily at low concentrations of sulfur compound in hydrogen; carbonyl sulfide reacted more readily at high concentrations because of the retardation caused by covering the catalyst surface by carbon disulfide. The reaction of methanethiol in large excess of hydrogen was shown[44] to be first order with respect to the sulfur compound and to proceed at an appreciable rate in the temperature range 200 to 250°C where activated adsorption of the methanethiol takes place[69]. The rate of methanethiol hydrogenation was found to be slower than the rate of carbon disulfide reaction, which makes possible the isolation of methanethiol from the products of the mild hydrogenation of carbon disulfide.

Moldavski and Kumari[72] studied the hydrogenation of several sulfur compounds dissolved in a petroleum fraction at 230°C, using a molybdenum disulfide catalyst and an initial hydrogen pressure of 30 atmospheres in two-hour runs. Benzenethiol was 94 per cent desulfurized and was less stable than ethanethiol and 3-methyl-1-butanethiol. Dibenzyl, diallyl, diethyl, dipropyl and diisoamyl sulfides fell in the order given with respect to increasing stability toward desulfurization by hydrogenation. Save for the dibenzyl compound, the sulfides were much more stable than the thiols.

Cawley and Hall[46] found that benzenethiol was more easily desulfurized than carbon disulfide which in turn was more easily desulfurized than thiophene in experiments at 20 atmospheres pressure and elevated temperatures, using molybdenum disulfide as the catalyst and a high hydrogen concentration. At a constant contact time of about two minutes, the temperatures required for complete desulfurization were 200°C for benzenethiol, 250°C for carbon disulfide and 300°C for thiophene. It was concluded that the relative ease of desulfurization could be predicted on the basis of the nature of the reactions involved. Benzenethiol was pictured to desulfurize in one step. Carbon disulfide was thought probably to hydrogenate to methanethiol before removal of the sulfur atom, and, as described above, thiophene probably undergoes hydrogenation to thiacyclopentane followed by ring opening to form a mercaptan before desulfurization takes place. Thus it was thought, in these particular instances, that the relative ease of desulfurization was tied up with the number of steps involved in the process.

Elgin[56] found that dipropyl sulfide is much more rapidly desulfurized than thiophene during atmospheric pressure hydrogenation of naphtha solutions of the sulfur compounds over a steady state nickel catalyst at 300°C. With respect to the mechanism of dipropyl sulfide decomposition, Elgin[56] was unable to decide whether reaction with free nickel on the catalyst surface or catalyzed reaction with hydrogen was involved. Meerbott and Hinds[73] found that 1-butanethiol was more readily desulfurized than thiophene in pressure hydrogenations of solutions of the two compounds in a mixed *n*-heptane and 1-octene solvent over a tungsten-nickel sulfide catalyst. Griffith, Marsh and Newling[51] observed that thiacyclopentane could be hydrogenated more rapidly than thiophene. In the atmospheric pressure runs which were made at 200°C with 260 ppm of sulfur compound in the hydrogen, thiacyclopentane was about 80 per cent converted over molybdenum disulfide catalyst whereas the conversion of thiophene was only about 60 per cent. Over a nickel subsulfide catalyst, a mixture of hydrogen and 280 ppm of sulfur compound gave conversions of thiacyclopentane of 41 per cent and 100 per cent at 200 and 350°C, respectively, and corresponding conversions of thiophene of 0 and 15 per cent, respectively. It was thought[51] that the more rapid decomposition of thiacyclopentane over the molybdenum disulfide catalyst might be the result of only single-point adsorption on the molybdenum surface being necessary in comparison with the stated requirement of two-point adsorption in the case of thiophene. Similarly, it was postulated that two-point adsorption of thiacyclopentane on nickel subsulfide could not be involved because nickel atoms in the 111-plane only are suitably spaced to give such adsorption, and, inasmuch as the nickel atoms in this plane are arranged in groups of threes, simultaneous adsorption of enough hydrogen atoms to lead to reaction would be impossible.

Griffith, Marsh and Newling[51] obtained additional information on the atmospheric pressure hydrogenation of thiophene. Data obtained with the nickel subsulfide catalyst, in the temperature range 350 to 500°C and three concentrations (206 ppm; 378 ppm; and 550 ppm) of thiophene in hydrogen, showed the conversion to be nearly first order with respect to thiophene. With molybdenum oxide-molybdenum disulfide catalyst, at temperatures in the range 200 to 300°C and also three concentrations (155 ppm, 275 ppm, and 500 ppm) of thiophene in hydrogen, the reaction order with respect to sulfur compound concentration was stated to be between 0.2 and 0.6. Data obtained with molybdenum disulfide catalyst, at 200°C at thiophene concentrations between 162 ppm and 690 ppm, indicated that the reaction was approximately zero order with respect to thiophene.

Russian investigators[54, 55] studied the pressure hydrogenation of thiophene in benzene solution over a molybdenum disulfide catalyst. The conversion was between zero and first order with respect to sulfur compound. The rate of hydrogenation increased with increasing hydrogen pressure. In atmospheric pressure work employing hydrogen pretreated 40 per cent cobalt sulfide-60 per cent molybdenum trioxide catalyst, Pease and Keighton[74] also observed that the reaction order for the hydrogenation of thiophene dissolved in benzene was less than the first with respect to sulfur compound. It was stated[74] that thiophene apparently extensively saturated the catalyst surface, or else its hydrogenation was inhibited by a by-product (e.g., hydrogen sulfide). In their work, discussed above, on the hydrogenation of thiophene alone over molybdenum oxide-molybdenum disulfide and molybdenum disulfide catalysts, Griffith, Marsh and Newling[51] concluded that the rate determining step was the activated adsorption of hydrogen on the molybdenum sulfide surface.

Petroleum Fractions Work. Some additional information on the relative rates of hydrogenation of various sulfur types and of the effect of molecular weight on their hydrogenation as well as on the mechanism of hydrodesulfurization is available from work on petroleum fractions.

With respect to sulfur type, Byrns, Bradley and Lee[75] investigated the hydrodesulfurization of a number of gasoline boiling range feed stocks, such as cracked gasolines, straight-run gasolines and gasoline extracts. It was observed that thiophenes were the most difficultly decomposible sulfur compounds. Casagrande, Meerbott, Sartor and Trainer[76] likewise found this to be the result upon hydrogenating a 135 to 385°F pressure distillate tops (0.34 per cent S) under pressure over a tungsten-nickel sulfide catalyst. Comparison of sulfur in 50°F fractions of both the charge and product both as regards total sulfur and sulfur types is shown in Figure 3. Aliphatic sulfur types were extensively removed from all fractions. Residual sulfur compounds, which would include those of the thiophenic type, were less readily removable with about a 50 per cent decrease in this type of compound occurring in the case of all fractions. In the author's laboratory, Kuwait Crude (2.7 per cent S) was catalytically hydrodesulfurized at 824°F and 515 psig. A Karr analysis[77] (with slight modifications) of the crude showed that the sulfur was mainly distributed between thiophenic compounds (i.e., simple thiophenes, benzothiophenes and dibenzothiophenes) which accounted for a major proportion of the sulfur, and aliphatic sulfides which accounted for a lesser proportion of the sulfur. Thiols and disulfides were essentially absent. The aliphatic sulfur compounds were about 95 per cent removed; whereas, the thiophenic type were only about 40 per cent removed.

With respect to the effect of molecular weight of sulfur compounds on the rate of their hydrodesulfurization, little information is available based on petroleum fractions work in addition to observations made generally that the difficulty of hydrodesulfurization increases with increasing molecular weight of the fraction being processed. In this connection, the type of sulfur compound as well as its molecular weight is important.

In the author's laboratory, a comparison was made of the pressure hydrodesulfurization of a straight-run 40.3°API West Texas furnace oil (0.61 per cent S) and a 25.2°API catalytic cycle stock (0.94 per cent S) over a supported cobalt molybdate type catalyst at constant conditions except for temperature. The somewhat lower molecular weight (estimated 178 avg.) straight-run stock was 90 per cent desulfurized at a reaction temperature of 700°F; whereas, the somewhat higher molecular weight (estimated 195 avg.) cracked stock, the sulfur content of which would be more thiophenic, was only 76 per cent desulfurized at a reaction temperature of 752°F. On the other hand, Hughes, Stine and Faris[78] found that a straight-run 29°API wide-cut West Texas gas oil (estimated* avg. mol. wt. 288; 1.1 per cent S) hydrodesulfurized less readily than a narrower cut, somewhat lower molecular weight (estimated* 271 avg.) 25°API West Texas catalytic gas oil (1.6 per cent S). In hydrogenation over a supported cobalt molybdate type catalyst at 750°F and 300 psi, the straight-run gas oil was only 72.7 per cent desulfurized in comparison with 78.2 per cent desulfurization for the cracked stock. Apparently an effect of molecular weight

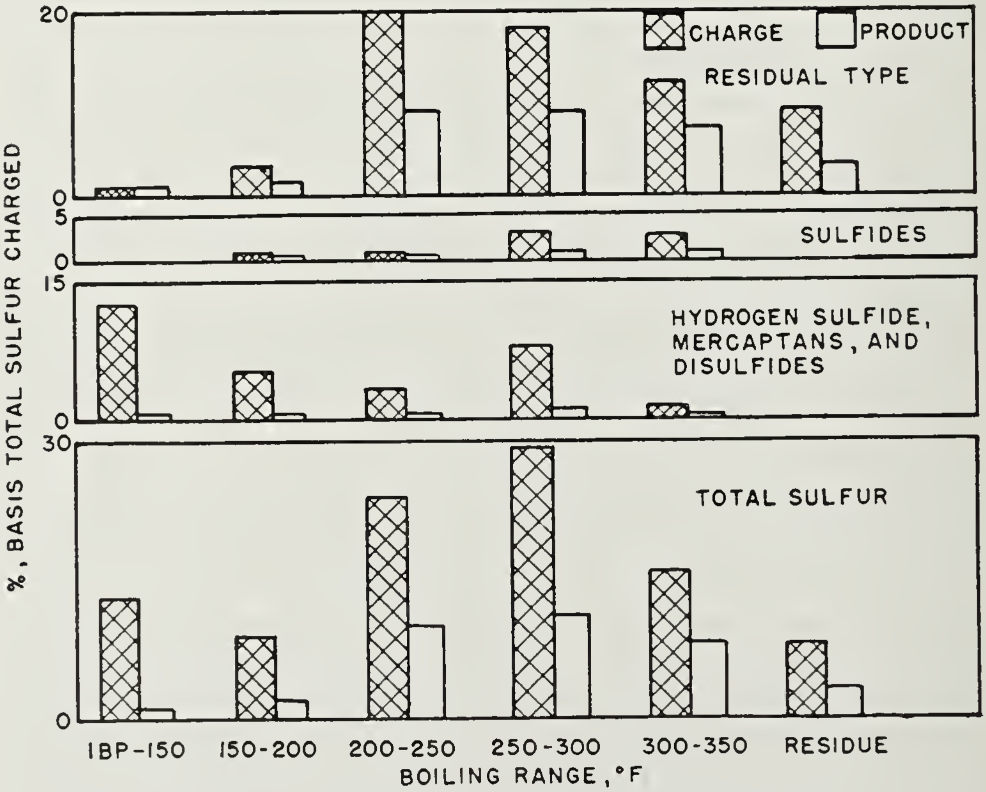


Figure 3. Comparison of 50°F. cuts of pressure distillate tops charge and product. (Derived from Ref. 76 with permission of the Editor of the *Industrial and Engineering Chemistry*).

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* By author from distillation data.

of the sulfur compounds being removed is indicated. Thus, the somewhat less thiophenic sulfur content of the straight-run oil was probably present in somewhat higher molecular weight compounds, and the effect of molecular weight could have been controlling in this comparison.

Hoog[79] specifically obtained an indication of an effect of molecular weight on the rate of hydrodesulfurization during a study of the processing of a full range 500 to 662°F Middle East gas oil (mol. wt. 236; 1.25 to 1.30 per cent S) and two narrow cuts from this gas oil, specifically a 554 to 572°F fraction (mol. wt. 233; 1.20 per cent S) and a 626 to 644°F fraction (mol. wt. 268; 1.76 per cent S). A supported cobalt molybdate catalyst was employed at 707°F; various contact times, 11 to 51 atmospheres pressure and hydrogen to oil mole ratios of from 6 to 60:1 were used. The data permitted a study of the kinetics of the hydrodesulfurization of the various charges. It was found that the rate of hydrodesulfurization of the heavier narrow fraction was considerably slower than the rate for the lighter fraction. It was stated that the phenomena of light-heavy selectivity might be connected with the occurrence of different types of sulfur compounds; however, it was preferred to believe that it was a matter of steric effects because "the higher the molecular weight of the sulfur compound, the more the sulfur atom may be shielded from the hydrogen atoms by hydrocarbon groups."

Hoog showed[79] that the hydrodesulfurization of the narrow fractions to a level of 95 per cent sulfur elimination could be described by the first order mechanism,

$$\ln \frac{p_s}{p_s^0} = -k_{p_{\mathrm{H}}p_0} \cdot \tau,$$

where p_s = partial pressure of sulfur compounds at the end of the catalyst bed,

p_s^0 = the corresponding partial pressure at the inlet to the catalyst bed,

τ = apparent contact time, and

$k_{p_{\mathrm{H}}p_0}$ = the rate constant which held only for a given hydrogen partial pressure p_{H}, oil partial pressure p_0, temperature, and catalyst combination.

More extensive elimination of sulfur than about 95 per cent was not observed, and it was thought that the remaining sulfur compounds might be a highly unreactive type. The desulfurization of the full range oil did not follow the postulated first order mechanism, and it was thought that any rate curve for desulfurization of the full-range oil was a "resultant of an integration of rate curves for a series of narrow cuts of increasing molecular weight." The intermediate position of the rate curve for the desulfurization of the full range oil when compared with rate curves, obtained under the same reaction conditions, for the two narrow cuts is shown in Figure 4.

In order to show the magnitudes of the effects of hydrogen and oil partial pressures, Hoog[79] calculated the first order rate constants for the hydrodesulfurization of the various fractions under each of various hydrogen and oil partial pressure conditions employed. For the full-range oil, a first order mechanism was assumed, and an initial rate constant, k_i, was approximated as being equal to the average rate constant between 100 and 50 per cent sulfur retention level. The dashed curve of Figure 4 shows a rate curve derived in this manner for one specific set of reaction conditions. The rate constants were plotted against the oil partial pressure on a semilog plot with stock and total reaction pressure as parameters. The results are shown by Figure 5. Light-heavy selectivity as well as the marked effect of hydrogen and oil partial pressures on the reaction rate are readily apparent. For a clearer presentation of the effect of hydrogen partial pressure, Hoog[79] made the comparison shown in Table 13 of the rate constants at infinite hydrogen dilution and at 2.5 atmospheres oil partial pressure deriving the values from Figure 5. It was concluded that, although the effect of hydrogen partial pressure was rather limited at infinite hydrogen dilution, it was substantial at finite oil partial pressures.

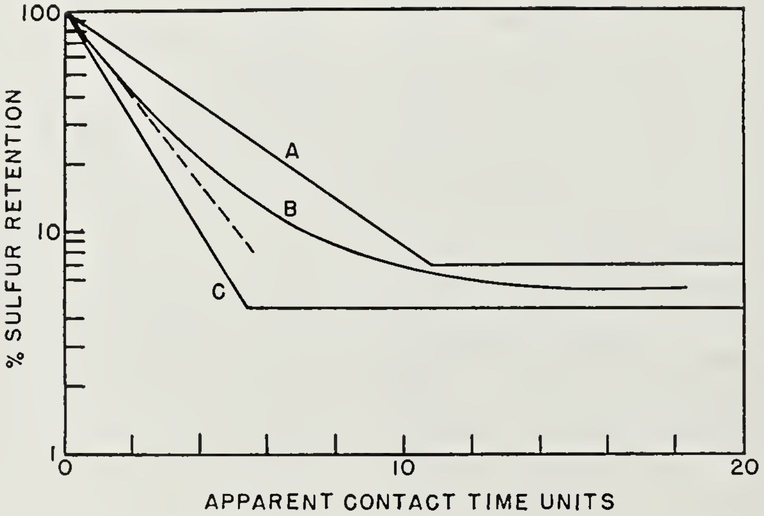


Figure 4. Hydrodesulfurization of Middle East gas oil fractions at 707°F., 51 atmospheres absolute pressure and a hydrogen to oil ratio of 3000 standard cubic meters/ton. Curve A, 626°–644°F. fraction; Curve B, 500°–662°F. full-range gas oil; Curve C, 554°–572°F. fraction. (Derived from Ref. 79 with permission of the Editor of the *Journal of the Institute of Petroleum*).

Among the theoretical speculations that Hoog[79] advanced to explain his findings was that the effect of oil partial pressure could be explained by assuming that oil molecules were preferentially adsorbed on the catalyst surface, leaving less surface available for the dissociation of hydrogen molecules to form hydrogen atoms for entering into desulfurization reactions.

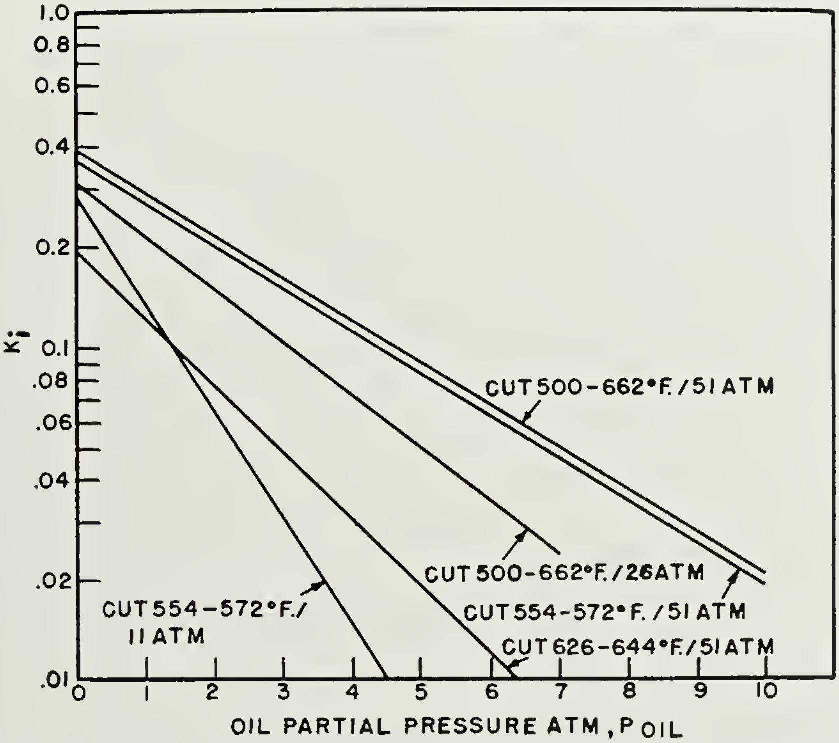


Figure 5. Correlation of reaction rate constants with oil partial pressure for the hydrodesulfurization of the indicated gas oil fractions at the indicated total absolute reaction pressures. (Derived from Ref. 79 with the permission of the Editor of the *Journal of the Institute of Petroleum*).

TABLE 13. COMPARISON OF RATE CONSTANTS FOR HYDRODESULFURIZATION OF GAS OIL FRACTIONS

Middle East Gas Oil	p_H, atm.	k_i at $p_0 = 0$	k_i at $p_0 =$ 2.5 atm.
Narrow Cut 554–572°F	48–51	0.38	0.18
Narrow Cut 554–572°F	9.5–11	0.29	0.04
Narrow Cut 626–644°F	48–51	0.19	0.06
Full Range 500–662°F	48–51	0.40	0.19
Full Range 500–662°F	22–26	0.32	0.13

Hoog[79] found that nitrogen inhibited the hydrodesulfurization, and he assumed that the retarding effect was due to competition of the nitrogen with hydrogen for free sites on the catalyst. However, he indicated that the magnitude of the inhibition effect showed that hydrogen was preferentially adsorbed with respect to nitrogen.

Some other studies on petroleum fractions bear on the kinetics and mechanism of hydrodesulfurization. Cole and Davidson[80] report that, for a given set of operating conditions, the per cent hydrodesulfurization of blends of thermally cracked gasoline and low-sulfur straight-run gasoline boiling in the aviation gasoline range is independent of original sulfur level when processing under pressure over a tungsten-nickel sulfide catalyst. Gary and Schweyer[81] made a similar observation relative to the cobalt molybdate pressure hydrodesulfurization of various gas oils including some West Texas, Kuwait, Columbia, and Venezuela stocks. Sulfur contents of the feeds varied between 0.51 and 3.36 per cent. At the constant conditions employed, product sulfurs varied between 0.37 and 2.34 per cent and sulfur removal was constant at about 27.5 per cent. Hammar[82] made a preliminary study of the kinetics of the hydrogenation of shale oil gasoline over a catalyst consisting of cobalt molybdate on alumina containing chromium as a promotor. Upon setting up rate equations according to the principles of Hougen and Watson[83] and determining the fit of calculated with experimental data, he concluded that hydrogenation of the olefins and of the sulfur compounds (mainly thiophenes) occurred on different parts of the catalyst. Inasmuch as this indicated the theoretical possibility of the existence of selective catalysts which would effect hydrodesulfurization without olefin saturation, a search for selective catalysts was conducted with the results given in a subsequent section.

Accompanying Reactions

Reactions of Hydrocarbons. Within the wide ranges of temperature and pressure utilized for hydrodesulfurization, it is apparent that many hydrocarbon reactions proceed concurrently with the sulfur compound reactions. Paraffin and naphthene isomerization reactions take place under all conditions, and hydrocracking increases as the temperature and pressure increase. At the higher temperatures and low pressures, some naphthenes dehydrogenate and some paraffins dehydrocyclize, and, at the lower temperatures and higher pressures, aromatics may be hydrogenated. Paraffins dehydrogenate to only a slight extent under the more severe conditions; whereas, olefins are readily hydrogenated under all conditions.

As explained more fully below, the nature of the catalyst is also a factor in determining the extent to which the various hydrocarbon reactions will occur. With the usual selective catalysts, the main reactions lead to the elimination of sulfur compounds and other heterocyclics, and, although some isomerization and hydrocracking may occur, the extent of such reactions is usually relatively minor. However, over certain catalysts and under favorable reaction conditions these latter reactions become important.

So far as applications which are considered in this chapter are concerned, hydrocracking is important in the conversion of residual oils and certain other stocks to lighter products. In certain applications of mild hydrodesulfurization, naphthene and heterocyclic dehydrogenation and paraffin dehydrocyclization act as a source of hydrogen for effecting desulfurization reactions. In this connection dehydrogenation of six-membered ring naphthenes is probably most important.

Accompanying hydrocarbon reactions of specific interest are olefin and aromatic saturation. As described below, it is desirable to remove sulfur and conjugated diolefins from cracked gasolines to increase quality and stability and, at the same time, to maintain high octane numbers by not saturating monoolefins to any great extent. In the case of aromatic distillates of suitable boiling range for inclusion in aviation gasolines, saturation of olefins and sulfur removal without aromatic hydrogenation is practiced.

Even though olefin hydrogenation is thermodynamically favored under all usual hydrodesulfurization conditions, it is possible to effect a degree of selective desulfurization without a corresponding degree of monoolefin saturation and, at the same time, to bring about substantial removal of conjugated diolefins. Thus, for example, in the pressure (75 psig) hydrodesulfurization of a 135 to 385°F pressure distillate tops over a tungsten-nickel sulfide catalyst, Casagrande, Meerbott, Sartor and Trainer[76] obtained sulfur, conjugated diolefin and monoolefin reductions of about 66, 89 and 21 per cent, respectively. In operation with this catalyst, it is indicated that the least branched olefins hydrogenate most rapidly[73] and that the unreacted olefins undergo considerable isomerization[76] of the double bond shift type[73]. The shift is toward the center of the molecule. No skeletal isomerization takes place[73]. The double bond shift improves the octane number. On the other hand, the more rapid hydrogenation of the least branched olefins tends to lower the octane number. However, this lowering is compensated for by the improvement due to the double bond shift.

The degree of selectivity obtainable for the hydrogenation of sulfur compounds is influenced by a number of factors besides catalyst and reaction conditions which are discussed below. Thus, Cole and Davidson[80], in studying the pressure hydrodesulfurization of fractions of Los Angeles Basin catalytic and thermal gasolines over a tungsten-nickel sulfide catalyst, noted that the rate of hydrogenation of olefins decreased more rapidly with increase in boiling point than the hydrogenation of sulfur compounds. Figure 6 shows the results in the case of three fractions of the thermal gasoline. These results, as well as the results on the catalytic gasoline, indicate that somewhat greater selectivity for desulfurization should be obtainable during processing of heavier fractions.

There is also apparently an effect of type of olefin. Thus it has been observed[73] (Figure 7) that greater selectivity is obtained for the hydrodesul-

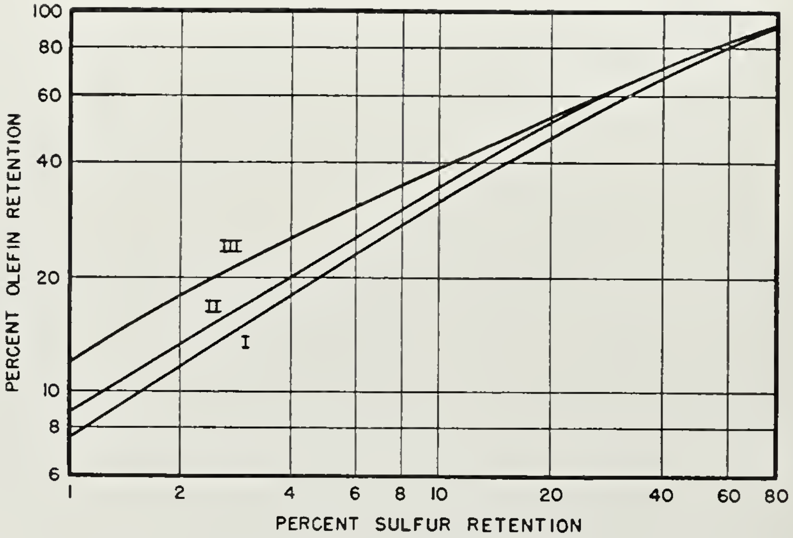


Figure 6. Variation of olefin retention with sulfur retention on hydrodesulfurization for three fractions of California thermal gasoline. Properties of charges were:

Fraction	*Boiling Range, °F.*	*Sulfur, Wt. %*	*Bromine No.*
I	110–210	0.41	92
II	180–290	0.66	87
III	290–370	1.04	50

(Reproduced from Ref. 80 with permission of the Editor of the *Industrial and Engineering Chemistry*).

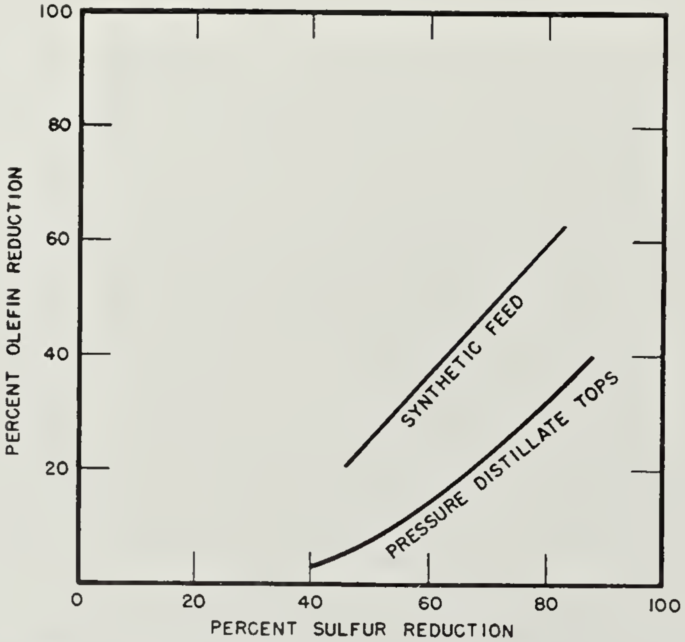


Figure 7. Selective hydrotreating of pressure distillate tops and synthetic feed over tungsten-nickel sulfide catalyst. (Reproduced from Ref. 73 by permission of the Editor of the *Industrial and Engineering Chemistry*).

furization of the above-mentioned pressure distillate tops (0.36 per cent S; ca. 80 bromine number) over tungsten-nickel sulfide catalyst than for a synthetic feed (0.30 per cent S; 70 bromine number) consisting of equal weights of n-heptane and octene-1 and containing added sulfur compounds. Apparently, the n-olefin hydrogenates more readily than the mixed olefins in the pressure distillate tops, although it has been alternatively suggested[73] that components in the pressure distillate tops may inhibit the hydrogenation of olefins.

The mechanism by which sulfur compounds may be selectively hydrogenated in the presence of olefins has not been definitely established. Both Cole and Davidson[80] and Meerbott and Hinds[73] found that sulfur compounds in the feed inhibit the hydrogenation of olefins. Data of Cole and Davidson[80] showing the extent of the inhibition are given in Figure 8, which represents the results of the addition of a concentrate of thiophenes to a blend of thermal and low-sulfur straight-run gasolines during pressure hydrodesulfurization over tungsten-nickel sulfide catalyst. It has been suggested[73] that this inhibitory effect might be attributed to more sucessful competition for the active catalyst centers by the sulfur compounds. However, it will be recalled that Hammar[82] concluded that hydrogenation of sulfur compounds and olefins may occur on different parts of a catalyst surface. Limited work indicates that olefins apparently have, at most, only a small inhibitory effect on the desulfurization process[73].

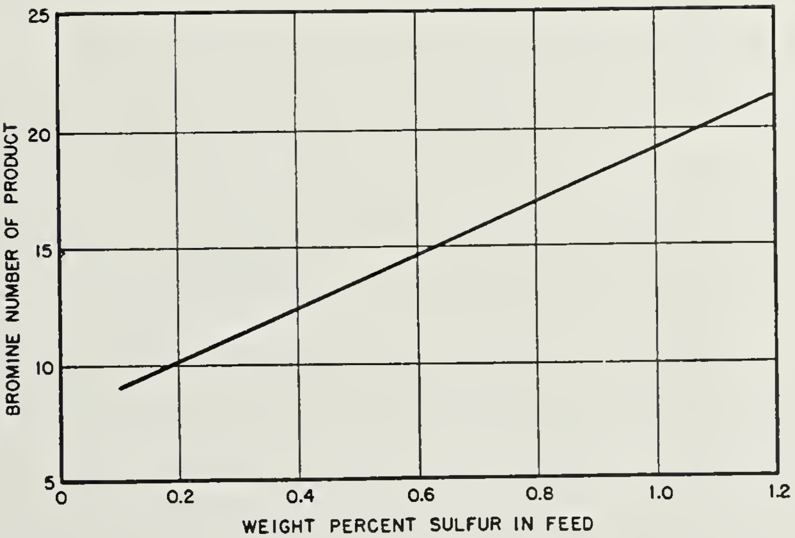


Figure 8. Effect of sulfur in feed on hydrogenation of olefins. (Reproduced from Ref. 80 by permission of the Editor of the *Industrial and Engineering Chemistry*).

Reactions of Heterocyclics. Charge stocks to be hydrodesulfurized frequently contain nitrogen, oxygen and metal compounds. The heterocyclic atom in all these compound types is extensively removed under hydrodesulfurization conditions. The nitrogen compounds which may be present are typified by pyridines and quinolines (basic) and carbazoles, indoles and pyrroles (non-basic). Oxygen may be found in preformed compounds such as phenols, fatty acids and naphthenic acids and in oxidation products, for example, hydroperoxides. Metals which may be present include arsenic, nickel and vanadium. In general, nitrogen is eliminated as ammonia, oxygen as water and metal as the metal itself, usually as a deposit on the catalyst.

Simultaneous removal of nitrogen compounds is a very important present and potential aspect of hydrodesulfurization. Marked deleterious effects of traces of these compounds on storage stability and amenability to processing of petroleum products have been observed. Basic nitrogen compounds in catalytic cracking charge stocks temporarily poison the activity of cracking catalysts by neutralizing acid centers with resulting decrease in gasoline yields[84, 85]. Nitrogen compounds also poison certain other catalysts including platinum containing hydroreforming compositions[86]. Some nitrogen compounds contribute to the instability of burner and diesel fuels. Thus pyrrole markedly increases the rate of deterioration of a blend of catalytic cycle stock and a virgin oil from Coastal Crude[87].

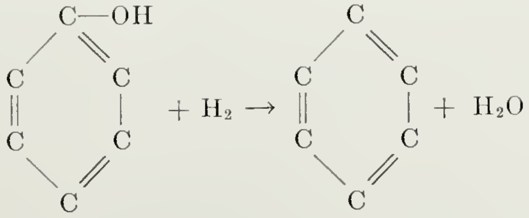
Certain oxygen compounds are also undesirable in petroleum fractions. Thus, for example, naphthenic acids are corrosive and hydroperoxides and gums represent stages of deterioration of hydrocarbons.

Arsenic is generally thought to be a marked poison for platinum hydroreforming catalysts. However, certain such catalysts have considerable tolerance for this metal[88]. Such tolerance is probably a fairly direct function of platinum content. The iron, nickel, vanadium and copper in catalytic cracking charge stocks poison the selectivity of cracking catalysts[89, 90].

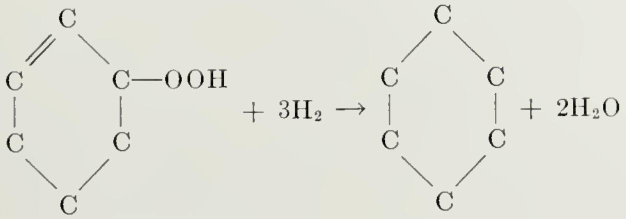
The specific illustrations shown in Table 14 of the over-all reactions involved in the mild hydrogenation of certain nitrogen and oxygen compounds over a cobalt molybdate-alumina type catalyst have been given by Grote, Watkins, Poll and Hendricks[86]. It has been stated[91] that, in general during hydrogenation, nitrogen is eliminated as ammonia less readily than oxygen is eliminated as water. Although this may be mainly true, it is also certainly a fact that some oxygen compounds react less readily than some nitrogen compounds. Thus, de Rosset, Riedl and Czajkowski[92] compared the rates of removal of thiophene, benzenethiol, pyridine, quinoline, aniline, piperidine, pyrrole, polyalkyl pyridines and *m*-cresol from a naphtha, upon mild hydrodesulfurization over a cobalt molybdate type catalyst. Pyridine, piperidine, pyrrole, thiophene and benzenethiol were relatively easily removed. *m*-Cresol, quinoline and aniline were more refractory, and this was particularly true in the case of *m*-cresol. The polyalkyl pyridines reacted

TABLE 14. TYPICAL REACTIONS OF OXYGEN AND NITROGEN COMPOUNDS

1.



2.

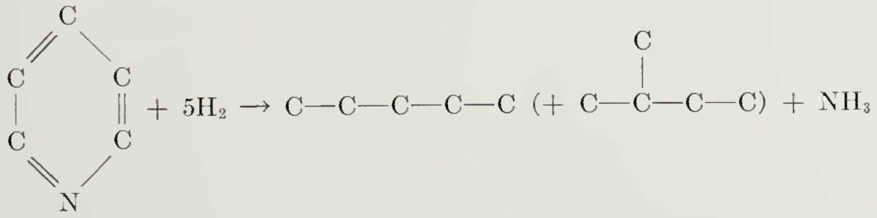


(Cyclohexene hydroperoxide)

3. $C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O$

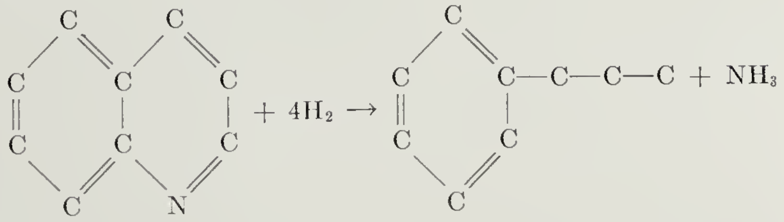
(Heptene hydroperoxide)

4.



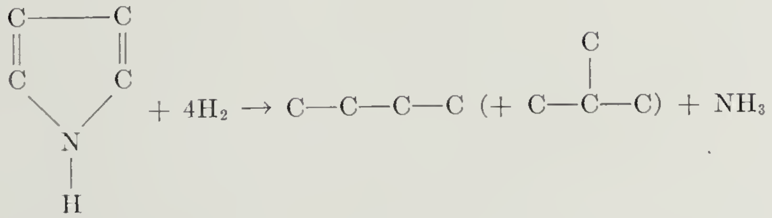
(Pyridine)

5.



(Quinoline)

6.



(Pyrrole)

at a rate similar to that for quinoline. On the other hand, Griffith, Marsh and Newling[51] noted that furane was decomposed to a greater extent by hydrogenation over a molybdenum oxide-molybdenum sulfide catalyst than pyrrole. Both tetrahydrofurane and furane were less refractory to hydrogenation than pyrrole over nickel subsulfide catalyst[51].

CATALYSTS

General Description

In general, any hydrogenation catalyst may be employed for the hydrodesulfurization of petroleum fractions. In the patent literature, such catalysts are often classified[93, 94, 95] broadly on the basis of the Periodic Table. Thus, one patent[93] indicates that suitable compositions contain oxides or sulfides of Groups II to VII, preferably of Group VI and preferably in conjunction with metals of Group VIII or with heavy metals of Groups I and II or their oxides or sulfides. Typical carriers for such catalysts are indicated to be active charcoal, fuller's earth, Florida earth, silica gel, alumina gel, pumice, bauxite and burnt fire clay. A basic U. S. patent[95] describes Group VI metal (molybdenum, tungsten, chromium and uranium) compounds which may be admixed with substances which may or may not have hydrogenating properties such as iron or cobalt or their compounds, or alumina, zinc oxide, magnesia or calcium carbonate. Another general classification[96] indicates catalytic agents to include oxides or other compounds of the related metals which possess their differentiating electron in the "second from the outermost shell" (shell immediately beneath the outer shell). Metals which are included[97, 98] are scandium, titanium, *vanadium*, *chromium*, manganese, *iron*, *cobalt*, *nickel*, copper, zinc, yttrium, zirconium, niobium, *molybdenum*, masurium, ruthenium, rhodium, palladium, silver, cadmium, lanthanum, hafnium, tantalum, *tungsten*, rhenium, osmium, iridium, *platinum*, gold, mercury, actinium, thorium and uranium. With the exception of copper, zinc, silver, cadmium, gold and mercury, these elements are of the transition type characterized by the fact that the outer two or three electron shells are incomplete. Copper, silver and gold in their polyvalent states also belong to the transitional class.

Obviously such broad classifications as given above are of sufficient scope to include materials of little value, or which have value only as promoters, and to cover substances which may only function as carriers. On the basis of frequency of mention in representative patent and other literature and of activity, the *italicized* members of the latter classification given above, when used alone or in certain combinations, assume an important position. Of the Group VIa and the Iron Group metal compounds, combinations of oxides or sulfides of cobalt and molybdenum or of sulfides of nickel and tungsten are used most frequently in the commercial applications considered in this chapter. Supported or unsupported combinations of cobalt oxide and molybdenum oxide may be mixtures of these compounds and/or the chemical compound cobalt molybdate. All such compositions are referred to as cobalt molybdate catalysts according to common usage.

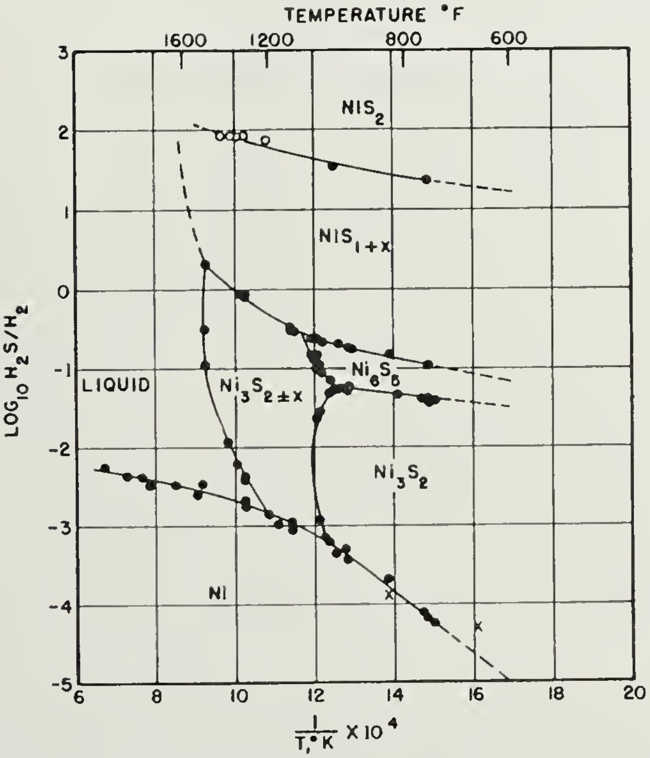


Figure 9. Hydrogen reduction equilibria of the nickel sulfides. Rosenqvist's[99] data and phase diagram taken directly. The data of Sudo[100] and Schenck and Von der Forst[101] are in substantial agreement with those of Rosenqvist for the Ni → Ni_3S_2 and Ni_3S_2 → Ni_6S_5 equilibria. Experimental points: ● Rosenqvist,[99] ○ Biltz, Voigt and Meisel,[102] and × Badger, Griffith and Newling.[103] The magnitude of the subscripts x in the formulae is of the order of a small fraction of one.

State of Equilibrium Catalysts

Although bulk thermodynamics probably are inapplicable to catalyst surfaces and to supported catalysts, such data are sometimes employed in considering what might be the gross state of the catalyst or in determining a proper concentration of hydrogen sulfide in hydrogen to convert a catalyst to a desired sulfide state or to maintain it in that state. In the case of catalysts used for hydrodesulfurization, only the hydrogen reduction equilibria of the sulfides need to be considered inasmuch as these are the final equilibrium states whether metals, oxides or sulfides are the starting points. Accordingly, the hydrogen reduction equilibria for several pertinent sulfides have been taken or calculated from the literature. For convenience the results are presented as the logarithm of the ratio of hydrogen sulfide to hydrogen necessary to maintain various sulfide states as a function of temperature. Figure 9 gives the data for nickel sulfides; Figure 10, the results for cobalt sulfides; Figure 11, the data for iron sulfides; and Figures 12 and 13, the results for molybdenum sulfides and tungsten sulfide, respectively. Although data have been presented for a wide temperature range for the sake of completeness, only those relating to the hydrodesulfurization temperature range of about 600 to 800°F are of prime importance for the present considerations.

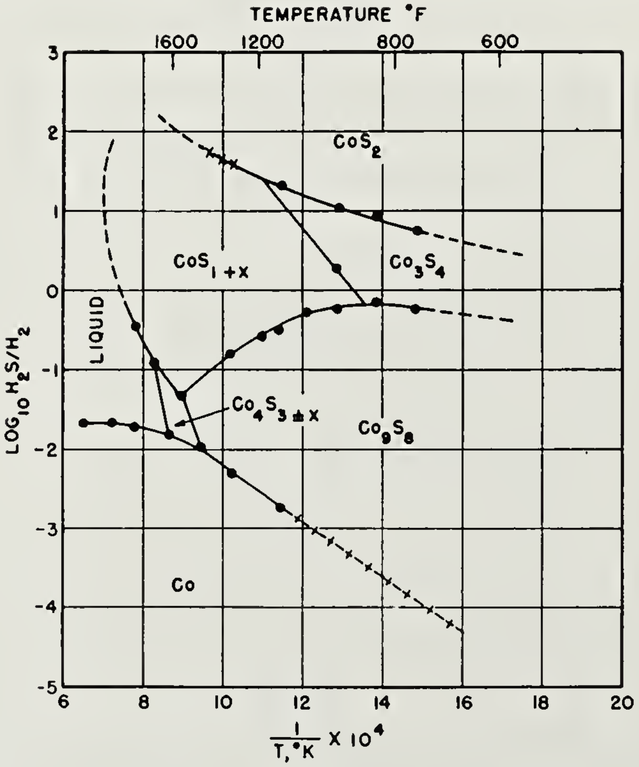


Figure 10. Hydrogen reduction equilibria of the cobalt sulfides. Rosenqvist's[99] data and phase diagram taken directly. Sudo's[104] data for the Co → Co_9S_8 equilibrium are in excellent agreement with those of Rosenqvist. Experimental points: ● Rosenqvist,[99] × Hülsmann et al,[105] and —+—+—+— Sudo (equation).[104] The magnitude of the subscripts X in the formulae is of the order of a small fraction of one.

The figures indicate that, in the hydrodesulfurization temperature range, only a small fraction of one per cent of hydrogen sulfide in hydrogen is necessary to convert the metals to the lowest indicated sulfides. Thus, the conversion of nickel to Ni_3S_2, cobalt to Co_9S_8, iron to FeS, molybdenum to MoS_2 and tungsten to WS_2 is expected even when relatively sulfur poor stocks are hydrodesulfurized due to the low hydrogen sulfide concentration required. In general, up to several per cent hydrogen sulfide may be present in the hydrogen with the stable state remaining as the indicated lower sulfide. This applies, for example, at two per cent hydrogen sulfide, a frequently encountered concentration.

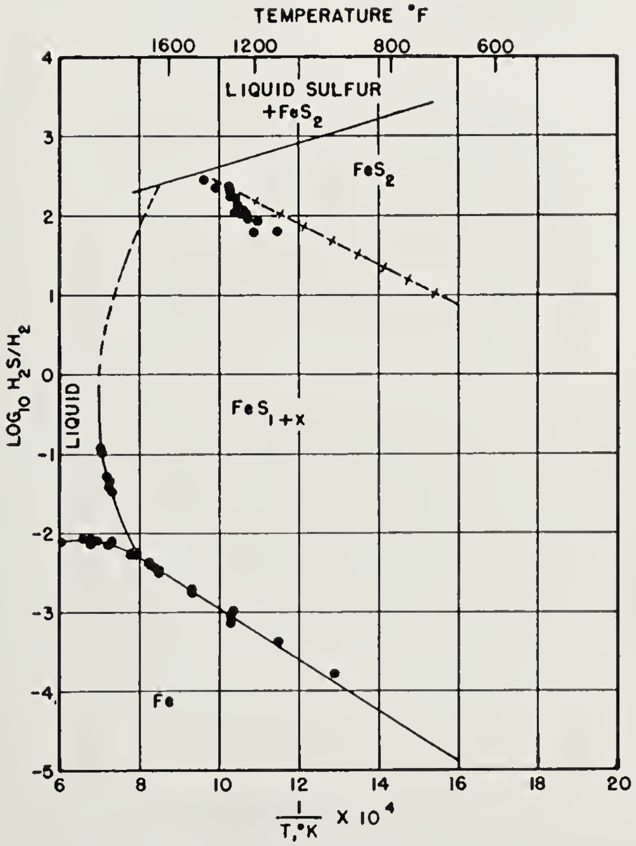


Figure 11. Hydrogen reduction equilibria of the iron sulfides. Rosenqvist's[99] data and phase diagram taken directly with the exception of an alteration of the $FeS_{1+x} \rightarrow FeS_2$ equilibrium. Wunderlich's[106] correlation of data for the dissociation pressure of FeS_2 is in good agreement with an earlier correlation by Kelley[107] and was, therefore, used to calculate this equilibrium. Results of investigations by Alcock and Richardson,[108] Sudo,[109] Matoba and Unotoro,[110] and Sano[111] are in excellent agreement with the data of Rosenqvist[99] for the $Fe \rightarrow FeS_{1+x}$ equilibrium. Experimental points: ● Rosenqvist[99] and —+—+—+— Wunderlich (correlation).[106] The magnitude of the subscript x in the formula FeS_{1+x} is of the order of a small fraction of one.

In connection with these thermodynamic data it is of interest that, for maintenance of maximum activity of tungsten disulfide and similar catalysts, a definite partial pressure of hydrogen sulfide is required. As judged by activity behavior, tungsten sulfide requires a lower partial pressure than molybdenum[116], although it appears on the basis of the present thermodynamic data that, for maintenance of the disulfide form which is pre-

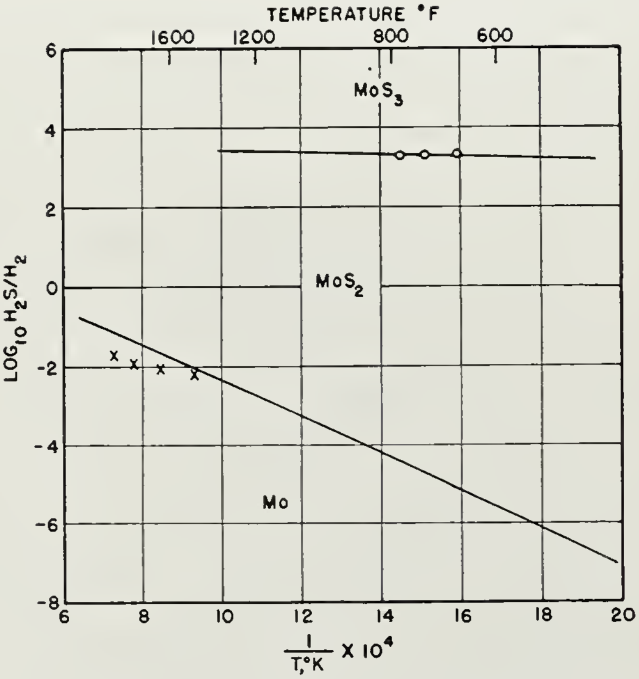


Figure 12. Hydrogen reduction equilibria of the molybdenum sulfides. Solid lines calculated using the heats of formation and entropies of Rossini et al[112] and the latest estimated heat capacities of the sulfides of Kelley.[113] Experimental points are those of Parravano and Malquori[114] as correlated by Kelley.[107]

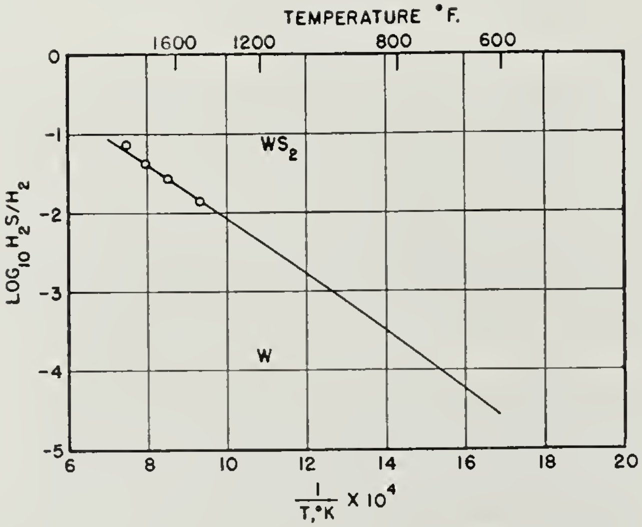


Figure 13. Hydrogen reduction equilibrium of tungsten sulfide. Data of Parravano and Malquori[115] as correlated by Kelley.[107]

sumably the active state, a lower partial pressure is required for molybdenum than for tungsten.

Carriers

Although there are numerous examples in which unsupported catalysts have been applied for hydrodesulfurization, many catalysts including the commercially employed cobalt molybdate type are of the supported type. The use of supported catalysts may be desirable because of the usual advantages which include greater stability, particularly during regeneration, and more advantageous use of the expensive hydrodesulfurization component. Carriers and resulting catalysts may be in pelleted or granular form suitable for use in fixed- or moving-bed operations or in finely divided form suitable for suspensoid or fluid operations.

Historically a wide variety of carriers has been employed. Low-area, porous carriers such as pumice, fire brick, and diatomaceous earth and high-area, porous carriers such as alumina, magnesia, silica, active charcoal, activated fuller's earth, silica-stabilized alumina gel, and gel type synthetic cracking catalysts are among those substances which have been mentioned as suitable. Very probably today, however, only high surface area carriers are used in preparing the preferred cobalt molybdate hydrodesulfurization catalysts, and actually γ-alumina or γ-alumina stabilized with a minor amount of silica appears to be most suitable. Good selectivity for desulfurization is obtained with catalysts prepared using such microporous carriers because of the mild conditions usually employed. Secondary reactions do not occur significantly as a result of the relatively long residence time of molecules in the microporous structure. For maximum selectivity, however, carriers with coarser pore structure may be used.

In one sense, the high area carriers may be classified on the basis of whether or not they contribute hydrocracking activity to the finished catalyst. Carriers which on account of their acidic nature are suitable as cracking catalysts contribute cracking activity when incorporated with a hydrogenation component to yield a catalyst which is active for hydrocracking. Examples of such carriers are fuller's earth activated by hydrofluoric acid and natural and synthetic silica-alumina cracking catalysts. Other carriers, such as alumina and magnesia, have little cracking activity and may be used to produce a catalyst having mainly hydrogenating activity. The preferred alumina and silica stabilized alumina carriers have minor hydrocracking activity and thus are particularly suitable for the preparation of catalysts having good hydrogenation activity, which is important for selective hydrodesulfurization, but minor hydrocracking activity. Of the two preferred γ-alumina supports mentioned above, the one stabilized with silica will have the higher cracking activity.

On the basis of electron microscope studies of molybdenum oxide hydroreforming and cobalt molybdate hydrodesulfurization catalysts utilizing synthetic alumina gel stabilized with about 5 per cent silica as the carrier, Nahin and Huffman[117] concluded that the active state was associated with microcrystals 50 to 200 Å in size. At 875 to 900°C for the molybdenum oxide catalyst and at 925 to 950°C for the cobalt molybdate catalyst, loss of surface area and metal oxide promoted transformation of the γ-alumina into the α-form resulted in loss of catalytic activity. Crystal growth accompanied these undesirable changes to give particles thousands of Angstroms in size.

An advantage of using the silica stabilized base for hydrodesulfurization catalysts is that resultant compositions are more heat stable; however. compositions containing unstabilized alumina will generally stand repeated regenerations and are adequate catalysts for mild hydrodesulfurization. Preferred methods of preparing the silica stabilized base involve precipitation of silica in the presence of the entire hydrous alumina gel or coprecipitation of silica and alumina with final drying and calcining of the resulting mixtures[96, 118]. Activated alumina impregnated with silica has poorer heat stability and this also applies to mechanical mixtures of dry silica and alumina gels. Coprecipitation is also advantageously employed[119] in the preparation of molybdena-alumina catalysts which are more stable than those obtained by impregnation. A degree of increased stability for alumina supported cobalt molybdate, molybdenum oxide and chromium oxide catalysts may be obtained by incorporating a minor amount (1 to 15 per cent of aluminum orthophosphate with the alumina carrier. The phosphate is added by precipitation in the presence of the hydrous alumina gel[120].

A molded alumina carrier of high mechanical strength which is particularly suitable for the preparation of cobalt molybdate catalysts has been described by Engel and Krijger[121]. Powdered alumina trihydrate, such as natural bauxite, is treated with an aqueous solution of an aluminum salt of a strong acid (e.g., aluminum chloride), extruded and calcined in a controlled manner to obtain γ-alumina. Activated alumina treated with about a 15 per cent solution of hydrochloric acid[122, 123] or with a 10 per cent solution of hydrofluoric acid[124] have been mentioned as suitable. It is stated that the hydrochloric acid treated carrier should be washed free of chlorine[123]. Cheap alumina carriers which may be employed include (1) trihydrate bauxite[125], (2) a special purity bauxite which contains <1 per cent iron oxide, <7.5 per cent silicon oxide, <4.5 per cent titanium oxide and <0.1 per cent sodium oxide with hydration preferably controlled to about 1 to 3 per cent[126], and (3) bauxite impregnated with alumina.[127]

Some other carriers may be mentioned as included among those which might be employed. Thus, Holder and Welty[128] use a zinc oxide-aluminum oxide spinel base. Zinc oxide impregnated on activated alumina[124] or on alumina stabilized with a minor amount of silica[124, 129] may also be suitable. A nonacidic carrier or promoter which has been employed to some extent is sodium aluminate[130, 131].

Promoters

Various substances are added as promoters in hydrodesulfurization catalysts. The examples given above relative to the stabilization of γ-alumina by minor amounts of silica or aluminum orthophosphate are examples of structural promotion which results in a more stable base. Also, the base may stabilize the active hydrodesulfurization component. An interesting example of this, in the case of supported nickel and cobalt catalysts, is given by Montgomery[132]. These transitional group metals are deposited in such an amount that less than 0.8 of a statistical monolayer exists on the support. Thus, the chance for the development of a crystal lattice on the catalyst surface is minimized and the resistance of the catalyst against powdering, which proceeds by the mechanism of carbon entering the metal lattice, is increased. Stabilization of supported nickel catalysts by the addition of copper has also been described[133].

One of the reasons for the high activity of catalysts comprised of Group VIa plus Iron Group metal compounds is probably mutual promotion; discussion of some preferred ratios for the components in certain of these catalysts is given below. A specific example of the promotional effect in the case of combined cobalt oxide and molybdenum oxide is available from the work of Byrns, Bradley and Lee[75]. Cobalt oxide, molybdic oxide, a mechanical mixture of cobalt oxide and molybdic oxide, and cobalt molybdate (all bentonite supported) were compared for atmospheric pressure hydrodesulfurization of cracked naphtha. Neither cobalt oxide nor molybdic oxide or the mixture of these displayed an activity comparable with that of the cobalt molybdate compound.

The promoting action of phosphorous, added for example as ammonium phosphomolybdate or cobalt phosphomolybdate, for cobalt oxide-molybdenum oxide-alumina catalysts has been recognized recently[134]. Also fluorine[135, 136] or both fluorine and phosphorous[137] are used as activating agents for such catalysts. Both phosphorous and fluorine increase desulfurization activity and also enhance the dehydrogenation potential of the catalyst[134, 136, 137] which latter is important in the equilibrium Autofining operation discussed below. Fleck[138] states that addition of the molybdic oxide as a heteropoly acid salt or a heteropoly acid minimizes the tendency of molybdic oxide to effect sintering of a γ-alumina carrier upon heating.

Sulfur Sensitive and Insensitive Catalysts

Catalysts employed in hydrogenation reactions have been classified as sulfur sensitive and sulfur insensitive. Sulfur sensitive catalysts are exemplified by iron, cobalt, nickel and platinum metal or oxide catalysts which effect hydrogenation reactions at low temperatures (e.g., below about 400°F). The active state of such catalysts for low temperature hydrogenations is readily poisoned by traces of sulfur, organic peroxides and unsaturated polymers usually present in petroleum products. Sulfur insensitive catalysts include vanadium, chromium, tungsten and molybdenum oxides and sulfides. These catalysts display their activity only at relatively high temperatures, but are quite active in the temperature range employed for hydrodesulfurization.

The sulfur sensitive catalysts upon sulfiding may also be active hydrogenation and hydrodesulfurization catalysts depending upon the conditions.

Table 15. Minimum Mole Per Cent Hydrogen Sulfide in Hydrogen to Give Various Nickel Sulfides

	Approx. Minimum Mole Per Cent at	
	600°F	800°F
Ni_3S_2	0.97×10^{-3}	1.1×10^{-2}
Ni_6S_5	2.8	4.2
NiS_{1+x}	6.2	11.8
NiS_2	94	97

For example, platinum catalysts generally are active at moderate hydrogen pressures and at temperatures above about 700°F in the presence of sulfur compounds and may be employed with little aging for saturative hydrogenation and hydrodesulfurization of cracked naphthas. At lower temperatures (e.g., 600°F), aging may be fairly rapid[139]. Also nickel subsulfide is active for both hydrogenation and hydrodesulfurization but does not display its activity below about 300°F[51, 140]. Thus by way of illustration, Maslyanskii[141] found that nickel hydrogenation catalysts were not poisoned for gasoline hydrodesulfurization at 392°F, 10 atmospheres pressure and 1.7 to 2.0 volume space velocity, if mole ratios of hydrogen to gasoline of 6:1 and 9:1 for gasolines of 0.15 per cent or less and 0.2 per cent sulfur, respectively, were used. In view of the extent of desulfurization obtained (e.g., charge, 0.12 to 0.15 per cent S; product, 0.012 to 0.018 per cent S) which would lead to equivalent hydrogen sulfide formation and an extrapolation of the nickel sulfide reduction equilibrium data of Figure 9, it can be calculated that the gross state of the nickel was nickel subsulfide. The data tabulated in Table 15, which were derived from the equilibrium data given in Figure 9, show that very low hydrogen sulfide percentages in hydrogen sulfide-hydrogen mixtures are required for maintenance of nickel in the Ni_3S_2 subsulfide form and that a higher sulfide is only possible at above about 3 to 4 mole per cent hydrogen sulfide over the usual hydrodesulfurization temperature range of 600 to 800°F.

Possibly with all sulfur sensitive catalysts, under sulfiding conditions in the presence of hydrogen, metal atoms or aggregates exist on the catalyst surface and are the seat of catalytic activity. This has definitely been shown to be a possibility in the case of nickel catalysts[142].

Susceptibility of sulfur sensitive catalysts to poisoning may be altered by complex or compound formation. Catravas[143] observed that, in the presence of hydrogen and hydrogen sulfide, nickel sulfide is formed on unsupported nickel catalysts, but not on those supported on kieselguhr or consisting of nickel silicate. In the case of cobalt oxide precipitated in the presence of a diatomaceous support, Johnson and Ries[144] present evidence for the existence of catalyst-support interaction to form a complex which, in part, is characterized by resistance toward reduction to cobalt metal. This complex should also possess resistance to sulfiding.

Hydrogenation and Hydrocracking Catalysts

As mentioned above in connection with the discussion of catalyst carriers, catalysts may be prepared which have mainly hydrogenation (and hydrodesulfurization) activity whereas others can be produced which have substantial hydrocracking activity simply by varying the nature of the support. Acidic supports give hydrocracking catalysts; nonacidic or basic supports give catalysts which, in general, have hydrogenation activity only. Thus, tungsten oxide or nickel oxide on hydrofluoric acid washed activated clay such as Super Filtrol[145], tungsten sulfide or a sulfided mixture of zinc, chromium and molybdenum on activated clay[146, 147, 148], and nickel oxide[149] or molybdenum oxide[150] on silica-alumina cracking support are active hydrocracking catalysts. On the other hand, zinc oxide-molybdenum oxide-magnesia, cobalt molybdate-alumina and molybdenum oxide-alumina compositions are hydrogenation catalysts. Varied activity with respect to hydrocracking is also found among single component catalysts. Notably tungsten disulfide is a strong hydrogenation and hydrocracking catalyst and may be more active[151], for example, than molybdenum sulfide which is similar in characteristics[91, 152].

Actually, tungsten disulfide is an extremely active and versatile catalyst. According to Pier[152], it may be used for olefin hydrogenation at above 200°C and for hydrogenation of aromatics at above 300°C. Practically quantitative reduction of nitrogen and sulfur compounds to hydrocarbons can be accomplished over the catalyst at 400°C. It also has considerable isomerization and cracking activity. Temperatures required for such latter reactions associated with disruption of C—C bonds are about 400°C or higher.

In general, catalysts that promote hydrocracking also promote isomerization reactions which are likewise strongly dependent upon the acidic characteristics of a catalyst. Little isomerization occurs over purely hydrogenation catalysts. In many instances with such latter catalysts, the extent of cracking may be only of the same magnitude as could be obtained by hydroprocessing without catalyst; however, the extent of saturation reactions is much greater than without a catalyst. The relative results obtained by the author for processing catalytic cycle stock thermally and with typical hydrocracking and hydrogenation catalysts are compared in Table 16 to illustrate some of the above statements. The much more extensive conversion of the stock which occurred over the molybdenum oxide-silica-alumina hydrocracking catalyst is readily apparent; the more extensive isomerization activity of the hydrocracking catalyst is reflected by the much higher ratio of iso- to *n*-butane in the gaseous products. The substantial equivalence of thermal processing and operating with a hydrogenation catalyst so far as cracking is concerned is obvious, and the higher hydrogen consumption and lower specific gravity of the residual cycle stock when the molybdenum oxide-alumina catalyst was employed as compared with thermal processing point up the greater saturation reactions which occur catalytically.

TABLE 16. HYDROGENATION OF LIGHT CATALYTIC CYCLE STOCK[a]

Catalyst	None	13% MoO_3-87% Al_2O_3	11% MoO_3-89% Houdry S-45 SiO_2-Al_2O_3
Products, wt. % of cycle stock			
C_4 and lighter	4.1	4.3	13.9
Gasoline[b]	17.9	19.9	46.5
Residue	78.7	77.1	41.3
Coke	—	0.2	0.3
Ratio of iso- to *n*-butane in gaseous products	0.29:1	0.33:1	0.94:1
Hydrogen consumption, wt. % of cycle stock	0.26	1.10	2.20
Properties of products			
Gasoline sp. gr. at 60°F/60°F	0.775	0.779	0.765
Residue sp. gr. at 60°F/60°F	0.9030	0.8816	0.8692

[a] Bomb runs at 830°F and 2000 psig for 108 minutes with 7.8 wt. % catalyst and 4.8 wt. % hydrogen based on the cycle stock.

[b] Including 4.7 wt. % gasoline in the charge.

Similar differences in activity between the two types of catalysts are noted upon processing a heavy stock providing the hydrogen partial pressure is high enough to prevent excessive coke formation and particularly if the operation is in the vapor phase such as was the case in the above examples. In liquid phase operation, liquid absorbed by the catalyst tends to be stagnant, and there is limited accessibility of hydrogen and unabsorbed liquid to the catalyst. This tends to minimize differences among the catalysts.

Varied amounts of hydrogenation components have been incorporated in hydrocracking catalysts. The German middle oil splitting catalyst 6434, used at 300 atmospheres pressure, was comprised of about 10 per cent tungsten disulfide on activated clay[148]. Catalysts K-534, 535 and 536[146] which were also used for this purpose at a higher pressure (700 atmospheres) consisted of about 5 parts zinc oxide, 2 parts chromium oxide and 0.7 parts molybdenum sulfide per 100 parts of activated support. The support consisted of 40 per cent bleaching (Terrana) clay and 60 per cent of the closely related AD 5 paste (both etched with hydrogen fluoride). The catalyst was presulfided before use. Synthetic aluminum silicate impregnated with 0.5 to 1.0 per cent molybdic acid has been used for hydrocracking residues, boiling up to 325°C, from hydroforming operations[153].

Actually, it is interesting that maximum hydrocracking activity in a supported catalyst for treating vaporized petroleum stocks generally appears in the range 2 to 4 per cent hydrogenation component concentration, with the optimum concentration decreasing with increased uniformity of impregnation. This is illustrated in Figure 14 which shows results obtained in the author's laboratory with molybdenum oxide-Houdry S-45 synthetic silica-alumina catalysts. In this comparison, optimum light catalytic cycle stock hydrocracking was observed at about 4.0 per cent molybdic oxide concentration in the case of a catalyst produced by static drying the base impregnated with ammonium molybdate solution prior to calcination in air. The general activity level was higher and the optimum activity was at about 3.0 per cent molybdic oxide concentration with catalysts produced by rotary drying, which was found to give more uniform impregnation. However, substantial hydrocracking activity exists at considerably higher hydrogenation component concentrations, and the use of a high concentration is justified when increased hydrogenation activity is desired. Such higher hydrogenation activity may be wanted when highly refractory stocks are being processed.

Selective Hydrotreating Catalysts

Mention was made above in the discussion of accompanying reactions of the problems of selectively hydrotreating cracked naphtha for desulfurization and conjugated diolefin removal without a corresponding degree of monoolefin saturation. Besides finding suitable reaction conditions, the problem of selective hydrotreating is obviously one of developing a selective catalyst, and attention has been paid to this aspect.

Hammar[82] concluded that there was the possibility of the existence of such selective catalysis which would desulfurize without saturating monoolefins on the basis of study of the kinetics of the hydrodesulfurization of shale oil gasoline (b.p. 183 to 367°F; bromine No., 76.7; 1.14 per cent S, 88 per cent of which was thiophenic) over a chromium promoted cobalt molybdate-alumina catalyst. In a search for such a selective catalyst, prereduced and presulfided CoMo-alumina (1.73), Mo-alumina (1.6–1.7), Co-Mo (1.5), CoMo-pumice (3.5), CoMo-synthetic Al_2O_3-SiO_2 (4.2), CrCoMo-alumina (1.7), NaCoMo-alumina (1.5), ZnCoMo-alumina (1.6–2.0), UCoMo-alumina (1.5), Cr-alumina (2.4), Fe-alumina (1.5), FeCr-alumina (1.7), CrVMo-alumina (0.7), W-alumina (0.8) and CoW-alumina (1.8) catalysts of undefined specific compositions were compared for the processing of shale oil gasoline at constant pressure (220 psig) and hydrogen to oil mole ratio (1.75:1), but, depending on the catalyst, at one or several temperatures in the range 300 to 475°C, and at one or several contact times. Hammar observed that, if sulfur content and olefin content of the product from hydrogenation over a given catalyst at different space velocities were plotted on a log-log chart, a straight line was obtained. This general sort of a plot had been employed previously (see Figure 6) by Cole and Davidson[80] for illustrating gasoline olefin saturation and desulfurization results

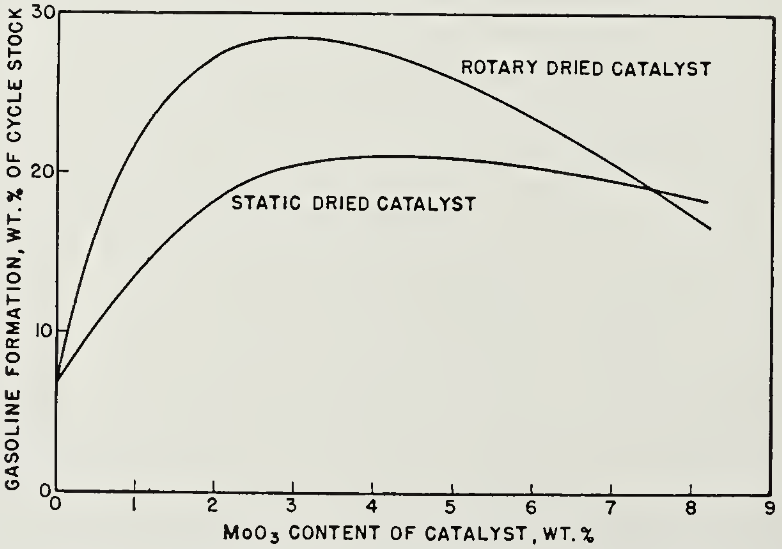


Figure 14. Effect of molybdenum oxide concentration and uniformity of impregnation on activity of molybdenum oxide-Houdry S-45 silica-alumina catalysts for light catalytic cycle stock hydrocracking. Reaction conditions: Bomb runs at 740°F. and 2000 psig. for 64 minutes with 8.0 wt.% catalyst and 4.9 wt.% hydrogen based on the cycle stock.

over tungsten-nickel sulfide catalyst, and Hammar uses the empirical relationship in the form of an equation to correlate the results of his catalyst studies. The mathematical expression, which should hold at least approximately, is best written as,

$$\log \frac{a_s^0}{a_s} = \alpha \log \frac{a_o^0}{a_o}$$

where a_s^0 and a_s are representative of initial and final concentrations of sulfur compounds, and a_o^0 and a_o are representative of initial and final concentrations respectively of olefins. The term α is a measure of catalyst selectivity and is the slope of the line on the log-log chart. If only sulfur compounds were hydrogenated (complete catalyst selectivity), the value of α would be infinite. If equal percentages of sulfur compounds and olefins were hydrogenated (no catalyst selectivity), the value of α would be one, and for the case of only olefin saturation (complete negative selectivity), the value of α would be zero. The selectivities noted by Hammar for the various catalysts which he examined are shown above in parentheses after the respective compositions. Although differences among the catalysts in this respect were observed, all effected substantial hydrogenation of olefins and no satisfactorily selective catalyst was found. The most selective catalysts (CoMo-pumice and CoMo-synthetic Al_2O_3-SiO_2) showed rapid deterioration at 425°C, the temperature at which they were tested, and Hammar suggests the possibility that they were "selectively poisoned" by sintering or coke deposition. This seemed possible, because he had observed, in tests under hydroreforming conditions (temperatures of 500°C and above), that the desulfurization reaction is much less susceptible to carbon on catalyst than either olefin saturation or aromatization.

Horne and Junge[154] found that an unprereduced 29.3 per cent NiO-70.7 per cent activated alumina catalyst was quite selective for the desulfurization of a West Texas cracked distillate at 100 to 500 psig, 1 to 6 volume space velocity, and hydrogen to oil ratios of from about 100 to 1000 scf/bbl (standard cubic feet per barrel). Prereduction of the catalyst is said[154] to decrease desulfurization efficiency. Sulfiding nickel containing catalysts increases their selectivity for desulfurization with respect to monoolefin saturation[155, 156] and for the hydrogenation of diolefins to monoolefins[157]. Thus, supported nickel sulfide catalysts have been used for selectively hydrotreating cracked gasolines[155, 158]. Sartor[158] states that such catalysts are superior, and particularly so if prepared by mixing dry nickel carbonate with diatomaceous earth followed by moistening the mixture with aqueous ammonium hydroxide to form a paste, then drying, pelleting, calcining and sulfiding. Such a preferred catalyst is more selective than one prepared in the same way except that the nickel was incorporated with the diatomaceous earth by impregnation using an aqueous solution of ammonium carbonate, ammonium hydroxide and nickel carbonate. It is also more selective than a cobalt sulfide-molybdenum sulfide-alumina catalyst. Data given by Sartor[158] to illustrate these facts are shown in Table 17. Iron catalysts are also selective in the sulfide state[159], and selectivity is shown by cobalt, iron and nickel catalysts upon partial sulfiding[160].

Many other catalysts have been mentioned in connection with selective hydrotreating, and it is probable that with any hydrogenation catalyst at least some selectivity will be apparent. Sartor[158] classified many sulfide catalysts with respect to desulfurization activity and selectivity. It appears that the most important catalysts have either fair activity for desulfurization and fair selectivity or good activity and poor selectivity. Catalysts with fair activity and fair selectivity are said to include cobalt and molybdenum sulfides supported on alumina gel, cobalt sulfide on active alumina as well as various modifications of supported nickel sulfide. Catalysts with good activity but poor selectivity are indicated to be platinum sulfide on silica gel, tungsten-nickel sulfide, molybdenum sulfide on active alumina and unsupported molybdenum sulfide. However, with respect to molybdenum sulfide, Carlile and Cawley[161] report that it can be employed with considerable selectivity for the hydrodesulfurization of crude benzene containing about 10 per cent unsaturated hydrocarbons. Engel and Hoog[123] confirm that tungsten-nickel sulfide, which has been used extensively[76, 162] in the development of a cracked gasoline selective hydrotreating process, has high activity but moderate selectivity. They present the data given in Table 18, which were obtained under optimum conditions for each individual catalyst, to show that it is less selective than two cobalt oxide-molybdenum oxide-bauxite catalysts which differ in that the one contains

TABLE 17. DESULFURIZATION OF A PRESSURE DISTILLATE GASOLINE[a]

	Preferred Nickel Sulfide-Diatomaceous Earth Catalyst[b]	Comparison Nickel Sulfide-Diatomaceous Earth Catalyst[b]	Cobalt Sulfide-Molybdenum Sulfide-Alumina[c]
Olefins Retained, %	99	99	84
Sulfur Retained, %	56	69	50
Maleic Anhydride Value of Product	1	5	1
Change in Clear Octane Number	+1.5	+0.5	−2.5

[a] Runs at 598–602°F, 75 psig, 8.0–8.3 LHSV, and a hydrogen to oil mole ratio of 1.74–2.00:1. Charge properties: Bromine number, 90; Sulfur, 0.363%; Maleic anhydride value (measure of conjugated diolefin concentration), 30; Clear octane number, 70.2.

[b] Contain about 70% nickel on a reduced basis.

[c] A very comparable but different distillate used with this catalyst.

potassium. As illustrated in the table, addition of potassium to such a catalyst has been found to increase selectivity[123, 163]. This increased selectivity is developed by heating the catalyst in the presence of oxygen at high temperatures (e.g., 750°C)[123].

Molybdates, Tungstates and Similar Catalysts

In the discussion thus far, the preferred cobalt molybdate and tungsten-nickel sulfide catalysts have not been described specifically. Because of their relative importance, a detailed description of their preparation and activity is justified. Thus, the following is devoted to this purpose as well as to comparable information on similar mixed catalysts.

Preparation. With respect to cobalt molybdate catalysts, the compound itself may be prepared[164, 165] by precipitation upon addition of a slightly ammoniacal solution of ammonium molybdate to an aqueous solution containing the equivalent number of moles of cobalt nitrate. Catalyst preparation may be completed by washing, drying at 200°F, pulverizing and pelleting. On the other hand, precipitated cobalt molybdate may be distended on a support[128, 164, 165]. Thus, Byrns suspended freshly precipitated hydrous alumina gel[164, 165] in a solution of cobalt nitrate. A solution of ammonium molybdate, equimolar with respect to the cobalt nitrate, was added and the mixed precipitate was washed and heated to produce the final catalyst. Supported precipitated iron, nickel or cobalt chromite and nickel or iron molybdate catalysts may be similarly prepared[165]. Thus iron, cobalt or nickel chromite may be formed from a solution of a soluble salt of iron, cobalt or nickel and ammonium dichromate upon making the solution alkaline with ammonium hydroxide and heating the precipitate formed to produce the chromite. A support such as bentonite[166] or undried hydrous

TABLE 18. SELECTIVE HYDROTREATING OF CATALYTIC GASOLINE

% Desulfurization	% Monoolefin Retention with		
	Potassium Promoted Cobalt Oxide-Molybdenum Oxide-Bauxite[a]	Cobalt Oxide-Molybdenum Oxide-Bauxite[a]	Tungsten-Nickel Sulfide
40	97	87	80
50	91	80	75
60	85	72	68
70	78	62	60
80	72	51	47

[a] Weight ratio of bauxite: molybdenum:cobalt:potassium was 100:6.5:0.8:0.4 in promoted catalyst; other catalyst the same but without potassium.

alumina gel[165] may be present as a suspension during the precipitation step, or a binding agent such as bentonite may be mixed with the precipitate after formation[166].

Supported cobalt molybdate and other mixed catalysts may also be prepared by the familiar impregnation technique. Thus, for example, the carrier may be coimpregnated with a solution containing compounds of both catalytic elements, followed by drying and calcining. In the case of cobalt molybdate catalysts, the dissolved compounds are suitably cobalt nitrate and ammonium molybdate. On the other hand, the catalytic agents may be deposited by double impregnation in which the support is first impregnated with a solution of a compound of one of the catalytic elements after which it is dried and calcined and then impregnated with a solution of a compound of the other catalytic element followed by the normal finishing procedures.

When utilizing the coimpregnation technique, one often encounters problems arising from the instability of the single solution. Nahin and Huffman[167, 168] discuss this problem in connection with the preparation of impregnated catalysts containing a Group VIa metal (chromium, molybdenum, tungsten or uranium) and a Group VIII metal (iron, cobalt or nickel). Specifically described are the preparations of solutions containing cobalt and molybdenum, nickel and tungsten, cobalt and chromium, and nickel and chromium. Although some modifications of their method of solution preparation are described, the basic procedure is to add a solution of the basic oxide-forming metal salt (e.g., cobalt nitrate) to ammonium hydroxide (the initial solvent) of required concentration to form the basic hydroxide and to redissolve it as the ammonium complex and then to add the acidic oxide-forming component (e.g., ammonium paramolybdate). For the usually employed concentrations of from 0.20 to 1.5 molar with respect to metal or metals, it is indicated that solution preparation must be adjusted to fulfill the following requirements if stability is to result:

1. The concentration of ammonia in the initial solvent should be between 8 and 15 molar and preferably between 12 and 14 molar.
2. The concentration of ammonia in the final solution should be between 5 and 15 and preferably between 7 and 9 molar.
3. The mole ratio of ammonia to Iron Group metal in this solution should be at least twice the ionic charge on this metal.

The author has found the Nahin and Huffman procedure to be generally applicable for the preparation of stable cobalt and molybdenum solutions from cobalt nitrate and ammonium paramolybdate but not for preparation of nickel and tungsten solutions from nickel nitrate and tungstic acid. In the latter case, only solutions up to 0.6 molar or less with respect to each metal could be prepared, and, at molarities of metals of about 0.6, ammonia molarity in the final solution could not exceed about 5. Also, at constant total metal oxide content of 15.1 per cent in the solution, stability decreased as the atom ratio of nickel to tungsten was increased from between 0.25:1 to 2:1. On the other hand, the author and Pardee[169] have found that perfectly stable solutions of any useful nickel and tungsten concentration, containing the metals in any ratio, can be prepared simply by mixing aqueous ammonium metatungstate and nickel nitrate solutions. The pH of the metatungstate solution is controlled between 2 and 5 as is the pH of the final solution.

Engel and Hoog[170, 171] have found that stable cobalt nitrate or nickel nitrate-ammonium tungstate and cobalt nitrate-ammonium molybdate solutions can be prepared by dissolving the acidic oxide-forming salt to form a 10 to 15 per cent solution in 50 per cent aqueous alkanol amine (e.g., ethanol amine) and then mixing in an aqueous 10 per cent solution of the basic oxide-forming metal salt. Apparently, no trouble was experienced in preparing solutions containing nickel and molybdenum and iron and tungsten even in the absence of alkanol amine; their method was not applicable for preparing solutions of iron and molybdenum.

Further problems in preparing supported mixed catalysts by impregnation techniques arise in attempting to gain uniformity of impregnation. Although catalysts with a fairly high degree of uniformity should result from a usual method of preparation which involves coimpregnating a carrier, drying, grinding, pelleting and calcining[122] or from mixing the powdered components and pelleting[172], such catalysts may possess inferior strength when compared with impregnated preformed strong pellets or granules. However, during impregnation of pellets or granules, the impregnant may be selectively adsorbed on the outside of the particle, or, if not, during drying, the impregnant may migrate away from the center. With respect to this problem, Engel and Hoog[173] have found that the uniformity of impregnation of molded alumina carrier[121] with cobalt and molybdenum or nickel and molybdenum by coimpregnation was markedly improved by the inclusion of a polyhydric alcohol (e.g., erythritol, pentaerythritol, sorbitol or mannitol) in the impregnation solution.

Relative to the preparation of unsupported tungsten-nickel sulfide, Archibald and Trimble[174] treat an ammoniacal solution of ammonium tungstate with hydrogen sulfide to form the thiotungstate and ammonium sulfide. Addition of an aqueous nickel nitrate solution results in the formation of nickel sulfide precipitate. Then tungsten trisulfide is precipitated by the addition of sulfuric acid to give a solution of pH of about 1.2. Alternately acidified nickel nitrate may be added to effect coprecipitation of the nickel and tungsten. Prior to being pelleted, the total precipitate is roasted in hydrogen to convert tungsten trisulfide to disulfide. Additional information on the preparation of this catalyst is given by Cole[175].

Method of Preparation and Activity. The method by which the mixed type catalysts are prepared has an effect on activity. Thus, Byrns found[164] that a catalyst prepared by precipitating cobalt molybdate on undried hydrous alumina gel is more active than a catalyst prepared by precipitating cobalt molybdate on dried alumina gel or than unsupported precipitated cobalt molybdate itself. However, cobalt molybdate catalysts prepared by impregnation are more active than those prepared by coprecipitation. Thus, Huffman[96] found that such catalysts prepared by coimpregnation of dried alumina or silica stabilized alumina gel were more active for gas oil hydrodesulfurization than comparable catalysts prepared by coprecipitation in the presence of undried alumina gel or a mixture of undried alumina and silica gels. Hendricks[176] confirms this superiority for the impregnated catalysts, but points out that activity varies with method of impregnation. Using cobalt nitrate and ammonium molybdate solutions or a mixed solution, he prepared silica stabilized alumina supported cobalt molybdate catalysts by coimpregnation and by double impregnation. With double impregnation, the order of impregnation was varied with the molybdenum being deposited both first and last. In comparison with the other catalysts, the composition prepared by depositing the molybdenum first showed some little superiority in hydrodesulfurization and/or dehydrogenation activity. Testing of a corresponding series of nickel molybdate catalysts[177] gave similar results with the catalyst prepared by double impregnation with deposition of the molybdenum first showing a degree of improved hydrodesulfurization and dehydrogenation activity.

Composition. The amount of mixed-type hydrogenation component in supported catalysts such as cobalt molybdate-alumina compositions as well as the ratio of the individual catalytic components one to another both have an affect on resulting catalyst activity. Similarly, the ratio of the individual constituents of unsupported mixed-type catalysts is important.

Workers of the Union Oil Co. have considered the composition of supported cobalt molybdate catalysts[75, 96, 168, 176]. Although they suggest that the atom ratio of cobalt to molybdenum can vary widely (e.g., 0.5 to 5: 1)[96] these investigators might appear to prefer a ratio of about 1:1[168] and illustrate the preparation of several catalysts containing the components in this approximate ratio[96, 168, 176]. Engel and Hoog[123, 178], associated with Shell Development Co. believe, however, that the optimum promotional effect of cobalt is reached with a relatively small amount of cobalt on an atom basis. Specifically, data are given[123] to show that the optimum ratio is about 0.2:1; thus, a bauxite supported catalyst (0.8 parts cobalt—6.5

parts molybdenum—100 parts carrier), containing the metals in this ratio, is considered a superior catalyst and is described in connection with the Shell trickle hydrodesulfurization process[179]. Efficient supported catalysts used for Autofining have also contained 0.2 atom of cobalt per atom of molybdenum[180], and actually a commercial catalyst prepared by The Harshaw Chemical Co. under Union Oil Co. patents contained only 0.6 atom of cobalt per atom of molybdenum[45].

With respect to optimum impregnant concentration in cobalt molybdate-alumina type catalysts, the same general activity behavior with increasing impregnant concentration is observed as with any other predominately hydrogenating catalyst. Thus, catalyst activity increases rapidly as the impregnant concentration is increased to a certain concentration, then further increases in concentration produce only slight additional increases in activity. The Shell catalyst described above contains about 9.7 per cent total impregnant concentration calculated as cobalt oxide and molybdenum trioxide. According to Engel and Hoog[123], higher concentrations would not produce a significantly more active catalyst. Union Oil Co. workers appear to prefer[168, 176] about 12 to 14 per cent impregnant in their silica stabilized alumina supported catalyst, although a composition containing as low as 7.0 per cent is described[96], and a broad useful range of impregnant concentration is indicated to be 8 to 20 per cent[96]. Obviously the amount can vary with the exact quantity being dictated by specific requirements. With the somewhat less desirable coprecipitated cobalt molybdate-hydrous gel catalysts, the preferred concentration is higher and is in the range 20 to 25 per cent, with in excess of 50 per cent being definitely undesirable[164]. Similar considerations apply in the case of other alumina supported mixed Iron Group plus Group VIa oxide or sulfide catalysts[152, 181]. Generally a preference for a deficiency of the Iron Group metal is indicated[152, 181, 182].

According to analytical data given by Cole and Davidson[80], the commercial unsupported tungsten-nickel sulfide catalyst, produced by Shell Oil Co. for hydrodesulfurization of catalytic aviation base and other stocks, contains nickel and tungsten in an atom ratio of 1.96:1. Cole[175] states that the preferred atom ratio is between about 1.5:1 and 1.8:1, which is approximately the same as the range of 1.5:1 to 2:1 stated by Archibald and Trimble[174] to be particularly desirable for dehydrogenation activity. However, maintenance of the ratio in this range does not appear to be necessary, at least for obtaining good dehydrogenation activity, inasmuch as in a German dehydrogenation catalyst (5615) which has been used commercially[148], the nickel to tungsten atom ratio is about 0.5:1.

Relative Activity. The work of Byrns, Bradley and Lee[75] which showed the superiority of cobalt molybdate over cobalt oxide or molybdic oxide alone or over a mechanical mixture of the two has already been mentioned. Earlier, Pease and Keighton[74] showed that a mechanical mixture of cobalt sulfide and molybdenum oxide had markedly better hydrodesulfurization activity than either of the compounds themselves. However, probably the first indication of uniqueness for such mixed catalysts was German work[183], which disclosed that a catalyst consisting of equimolar proportions of molybdenum sulfide and cobalt sulfide was active for benzene hydrodesulfurization even at ordinary pressure.

With respect to molybdates themselves, Byrns, Bradley and Lee[75] compared that of cobalt with those of several other metals for the hydrodesulfurization of cracked naphtha at 650°F. Lined-out relative activities estimated from curves presented by these investigators are compared in Table 19, whereby the superiority of cobalt molybdate over the corresponding zinc, iron, copper or aluminum compound is obvious. By use of a similar testing procedure and stock, Byrns[166] established that cobalt molybdate was also more active than nickel chromite.

TABLE 19. RELATIVE ACTIVITIES OF SEVERAL MOLYBDATE CATALYSTS

Catalyst	Approximate Relative Desulfurization Activity[a] of Equilibrium Catalyst
Cobalt molybdate	100
Zinc molybdate	36
Iron molybdate	34
Copper molybdate	21
Aluminum molybdate	6

[a] $\frac{\%\text{ Desulfurization with specific catalyst} \times 100}{\%\text{ Desulfurization with cobalt molybdate}}$.

Supported nickel molybdate compositions, although somewhat less active, compare favorably with similar cobalt molybdate catalysts. This is illustrated by Table 20, which presents the author's data for the activities of these two types of catalysts prepared by coimpregnation when used for the hydrodesulfurization of Kuwait furnace oil distillate. The nickel molybdate catalysts effected about 89 per cent desulfurization as compared with 91 to 93 per cent with the cobalt molybdate catalysts. As would be expected, activity was fairly independent of nickel molybdate or cobalt molybdate concentration between 6 to 7 per cent calculated as metals and about 10 to 11 per cent (compare catalyst 2 with 1 and catalysts 5 and 6 with 3 and 4). Hendricks presents data[176, 177] which afford a comparison of silica stabilized alumina supported nickel molybdate and cobalt molybdate catalysts for straight-run Santa Maria Valley gas oil hydrodesulfurization and which confirm the author's observations of similar desulfurization activity.

Unsupported tungsten-nickel sulfide of the type employed by Shell Oil Co. is more active for hydrodesulfurization, saturative hydrogenation, and hydrocracking than cobalt molybdate-alumina compositions. When processing aromatic-containing unsaturated distillates boiling in the gasoline range over fresh tungsten-nickel sulfide, one generally finds it necessary to operate at temperatures in the low part of the range 450 to 800°F or at high space velocities, if one wishes to control aromatic saturation[80]. The tungsten-nickel sulfide is also an active catalyst for saturation of aromatics boiling in the gas oil range. Hoog, Klinkert and Schaafsma[179] show its greater desulfurization activity with respect to cobalt molybdate-alumina compositions by the data presented in Table 21. A lower operating temperature is possible for equivalent desulfurization with the tungsten-nickel sulfide.

TABLE 20. COMPARISON OF ALUMINA SUPPORTED CATALYSTS FOR HYDRODESULFURIZALION OF KUWAIT STRAIGHT-RUN FURNACE OIL DISTILLATE[a]

Catalyst	Composition[b]	Product Properties		% Desulfurization
		Sp. Gr. at 60°/60°F	Sulfur, Wt. %	
1	4.1% Ni—6.2% Mo (Ni:Mo = 1.08:1)	0.8201	0.11	89.3
2	1.8% Ni—4.3% Mo (Ni:Mo = 0.68:1)	0.8184	0.11	89.3
3	3.7% Co—6.4% Mo (Co:Mo = 0.94:1)	0.8180	0.08	92.2
4	4.0% Co—6.6% Mo (Co:Mo = 0.99:1)	0.8196	0.07	93.2
5	2.5% Co—3.6% Mo (Co:Mo = 1.13:1)	0.8196	0.08	92.2
6	2.4% Co—4.2% Mo (Co:Mo = 0.93:1)	0.8198	0.09	91.2

[a] Tests at 780°F, 200 psig, 1 LHSV, and a hydrogen to oil ratio of 4000 scf/bbl for 12-hour process periods using prereduced catalysts. Charge properties: Sp. Gr. at 60°/60°F, 0.8314; S, 1.03%.

[b] Ratios on an atom basis.

Pier[152], in discussing the activity of a specific fresh unsupported tungsten-nickel sulfide catalyst, stated that it had activity similar to that of tungsten disulfide for combined hydrogenation plus hydrocracking when operated at temperatures below 400°C. When used at higher temperatures (e.g., 425°C), the material underwent a transformation to make it comparable to a hydrogenation catalyst. This transformation was not accompanied by any change observable by x-ray diffraction analysis; however, a change in the surface of the catalyst was apparent on the basis of electron diffraction study. Fresh catalyst showed only lines for tungsten disulfide. Aged catalyst showed both tungsten disulfide and the nickel compound additive.

Among additional information on these mixed-type catalysts, Pease and Munro[184] have noted interesting activity behavior for a coprecipitated cobalt sulfide-chromium oxide catalyst. It was as effective as a mixed cobalt sulfide-molybdenum oxide catalyst and could be used for the quantitative hydrodesulfurization of a benzene-thiophene mixture at atmospheric pressure. The excellent hydrogenation activity of alumina supported nickel sulfide-molybdenum sulfide and nickel sulfide-tungsten sulfide type catalysts is well recognized[152]. A specific example of such a composition is German catalyst 8376[185] containing about 3 per cent nickel sulfide, 27 per cent tungsten sulfide and 70 per cent alumina. Hydrogenation activity of the tungsten sulfide is promoted by the addition of nickel sulfide and cracking activity is decreased by dilution with the alumina carrier[152]. The multipurpose German hydrogenation catalyst (S-3510), consisting of molybdenum oxide, zinc oxide and magnesia, is not as suitable as alumina supported cobalt molybdate catalyst for low-pressure selective hydrodesulfurization[179].

TABLE 21. COMPARISON OF TWO CATALYSTS IN TRICKLE HYDRODESULFURIZATION OF STRAIGHT-RUN MIDDLE EAST GAS OIL

Catalyst	Cobalt-Molybdenum-Alumina		Tungsten-Nickel Sulfide	
Temperature, °F	708		663	
Pressure, psia	750		750	
Space velocity, vol./vol./hr	2.4	3.6	2.4	3.6
	Sulfur Removal, %			
Hydrogen to oil ratio, scf/bbl				
1250	89	84	—	82
625	87	—	90	78

Other Catalysts

Inasmuch as any hydrogenation catalyst can be employed with more or less success, a very considerable number of other compositions could be described as additional specific examples of the general types which have been discussed above. A complete tabulation, however, would serve little purpose, because fairly comprehensive information is already available[186, 187, 188, 189] and a large proportion of the specific catalysts are not pertinent considering potential or presently practiced commerical hydrodesulfurization processes. Actually some of these compositions have been described above, and others are illustrated in the table given at the end of this chapter which contains supplemental hydrodesulfurization information. Included are compositions containing nickel, cobalt, iron, platinum, ruthenium, tin, chromium oxide, chromium oxide and molybdenum oxide, vanadium oxide, and molybdenum disulfide.

Mention should also be made of commercial hydroreforming catalysts. These are, of course, excellent naphtha hydrodesulfurization catalysts under hydroreforming conditions which includes the use of a relatively high temperature in comparison with that employed for mild hydrodesulfurization. In general, they are also excellent for lower temperature operations, as for example, in such processes as pretreating naphthas for desulfurization and olefin saturative hydrogenation. Besides the cobalt molybdate type catalyst used in Hyperforming, these catalysts include (1) those of the supported platinum type used in Platforming, Catforming, Houdriforming, Ultraforming and Sinclair-Baker hydroreforming, (2) those of the molybdena-alumina type used in Orthoforming and Fluid Hydroforming, and (3) the chromia-alumina bead catalyst used in Thermofor hydroreforming[190]. These catalysts will be discussed in detail in a chapter on hydroreforming in Volume VI of this series.

Some additional catalysts are bauxite impregnated with silicomolybdic acid[191], unglowed chromium oxide[192], Raney cobalt[193, 194], and rhenium heptasulfide and rhenium disulfide[49]. Among these, rhenium heptasulfide is a special catalyst in that it can be employed for the saturative hydrogenation of sulfur compounds, such as allyl phenyl sulfide and thiophene, without carbon-sulfur bond hydrogenolysis. It can also be employed for the partial hydrogenation of disulfides, such as diphenyl disulfide, to thiols. Rhenium disulfide has activity parallel to but lower than that of rhenium heptasulfide.

Catalyst Regeneration and Preactivation

Although in most instances hydrodesulfurization processes operate for long process periods, none is of a completely nonregerneative character because of catalyst deactivation. This deactivation occurs because of accumulation of carbonaceous deposits which must be removed in a reactivation process.

In general, regeneration of the catalysts when contained in fixed beds may be accomplished by the following steps:

1. Purging with steam or inert gas to eliminate oil and hydrogen.

2. Burning off the deposit and incidentally oxidizing the catalyst by passing a steam-air or inert gas-air stream through the bed until the hot burning zone proceeds through it.

3. Purging with steam or inert gas to eliminate air from the system and subsequently carrying out any other preactivation of the catalyst which is necessary.

With most catalysts, it is necessary to limit the maximum temperature in the burning zone to about 1150 to 1250°F to insure against deactivation of the catalyst by sintering, and in some instances this maximum permissible temperature may be lower. The temperature is regulated by the rate of addition of air or oxygen. Similar considerations apply in the regeneration of catalysts in fluid beds. However, in this case a hot burning zone will not exist because of the intimate mixing of the catalyst. Likewise moving-bed systems, incorporating reactor-regenerator combinations, may be designed to avoid the hot zone type of regeneration.

With respect to cobalt molybdate-alumina catalyst, Berg, Bradley, Stirton, Fairfield, Leffert and Ballard[195] of the Union Oil Co. indicate that about 1150°F is a suitable burning temperature in a fixed-bed. Porter and Rowland[196] of British Petroleum Co., Ltd. (formerly Anglo-Iranian Oil Co., Ltd.) in regeneration of fluid catalyst regulate the oxygen content of the regeneration gases so as to never exceed a temperature of 1100°F, and this maximum temperature appears to be the preference of British Petroleum Co. workers for fixed-bed regeneration also[197]. Regeneration may be accomplished at elevated[198] as well as at low pressures.

Pretreatment of the oxidized catalyst by reduction is accomplished during hydrogen pressuring up operations and during any additional hydrogen contact with the catalyst. Activity for desulfurization is increased by presulfiding[53]. However, the activity of the catalyst is good even in an unsulfided state, and, inasmuch as the catalyst soon becomes sulfided in use, it is not usually necessary to carry out this specific preactivation. In this connection, Porter and Haresnape[199] noted that a presulfided catalyst had increased dehydrogenation activity when employed in low pressure operation. The low dehydrogenation activity of the unsulfided catalyst is more noticeable at low feedstock velocities and when processing heavier feedstocks[200].

The air-steam regeneration of the Shell commercial tungsten-nickel sulfide catalyst is carried out at a maximum hot-spot temperature of 1250°F[80]. The catalyst is then resulfided[80]. The number of times the catalyst may be regenerated is limited only by its mechanical strength[76]. Interesting details of the oxidative and resulfiding reactivation of such a catalyst are given by Cole[201]. Apparently the regeneration may also be effected with sulfur dioxide at 400 to 600°C[174]. Prior to use in selective hydrotreating of cracked gasoline, it has been regenerated by burning in an air-steam mixture at 800°F and resulfiding with hydrogen sulfide at the same temperature[76]. The catalyst is advantageously preconditioned by using it for dehydrogenation prior to employing it for catalytic aviation base stock hydrodesulfurization[175].

Specific information is available on special regenerations and activations of numerous other hydrodesulfurization catalysts. In this field, Garwood[202] found that a chromium oxide-alumina catalyst was more selective for the hydrodesulfurization of a gas oil if it was prereduced and then presulfided. Coke formation decreased while desulfurization efficiency was maintained. Myers[203] reports that chromium oxide-alumina and chromium oxide-alumina-beryllium oxide catalysts have improved efficiency for desulfurization if pretreated with a hydrocarbon fraction containing 0.05 to 5.0 per cent sulfur. Johnson and Stuart[204] propose a multi-step regeneration of a supported molybdenum disulfide catalyst. After being oxidized by air-burning, it is treated successively with ammonium hydroxide and hydrogen sulfide to form ammonium thiomolybdate which is reduced to regenerate molybdenum disulfide.

Among other information on the subject, Montgomery and Brown[205] found that treatment of a nickel oxide-silica-alumina catalyst with wet steam causes an increase in activity for hydrodesulfurization and a decrease in activity for gas and coke formation. Hendel[206] regenerates a used sulfided nickel oxide-silica hydrofining catalyst by blowing it with gases containing hydrogen with or without the addition of steam. McAfee[207] proposes to hydrocrack off part of the carbonaceous deposit from a spent nickel containing hydrodesulfurization catalyst prior to regeneration with an air and steam mixture. Apparently, carbon deposits on the Shell tungsten-nickel sulfide catalyst are also reduced by reaction with hydrogen; thus, partial reactivation may be accomplished by hydrogen flushing[80]. Actually, hydrogenation is frequently employed to reactivate hydrodesulfurization and other catalysts to a greater or lesser extent[208-213].

General Process Considerations

Low-pressure hydrodesulfurization is applicable to such distillate stocks as straight-run and cracked naphthas, kerosenes, diesel fuels, straight-run and catalytic furnace oil distillates and heavy straight-run and catalytic distillates. It has also been described in connection with the processing of whole crudes and residues.

Processing Method

So far as processing method is concerned, apparently all commercially available low-temperature distillate hydrodesulfurization processes are of the fixed-bed type. However, proposals have been made of moving-bed[7, 214, 215, 216] and fluid operations[196, 208, 209, 217], and Union Oil Co. Hyperforming[7, 216], one of the moving-bed processes, is actually being employed[218] in a plant build for high-temperature naphtha hydroreforming and desulfurization. The preference for fixed-bed processing results in a large degree from the simplicity of operation and the long process periods which are possible between regenerations. Similar processing methods, as well as suspended catalyst operation, are applicable to whole crudes and residues. Since process period lengths are usually not long at high catalyst efficiency when charging whole crudes and residues, and particularly at higher temperatures in residue hydrogenation, continuous fluid and suspended catalyst processes offer advantages from the standpoint of catalyst regeneration. However, a fluid operation has the limitation that the stock must be completely converted to vaporized products in order to maintain catalyst fluidity. Of course at high pressure, it is possible to operate for long process periods in fixed-bed operation even at fairly severe temperature conditions and with active catalysts.

Distillate Hydrodesulfurization Processes

Some of the distillate hydrodesulfurization processes which are in commercial operation or which are available are tabulated in Table 22 together with examples of stocks which have been reported as treated and general information relative to reaction conditions under which they operate. Included are the Shell vapor-phase hydrodesulfurization or gasoline fractions process (Shell Oil Co.)[76, 80, 162, 219], Shell trickle hydrodesulfurization (Shell Oil Co.)[179, 220, 221, 222], Autofining (British Petroleum Co.)[136, 180, 220, 223, 224, 225], Gulfining (Gulf Oil Corp.)[226, 227], Hydrofining (Esso Research and Engineering Co.)[219, 220, 228, 229, 230, 231], Hydrogen Treating (Sinclair Refining Co.)[219], Diesulforming (Husky Oil Co.)[219, 232, 233], and Unifining[86, 219]. Both Universal Oil Products Co. and Union Oil Co. offer Unifining as a joint development. The original Union Oil Co. version was their cobalt molybdate process[7, 53, 75, 195], and an original Universal Oil Products Co. process was called Hydrobon. Other processes are available besides those listed in Table 22. Those in the United States include[234] Sovafining (Socony Mobil Oil Co., Inc.), Hydrotreating (The Texas Co.), Hydropretreating (Houdry Process Corp.), and unnamed processes (Standard Oil Co. of Indiana, Phillips Petroleum Co., Ashland Oil & Refining Co. and Sun Oil Co.).

One of the operations possessing a unique feature is Shell trickle hydrodesulfurization, a flow diagram of which is shown by Figure 15. Gas oil charge and recycle hydrogen are preheated by exchange with reactor effluent and further heated in a gas- or oil-fired furnace. The charge passes down over several beds of catalyst with the number of beds depending upon the sulfur content of the charge and the degree of desulfurization desired. Cold charge oil may be injected between the beds to take up exothermic heat of reaction. After heat exchange with the feed, the reaction products are cooled further and passed to a high-pressure separator. The gas phase plus make-up hydrogen constitute the recycle hydrogen. The liquid is flashed in a low-pressure separator and is then led into a fractionator for removal of hydrogen sulfide and light material. If desired, the gas from the low pressure separator may be passed to a gas purification system for hydrogen sulfide removal; this hydrogen sulfide may be converted into sulfur in a Claus plant. The main distinctive feature of this process is operation at a recycle hydrogen to oil ratio of 250 to 1500 scf/bbl which permits partial liquid phase operation and trickling of liquid down over the catalyst beds. Little decrease in sulfur removal is observed in operating in this manner below that which would be obtained in vapor phase operation at 5000 to 10,000 scf of hydrogen recycle, and capital and operating costs are said to be smaller[179]. In this trickle type of operation the ratio of the height of catalyst to effective diameter should be at least 5:1[122].

The distinguishing feature of the Autofining process is that the pressure and temperature of the operation are such that dehydrogenation of naphthenes occurs to supply the hydrogen required for hydrodesulfurization. In a simple modification[180], recycle gas plus cold feed pass through a heater to a reactor. Reaction product is cooled and separated in a high pressure separator into liquid and gaseous products which latter are recycled. Inasmuch as more hydrogen may be made than is consumed, provision is made for withdrawing this excess gas. With naphtha feed stock, operation can be started at atmospheric pressure. In processing gas oils, the unit may be first started up by processing naphtha until the desired pressure is attained before starting the gas oil feed; alternately the unit may be first pressurized with excess recycle gas produced in a previous run. Normally, even with gas oils there is hydrogen made during the first several hours, so that, if gas is not bled from the system, pressure will increase. Advantage of this is taken in the equilibrium-type of operation[136, 180, 199, 235] in which the unit is shut in and the pressure allowed to increase to an equilibrium value usually in the range 200 to 500 psig[136, 219]. More efficient desulfurization results at the higher pressure.

According to published information there is nothing particularly novel processing-wise relative to the other methods which have been listed. In some instances, such as in naphtha pretreating, the desulfurization system can float on a reforming unit and thus operate at pressures (about 300 to 500 psig) and hydrogen rich gas rates which are available from a reformer. It is said[236] that this type of operation is the most economical which can be

TABLE 22. SOME MAJOR DISTILLATE HYDRODESULFURIZATION PROCESSES

Name	Examples of Stocks Treated	Example of Catalyst Employed	Typical Reaction Conditions
Shell Vapor-Phase Hydrodesulfurization or Gasoline Fractions Process	Cracked and straight-run gasolines.	Tungsten-nickel sulfide	Up to 427°C (800°F), 1000 psig and 15 LHSV using various H_2 recycle rates.
Shell Trickle Hydrodesulfurization	Straight-run gas oil and catalytic cycle oil.	0.8 parts Co, 6.5 parts Mo, 100 parts bauxite and cobalt-molybdenum on alumina.	Broadly 349–388°C (660–730°F), 315–765 psig, various LHSV's, 250–1500 scf recycle gas/bbl of feed; for deep desulfurization 366–382°C (690–720°F) and 615–765 psig.
Autofining	All straight-run distillates up to 371°C (700°F) end-point, sulfur dioxide extracts, and blends of straight-run and cracked distillates.	Mixed cobalt and molybdenum oxides on alumina suitably fluorine promoted.	399–427°C (750–800°F), 50–200 psig, 1–5 LHSV, 2000–4000 scf recycle gas/bbl of feed.
Gulfining	Virgin and cracked furnace oil fractions and other distillates.	—	Various including 316–427°C (600–800°F) and up to 1000 psig.
Hydrofining	Straight-run and cracked naphthas, kerosene, tractor and diesel fuels, virgin and cracked gas oils, and lubricating oils.	Cobalt and molybdenum oxides on alumina and other catalysts.	Various including 204–427°C (400–800°F), 50–1600 psig, 0.5 to more than 16 LHSV, and up to about 3500 scf H_2/bbl of feed.

Hydrogen Treating	Various including straight-run and cracked naphthas and light catalytic cycle stock.	Extruded cobalt and molybdenum on alumina.	304–416°C (580–780°F), 200–800 psi, 2–8 LHSV, and 2000–5000 scf recycle gas/bbl of feed.
Diesulforming	Diesel fuels and other distillates.	—	316–427°C (600–800°F), 300–500 psi, 1–2 weight hourly space velocity and 5000 scf recycle gas/bbl of feed.
Unifining	Straight-run and cracked naphthas, straight-run and cracked middle and heavy distillates, aromatic distillates and lubricating oils.	Cobalt and molybdenum supported on alumina and other catalysts.	Up to 538°C (1000°F) and below 1000 psi but usually 260–399°C (500–750°F) and 300 to 800 psi or higher.

devised because of the elimination of costly gas compression. In general, the other processes provide for charging, reaction, product separation, make-up hydrogen and gas recycle. With all processes, regeneration of catalyst along the lines already indicated may be accomplished.

Process Variables

The exact conditions which are employed depend on the boiling range and character of the stock and upon the degree of desulfurization desired and the catalyst employed. Processing period lengths will likewise depend upon these variables. Inasmuch as for the most part it is difficult to present a picture of processing conditions apart from specific stocks to be desulfurized, certain details are discussed in connection with the applications of hydrodesulfurization. However, some generalities are presented below.

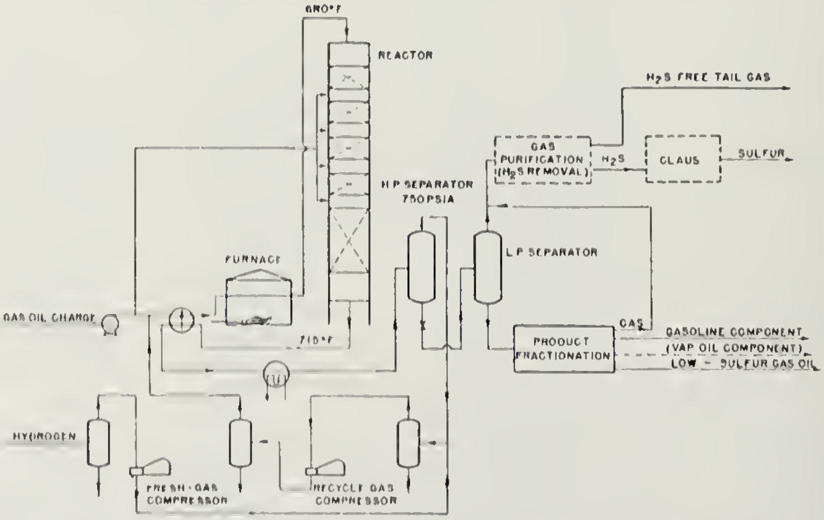


Figure 15. Flow diagram of a commercial hydrodesulfurization plant. (Reproduced from Ref. 179 by permission of the Editor of the *Petroleum Refiner*).

The over-all reaction involved in hydrodesulfurization may be exothermic as indicated by Table 11. Desulfurization itself, olefin saturation, and hydrocracking and aromatic saturation, when the latter occur, are all exothermic. On the other hand, naphthene dehydrogenation is endothermic. Thus, in processes operating at relatively high pressures without extensive naphthene dehydrogenation, the over-all reaction will be exothermic. This exothermicity will increase with increased unsaturation in the stock being treated and with increased hydrocracking[195]. In low-pressure operation, with extensive endothermic naphthene dehydrogenation such as occurs in Autofining, the over-all reaction is substantially thermoneutral[180].

The usual reaction variables of temperature, pressure, liquid space velocity, hydrogen to hydrocarbon ratio or recycle rate of hydrogen rich gas, and recycle gas composition all affect the desulfurization reaction. With respect to temperature, this should be such that effective desulfurization results and generally should be above 650°F as suggested by Byrns, Bradley and Lee[75]. Increasing the temperature improves desulfurization; however, as previously mentioned, to avoid substantial hydrocracking, the upper temperature limit should be held to 800°F or perhaps somewhat lower. Improved desulfurization will result with increasing total pressure or increasing hydrogen partial pressure[180, 195]; at the higher pressures processing cycle length will increase.

At other constant given conditions, changes in liquid space velocity vary contact time. The decreased contact time at higher space velocities will result in poorer desulfurization. Increasing the hydrogen to hydrocarbon ratio at constant liquid space velocity in vapor phase or essentially vapor phase operation also decreases contact time. Desulfurization may be improved somewhat because of the higher hydrogen partial pressure[180], or it may decrease because of decreased contact time[195]. Actually at a given contact time in gas oil hydrodesulfurization, improved results are reported[79, 237] at increased hydrogen rates. Though gas rates employed are generally higher, adequate desulfurization of many distillate stocks may be obtained at recycle rates as low as 250 to 1000 scf/bbl[179, 236]. In liquid phase hydrodesulfurization of heavy petroleum fractions, it has been suggested[238] to use sufficient hydrogen to combine with the sulfur and to satisfy the requirements of hydrogen solubility in the oil, and recycle rates of about 2400 to 4100 scf/bbl have been found to be adequate[238]. Actually, in liquid phase desulfurization, the rate is probably dependent to a considerable extent on the rate of diffusion of hydrogen through the liquid film on the catalyst surface. So far as this mechanism is concerned, all that can be done is to maintain the desired hydrogen partial pressure on the film.

With respect to recycle gas purity, the prime consideration is hydrogen partial pressure and actual hydrogen content can vary over a wide range with the degree of desulfurization controlled by adjusting temperature, space velocity and total pressure. Although the hydrogen content is preferably high, Porter and Hyde point out[239] that scrubbed exit gas from a naphtha thermal reforming unit containing only about 20 per cent hydrogen may be employed for the hydrodesulfurization of Iranian gas oil over a cobalt molybdate type catalyst in 780°F and 1000 psig operation. Hoog and Koome[240] indicate that hydrogen of 20 to 60 per cent purity may be employed in the Shell trickle hydrodesulfurization process. An excess of gas must be employed to effect a good flow of liquid over the catalyst, but this excess does not need to be hydrogen. It is only required that the gas be a substance, such as saturated hydrocarbon gas or nitrogen, which does not adversely affect the catalyst. Actually, as indicated in the introduction, the hydrogen generally available for hydrodesulfurization will be that available from hydroreforming operations. This will vary in purity from about 60 to 85 volume per cent hydrogen or higher depending on the severity and type of hydroreforming. Obviously, for most purposes this purity is adequate. In operations in which the hydrogen content of the recycle gas tends to be depleted below the desired level, resort may be had to bleeding recycle gas and replacing it with fresh hydrogen. Alternately, suitable absorption towers may be employed for concentrating the hydrogen.

Besides hydrocarbon gases, the other main impurity in recycle gas is hydrogen sulfide. Additional impurities such as water and ammonia derived from reduction of oxygen and nitrogen compounds may be present in small amounts. All these nonhydrocarbon impurities may be removed by proper scrubbing of the recycle gas or in solution or admixture with the liquid product.

Hydrogen sulfide in the recycle gas would be expected to exert a mass action effect on the desulfurization and to combine with unsaturates, when these are contained in the feed, to synthesize new sulfur compounds which would need to undergo subsequent desulfurization. Data obtained by Union Oil Co. workers[195], using a supported cobalt molybdate catalyst, show that increasing the hydrogen sulfide content of the recycle gas from 0 to 20 volume per cent only decreased the extent of desulfurization of a coker gasoline (3.07 per cent S) from about 98 to about 95 per cent, and this decrease was observed to be fairly linear with hydrogen sulfide concentration. In the case of a heavy coker gas oil (4.15 per cent S) the decrease was more substantial. Desulfurization was lowered from about 90 to about 70 to 75 per cent depending on the reaction conditions as the hydrogen sulfide content of the recycle gas was increased between 0 and 10 volume per cent. Actually, in commercial distillate hydrodesulfurization processes[180, 195, 241], the equilibrium concentration of hydrogen sulfide is not sufficiently high to affect desulfurization except to a minor degree. This is due to the solubility of hydrogen sulfide in the liquid product in the high pressure separator. This dissolved hydrogen sulfide is released upon transferring the liquid to the low pressure separator and to a lesser extent upon stripping to remove light components when products are so treated. This general method of removal of hydrogen sulfide from the recycle gas stream has been known for some time[242], and a specific recent example of its application during the hydrodesulfurization of Iranian gas oil over molybdic oxide on alumina catalyst in 1000 psig operation has been described by Strang[241]. Recycle gas contained only 1.1 volume per cent hydrogen sulfide; whereas, gas from the low pressure separator contained 42 volume per cent.

Process References

In the subsequent text, details of the application of hydrodesulfurization to various stocks and the results obtained are discussed. Certain supplemental information on processing various stocks has been collected in the table given at the end of this chapter.

GASOLINE PROCESSING

Hydrodesulfurization may be applied to light stocks boiling in the gasoline range for several purposes. Straight-run distillates may be treated to improve octane number and lead susceptibility to produce components for blending purposes or to obtain special products such as solvent naphthas having rigid sulfur and odor limitations. Low-grade straight-run or cracked naphthas of high sulfur, high nitrogen and/or high metals content may be pretreated to provide suitable charge stocks for platinum reforming operations. Cracked stocks containing substantial amounts of aromatics may be hydroprocessed to effect desulfurization and olefin saturation to produce aviation gasoline blending components. The clear octane number is decreased, but lead susceptibility is increased so that no loss of leaded lean mixture rating is observed. Cracked gasolines generally may be partially hydrogenated to improve quality as gasoline blending components. Miscellaneous applications of hydrodesulfurization to light stocks include the removal of sulfur compounds from olefin polymers and removal of sulfur compounds from crude benzene.

TABLE 23. CONDITIONS FOR MILD HYDRODESULFURIZATION OF STRAIGHT-RUN DISTILLATES

	Autofining	Union Oil Co.
Temperature, °F	780	745–765
Pressure, psig	100	450
Space velocity, vol./vol./hr.	5.0	0.95
Hydrogen to oil ratio, scf/bbl	2000	3350

Straight-Run Distillate

In general, reaction conditions are mild for the hydrodesulfurization of any straight-run stock boiling within the full-range gasoline limits and may be exemplified (Table 23) by those employed[180] in Autofining Iranian straight-run gasoline (0.081) per cent S) or naphtha (0.116 per cent S) and those used[195] by the Union Oil Co. for desulfurizing Santa Maria Valley straight-run gasoline (0.46 per cent S). Sulfur removal of 98 per cent is easily accomplished, and, under fairly severe conditions, products containing only a few parts per million sulfur may be obtained. Processing periods of several months are possible.

A possible application involves treating light naphthas for sweetening and desulfurization. This results in a marked increase in the lead susceptibility. However, the degree of practical realization of this improvement depends upon the sulfur content of the finished gasolines containing the desulfurized naphthas as blending components and there is the problem of whether such relatively low-quality naphthas can be used at all in view of present-day octane number requirements for motor fuels. Several examples are available of the quality improvements effected in straight-run gasolines and light naphthas by hydrodesulfurization[80, 86, 180, 195, 243, 244]. Those presented by Baeder and Siegmund[244] are given in Table 24. In connection with this type of treatment, it should be mentioned that vapor-phase bauxite desulfurization[245, 246, 247, 248] is effective if the stock does not contain an appreciable amount of thiophenes. Mild hydrodesulfurization, on the other hand, is applicable to stocks containing thiophenes for substantially quantitative desulfurization.

TABLE 24. MILD HYDRODESULFURIZATION OF VIRGIN NAPHTHAS

	West Texas 200–320°F		Iranian 170–330°F		Iran 216–300°F	
	Feed	Product	Feed	Product	Feed	Product
Sulfur, wt. %	0.12	0.01	0.10	0.004	0.06	0.006
Mercaptan number	33	0	18.3	0	1.4	0
Research octane number[a]						
Clear	63.5	64	48	50	40	45
+2 ml TEL	75	80.5	64	70	59	65
Motor octane number[b]						
Clear	—	—	51	51	43	46
+2 ml TEL	—	—	63	72	61	68
Yield, vol. %	—	100	—	100	—	100

[a] ASTM D 908.
[b] ASTM D 357.

Other important applications of mild hydrodesulfurization to light straight-run distillates include pretreating heavy naphthas to prepare low sulfur, premium charge stocks for platinum hydroreforming operations, and desulfurizing solvent naphthas to reduce sulfur content and to improve odor. These objectives are easily achieved[86, 180, 244].

Cracked Distillates

With Monoolefin Saturation. The principal applications of processing cracked distillates to effect substantially complete desulfurization and monoolefin saturation are pretreating such naphthas to prepare them as feeds for platinum hydroreforming operations and in processing light catalytic naphthas and similar feeds to permit their inclusion in aviation gasolines. Comparatively mild reaction conditions are adequate and cycle length is long. Thus Cole and Davidson[80] disclose that suitable conditions when using tungsten-nickel sulfide as catalyst are broadly 450 to 800°F., 700 to 1000 psig (at least 650 psig), 5 to 15 volume space velocity, and a hydrogen to oil mole ratio above 2:1. Specifically, processing of light catalytic naphthas was done at 650°F, 720 psig, 10 volume space velocity, and a hydrogen to oil mole ratio of 7:1. Cycle lengths before regeneration extended to 15,000 to 25,000 volumes of naphtha/volume of catalyst. Correspondingly long cycle lengths are also possible when processing cracked distillates with alumina supported cobalt molybdate type catalysts. Operating conditions include temperatures in the range 600 to 800°F and pressures in the range of about 50 to 800 psig.

Numerous examples[86, 244, 249] are available of the results of pretreating cracked naphthas. The operation is generally integrated with the platinum hydroreforming operation in that hydrogen rich gas from the reforming operation is employed in the desulfurization stage[249, 250, 251, 252, 253]. Successful operation is possible with several catalysts, including those of the platinum hydroreforming type[249, 250] and supported cobalt molybdate compositions[86]. Thermally cracked, visbreaker and coker distillates and blends of straight-run and cracked stocks are suitable upgraded. Actually, processing of such blends is a preferred procedure because milder operation is possible, and the substantial exothermic reaction which results when undiluted cracked naphthas are processed is overcome to a degree. Of the cracked stocks, coker distillate is a preferred material to pretreat because of high content of cycloolefins[244]. These cycloolefins are converted to naphthenes as a result of pretreating and later to desired aromatics during reforming. In addition to adequate desulfurization of stocks, nitrogen and metals contents can be reduced to suitably low levels by pretreating[86].

The application of substantially complete desulfurization and olefin saturation to light catalytic naphthas and similar feeds was important during World War II[80, 162, 254] when refiners were called upon to supply large quantities of grade 100–130 aviation gasoline. Light catalytic naphthas and such stocks as distillate produced as a by-product of butadiene synthesis by high temperature vapor-phase cracking of naphtha[80, 162] are of high aromatic content and are suitable for increasing the rich mixture rating. However, high olefin, and, in most cases, high sulfur contents make them unsuitable for blending because stability is poor and leaded ASTM D 614 lean mixture rating is low[80, 162, 254].

Processes developed by the Shell Oil Co.[80, 162] and Standard Oil Development Co.[254] were both applicable for effecting the desired desulfurization and monolefin saturation to produce stocks of improved stability, generally improved leaded lean mixture rating, and unreduced ASTM D 909 rich mixture rating. As would be expected diolefins were substantially eliminated[80], a fact which was probably largely responsible for the increased stability of the hydrogenated products. The Shell Oil Co. process utilized tungsten-nickel sulfide catalyst under conditions given above. The Standard Oil Development Co. process was operated with undisclosed catalysts. One which was fairly inactive was employed at 3000 psi; a more active catalyst was used at 150 psi[254]. As is usual in the case of mild hydrodesulfurization, there was no aromatic saturation as a result of processing in either of these operations. Apparently as long as the bromine number of the product does not drop below about 3, aromatic saturation is substantially inhibited[80]. Autofining has also been applied for the production of aviation gasoline components[180]. In this case liquid sulfur dioxide extracts of straight-run naphthas are processed.

Table 25. Effect of Desulfurization and Saturative Hydrogenation on Quality of Various Cracked Distillates

	Light Catalytic Naphtha 110–300°F		Heavy Catalytic Naphtha 270–430°F		Thermally Cracked Distillate 159–415°F	
	Feed	Product	Feed	Product	Feed	Product
Sulfur, wt. %	0.131	0.003	0.429	0.024	0.77	0.04
Bromine number	127	<1.0	62	4.0	71	2.0
Motor octane number						
Clear	78.2	71.2	77.4	64.3	60.5	47.0
+3 ml TEL	81.6	86.2	81.4	78.2	69.2	70.0
Research octane number	92.7	72.4	86.9	69.7	68.8	47.4
+3 ml TEL	98.0	89.0	93.6	86.1	76.4	71.6

Unfortunately, processing with complete olefin saturation is not applicable generally for upgrading cracked naphthas for inclusion in motor gasolines. Although stability is substantially improved, both clear Motor[80] and clear Research octane numbers are markedly decreased with the decrease being greater in the case of the Research value. Leaded (+3 ml TEL) Motor octane number is usually retained or increased[75, 195] due to the increased lead susceptibility because of sulfur removal and olefin saturation; however, at lower levels of added TEL (e.g., 1 or 2 ml) Motor octane number is usually lower and leaded Research octane number is lower even at the 3 ml of added TEL level. The author's data for the magnitude of some of these changes with certain light and heavy catalytic naphthas and a thermally cracked distillate are shown in Table 25.

With Minor Monoolefin Saturation. The general decrease of clear and leaded Research octane numbers and of clear Motor octane number upon complete saturation has led to selective hydrotreating to remove sulfur compounds and concomitantly conjugated diolefins without a corresponding degree of monoolefin saturation as discussed under accompanying reactions. Retention of a substantial proportion of the monoolefins maintains octane number. At the same time tendency for formation of gummy deposits is reduced, stability is improved and the naphtha has less tendency to leave deposits in engines.

In general, the degree of selectivity obtainable will depend upon catalyst, operating temperature and pressure, feed rate, hydrogen to oil ratio and stock. No complete picture can be presented to interrelate all these variables as only scattered information is available. With respect to catalyst, a number of compositions have been discussed above. Most information is available on the action of tungsten-nickel sulfide[76, 80, 123, 162]. With this catalyst and others, it is indicated, in general[76, 244], that the operating pressure should be low and the liquid feed rate high for best selectivity. Casagrande, Meerbott, Sartor and Trainer[76] found that optimum conditions for processing 135 to 385°F pressure distillate tops from thermally cracked mixed East-West Texas residue over regenerated tungsten-nickel sulfide catalyst were 600°F, 75 psig, 10 volume space velocity, and a hydrogen to oil mole ratio of 2 to 3:1. The operation resulted in about 60 per cent desulfurization, approximately 90 per cent conjugated diolefin removal and and only about 20 per cent monolefin saturation, with maintenance of the clear Motor octane number level and appreciations in both leaded Motor and leaded Research octane numbers. This degree of selectivity corresponds to that reported by Abbott, Liedholm, and Sarno[162] for the hydrodesulfurization of heavy thermal or heavy catalytic gasoline over both fresh and used tungsten-nickel sulfide catalysts. These latter investigators indicate that the normal reactor inlet temperature is between 450 and 650°F and that the normal operating pressure is between 500 and 700 psig. However, Engel and Hoog[123] confirm the importance of the use of a lower pressure by stating that optimum conditions for treating catalytic gasoline over tungsten-nickel sulfide include 599°F, 78 psi, and a hydrogen to oil mole ratio of 2:1. The selectivity obtained by all these investigators for the stocks indicated appears to be defined by the tungsten-nickel sulfide data for catalytic gasoline given in Table 18.

Engel and Hoog[123] state that the approximate optimum selective hydrotreating conditions, when employing a cobalt oxide-molybdenum oxide-bauxite catalyst or a corresponding potassium promoted composition for catalytic gasoline processing, are 842°F, 150 psi, a hydrogen to oil mole ratio of 2:1 and a variable space velocity adjusted to give the desired result. The very selective nickel sulfide-diatomaceous earth catalyst (Table 17) was employed[158] at 602°F, 75 psig, 8.0 volume space velocity and a hydrogen to oil mole ratio of 1.74:1 for pressure distillate gasoline hydrotreating. In general, pressures below about 75 psig and hydrogen to oil mole ratios below about 2:1 are to be avoided in selective hydrotreating because of excessive catalyst deactivation and/or impaired desulfurization and diolefin removal[76, 244]. At 75 psig operating pressure, it is estimated that cycle length for processing pressure distillate tops over tungsten-nickel sulfide catalyst can be extended to about 9500 volumes of feed/volume of catalyst[76].

TABLE 26. SELECTIVELY HYDROTREATING VARIOUS CRACKED NAPHTHAS[a]

Naphtha	Feed		% Br No. Reduction	% Desulfurization	Octane Number							
					Motor				Research			
					Clear		+2 ml TEL		Clear		+ 2ml TEL	
	Br No.	S, Wt. %			Feed	Product	Feed	Product	Feed	Product	Feed	Product
150–430°F Visbreaker	50	1.00	54	90	66.2	62.4	71.8	73.6	71.2	63.6	76.4	75.7
150–430°F Visbreaker + Coker	48	1.03	31	85	66.0	64.9	72.4	76.1	70.7	66.9	76.2	77.8
250–442°F Heavy Catalytic	23	0.24	26	71	—	—	—	—	92.5	90.5	96.0	95.5
300–450°F Heavy Thermal	34	0.28	29	57	—	—	—	—	59.5	52.5	70.0	69.0
200–350°F Light Catalytic	71	0.18	54	89	77.5	77.5	83.3	83.3	88.9	85.9	94.2	93.2
135–385°F Pressure distillate tops	80	0.34	25[b]	65	67.8	66.6	73.7	75.3	75.4	73.0	82.0	82.2

[a] Data of Casagrande, Meerbott, Sartor, and Trainer[76] for pressure distillate tops; all other data from Baeder and Siegmund[244].

[b] Monoolefin reduction.

Data are available on the selective hydrotreating of thermal and catalytic gasolines, visbreaker and coker distillates and some miscellaneous stocks and blends[76, 80, 123, 158, 162, 244]. These stocks are improved in properties as indicated above and their sulfur level greatly reduced so that they become improved for blending in the gasoline pool from this consideration alone. Some results which have been obtained in this type of processing are given in Table 26.

MIDDLE AND HEAVY DISTILLATE PROCESSING

Hydrodesulfurization under mild conditions to remove oxygen, nitrogen and sulfur compounds as applied to middle and heavy distillates is receiving considerable attention in commercial applications or potentially commercial applications. Thus tractor fuels and kerosenes are prepared from otherwise unsatisfactory stocks. Stove or range oils, furnace oil distillates, diesel fuels and heavy fuel oil stocks are suitably upgraded in properties including stability, color and blending characteristics. Light and heavy catalytic recycle stocks as well as straight-run charges may be upgraded for cracking. Miscellaneous stocks such as full range coker distillates and shale oil may also be processed to obtain valuable products.

Tractor Fuels

These fuels generally consist of a naphtha-kerosene blend containing aromatic stocks such as aromatic extracts, heavy catalytic gasoline, and light catalytic heating oil in sufficient proportions to give adequate octane number. Generally, the cracked and aromatic materials have high sulfur contents. Mild hydrodesulfurization which removes a substantial part of the sulfur and improves color and oxidation stability without affecting the octane number-contributing aromatic content is thus a very valuable procedure for treatment of such blends or the components thereof[180, 244].

Fairly mild operation usually suffices for effecting the desired improvements, with the exact conditions being dictated by the composition of the feed. Thus, tractor fuels containing aromatic extracts respond more readily than those containing components from catalytic cracking. In Autofining, suitable conditions for treating such fuels or their aromatic components are 780 to 800°F, about 100 psig, 0.5–3.0 volume space velocity and a recycle gas to feed ratio of 2000 to 7000 scf/bbl[180]. Processing of a 304 to 558°F tractor fuel blend which contained 45 volume per cent of a sulfur dioxide aromatic extract resulted in a sulfur reduction of from 0.58 per cent in the charge to 0.13 per cent in the product and an increase in clear Motor octane number from 48.1 to 51.2 for a processing period length of 1200 volumes of feed/volume of catalyst.

Kerosenes and Stove Oils

Kerosenes are petroleum distillates having a boiling range of about 320 to 500°F. They should be low in aromatics and sulfur, give low wick char and have a light color, an agreeable odor, and a low smoking tendency. Such materials may be distilled from low-sulfur paraffinic crudes directly, or they may, in general, be produced from any suitably boiling petroleum distillate by hydrodesulfurization. In either case, solvent extraction to reduce the aromatics to the desired low level is usually necessary. In general, mild processing conditions similar to those described as suitable for straight-run gasoline hydrodesulfurization may be employed and processing period lengths before regeneration are long.

Both Porter[180] and Morbeck[255] give examples of the hydrodesulfurization of kerosene fractions. Porter[180] shows the desirable effect of Autofining an Iranian kerosene. Morbeck[255] gives results of hydrofining a mixed sweet crude kerosene and one from West Texas Crude. Improvements in sulfur content, odor, color and wick char were obtained for the charges from both sources. With that from West Texas Crude, sulfur content was reduced from 0.55 per cent to 0.02 to 0.10 per cent, wick char was reduced from 65 to 20, and color was improved from +3 to +24 Saybolt.

Petroleum fractions boiling generally over the same range as kerosenes are employed as stove or range oils. For this particular purpose, the stock may contain more aromatics than a normal kerosene but should preferably conform to one in other respects. Substantial upgrading of such fractions is possible by hydrogenation[86, 233, 256]. Grote, Watkins, Poll and Hendricks[86] show the results which may be expected from Unifining a 42.3°API Montana stove oil. Gravity increased 0.5°API, volatility remained essentially unchanged, total sulfur decreased from 0.18 to 0.01 per cent, mercaptan sulfur decreased from 240 to 0.8 ppm, and color improved from +21 to +30 Saybolt. Zimmerschied, Hunt and Wilson[256] found that mild hydrodesulfurization of West Texas stock improved its quality to that of Mid-Continent distillate. Severe processing produced an even superior product which had a considerably higher smoke point and which gave considerably less burner deposits than observed for Mid-Continent stock.

Fuel Oils

Besides range or stove oils just described, distillate fuel oils include higher boiling straight-run and thermal and catalytic stocks. Furnace oils, light catalytic cycle stocks, etc. (No. 2 distillates) boil within the range about 400 to 700°F and heavy distillate stocks contain components boiling up to about 1000°F.

Because of the wide variety of stocks represented by the middle and heavy distillates and different objectives relative to their treatment, a wide variety of reaction conditions are employed. Some suitable specific levels of variables for processing light catalytic cycle stock, straight-run gas oil and heavy coker gas oil, all with supported cobalt molybdate type catalysts, are given in Table 27[179, 180, 195]. Even a fairly low molecular weight and susceptible stock such as Iranian straight-run gas oil cannot be desulfurized for extended periods in the low-pressure Autofining process. Catalyst regeneration is necessary after a throughput of 400 volumes of feed/volume of catalyst. High molecular weight, more refractory stocks such as the coker distillate are fairly difficult to process; however, throughputs considerably in excess of the 24 indicated in Table 27 are possible, under the tabulated conditions or at higher pressure, with adequate desulfurization. In the relatively high-pressure Shell trickle hydrodesulfurization operation, light catalytic cycle stock, which is more refractory than Iranian straight-run gas oil, may be processed for a throughput per cycle of 4000 with only slight catalyst deactivation. In the trickle process, the throughput per cycle possible when desulfurizing straight-run gas oil is 20,000.

Middle Distillate Stocks. One of the major applications of mild hydrodesulfurization is for the improvement of No. 2 distillates. As a result of processing, these stocks are stabilized against sludge formation and color deterioration and, in addition, burning properties are improved, corrosiveness reduced and blending characteristics enhanced.

The severity of processing will vary with specific requirements of individual refiners. If sulfur level is not a problem, mild processing with relatively little desulfurization will markedly improve cracked stocks and will hydrogenate mercaptans to effect sweetening of straight-run distillates[255, 257] Thus, Morbeck[255] has shown that, with 7 per cent desulfurization in the case of a catalytic stock and with 25 per cent desulfurization in the case of a thermal charge, color and stability were improved and there was a marked decrease in the carbon residue of the 10 per cent bottoms. The products were also compatible with doctor-sweetened West Texas virgin heating oil. Incompatible stocks, typified generally by unprocessed catalytic and other cracked furnace oils[258], have high blending carbon residue values due to interaction of unstable compounds which are present in them with converted (by doctor sweetening) sulfur compounds in a doctor-sweetened virgin stock. Inasmuch as carbon residue on the 10 per cent bottoms correlates with carbon deposition burning characteristics[255], carbon residue values should be low on final blended commercial oils and any enhancement in

TABLE 27. SUITABLE CONDITIONS FOR UPGRADING CERTAIN STOCKS WITH SUBSTANTIAL DESULFURIZATION

	Shell Trickle Hydrodesulfurization of 446–650°F Light Catalytic Cycle Stock (2.90 Wt. % S)	Autofining 406–675°F Iranian Straight-Run Gas Oil (0.72 Wt. % S)	Union Oil Cobalt Molybdate Processing of Santa Maria Valley Heavy Coker Gas Oil (70% point, 756°F; 4.15 Wt. % S)
Temperature, °F	710	780	700[a]
Pressure, Psig	750	100	450
Space velocity, Vol./vol./hr.	1.6	2.0	1.0
Hydrogen to oil ratio, scf./bbl.	1350	2000	4240
Run length, hours	>2500	200	24
Desulfurization, %	89	50	89

[a] Inlet temperature; temperature rise in bed was 84°F.

value for a component of the blend is quite undesirable. The value of very mild hydrogen treating in this connection is obvious. In addition to the desirable results described above, virgin stocks sweetened by hydrodesulfurization are compatible with caustic washed cracked furnace oils[255].

Generally, it is desirable to carry out the desulfurization of middle distillate fuel oils under more severe conditions to obtain substantial sulfur removal and a greater increase in desirable properties. Many examples are available of processing both cracked and straight-run stocks at high levels of desulfurization[53, 75, 78, 86, 179, 180, 195, 237, 255, 259, 260, 261]. Desulfurization of from about 60 to over 90 per cent can be obtained easily. Results given in Table 28 for processing Kuwait catalytic and straight-run furnace oils illustrate changes which may be effected[261]. Gravity (°API) is increased somewhat due to desulfurization and a minor amount of hydrocracking. Substantially complete elimination of mercaptan sulfur accompanies the marked decrease in total sulfur. Carbon residue on the 10 per cent bottoms is reduced. Color is better for products from cracked distillates. As indicated by neutralization numbers on products, oxygen compounds are substan-

TABLE 28. MILD HYDRODESULFURIZATION OF KUWAIT FURNACE OIL DISTILLATES

Typical Product Inspections

	Catalytic Furnace Oil		Straight-Run Furnace Oil	
	Untreated	Treated	Untreated	Treated
Inspection data:				
Gravity, °API	23.0	26.8	38.9	40.4
Color, ASTM Union	2	2–	1–	1–
Doctor	Sour	Sweet	Sour	Sweet
Sulfur, %	2.52	0.50	1.13	0.33
Mercaptan sulfur, %	0.003	0.001	0.021	0.001
Carbon residue, Conradson on 10% bottoms, %	0.36	0.07	0.03	0.03
Neutralization No.	0.03	0.01	0.04	0.01
Bromine No.	32.3	13.9	7.4	4.3
Aniline point, °F	80.9	88.6	155.5	157.8
Cetane index	27.8	33.5	55.7	58.1
Stability (210°F, 16 hr. insoluble sludge), mg./600 g.	4.2	1.0	0.5	0.1
Color, ASTM Union	4½–	2½–	1–	1–
Distillation, °F				
IBP	434	395	366	359
10%	481	463	427	433
50	533	523	507	502
90	603	606	599	596
EP	642	640	643	636

tially eliminated. Olefins undergo considerable saturation but aromatics are not saturated to any great extent.

Because of the formation of some light ends, desulfurized products must generally be stripped to meet flash specifications. These light ends have been found to be highly aromatic and of high octane number quality (e.g., clear Research number of 100+) when produced from light catalytic Middle East and other light catalytic cycle stocks[26, 179]. This results from the formation of alkyl aromatics from alkylbenzothiophenes according to type reaction V (Table 12). Such an alkyl aromatic boils some 145°F lower than the parent sulfur compound and thus will be in the gasoline boiling range if the sulfur compound boils lower than about 145°F above gasoline endpoint[26].

Table 29. Unifining Heavy Distillates

	Santa Maria Coker Distillate		Virgin Heavy Vacuum Gas Oil	
	Charge	Product	Charge	Product
Gravity, °API	26.9	39.0	23.6	27.2
Distillation, °F				
IBP	210	170	576	440
10%	318	285	674	600
50%	569	467	793	760
90%	870	722	879	870
95%	901	759	—	—
Maximum	—	—	902[a]	894[a]
Sulfur, %	3.9	0.05	1.94	0.39
Bromine No.	—	0.5	—	—
Nitrogen, %	0.24	0.05	—	—
Liquid yield, Vol. %	—	102	—	100.4

[a] 97% over.

Alkylbenzothiophenes constitute essentially the only sulfur type in the high sulfur content Middle East cycle stock which explains the desirable results which can be obtained with it[26], and other stocks will give the same results insofar as they conform to Middle East feed in sulfur content and type of sulfur compounds. In general, the sulfur compounds in light catalytic cycle stocks are concentrated disproportionately in the 392 to 572°F fraction[29], thus are usually of proper boiling point to yield gasoline components upon hydrodesulfurization.

Heavy Distillate Stocks. Heavy distillate stocks may also be processed to obtain premium stocks for blending in fuel oils. Table 29[86] shows results of Unifining Santa Maria coker distillate and a heavy virgin gas oil. The sulfur in the Santa Maria stock was reduced over 98 per cent; nitrogen removal, which is more sensitive to changes in processing conditions, was 79 per cent. Desulfurization of the virgin stock amounted to 80 per cent.

Diesel Fuels

High-speed diesel fuels correspond in general to No. 1 and No. 2 fuel oils. The present day tendency is toward products of lower sulfur content. Although suitable fuels may be obtained directly by distillation of sweet crudes, stocks from high-sulfur crudes and most cracked stocks require desulfurization. Processing conditions which involve the use of pressures of under 1000 psig have been used extensively for this type of operation. In general, the cetane number does not vary much as a result of this mild operation which reduces sulfur, oxygen, nitrogen and olefin contents. Much of such improvement as does occur probably comes about from converting heterocyclic ring compounds into higher cetane number open-chain compounds[262]. Additionally some increase would be expected from olefin saturation.

TABLE 30. EFFECT OF HYDRODESULFURIZATION ON SEVERAL DIESEL OILS

Stock	Charge		Product	
	S, Wt. %	Cetane Number	S, Wt. %	Cetane Number
362–640°F West Texas Catalytic[a]	0.94	28.5	0.19	28.7
366–643°F Kuwait Straight-Run	1.13	54.3	0.33	54.8
452–640°F Wyoming Straight-Run	2.1	46.0	0.14	52.0
363–694°F Arabian Straight-Run	0.99	56.0	0.10	56.8
478–634°F Elk Basin Straight-Run	1.3	46.0	0.25	46.0
495–682°F Mixed Catalytic (17%) and Arabian Straight-Run (83%)	1.6	51.0	0.35	52.0
361–666°F. Oregon Basin Straight-Run	1.32	47.0	0.21	50.0
West Texas Straight-Run[b]	1.0	51.0	0.07	56.0

[a] Predominantly of the source indicated.

[b] 10% point 500°F; 90% point 660°F.

Table 30 gives some results reported in the literature of such mild processing on Wyoming[86], Arabian[255], West Texas[262] and Oregon Basin[232] straight-run charges. Also included are data for a mixture of Arabian straight-run and catalytic stocks[255] and the author's data for Kuwait straight-run and West Texas catalytic stocks. Accompanying substantial desulfurization, cetane number improvement varies between 0 and 6 numbers in the case of the straight-run stocks. The low cetane numbers are not appreciably increased in the case of catalytic stocks; however, mild processing increases the amount of them which can be used because of sulfur, stability, corrosion and cleanliness considerations.

It should be noted in connection with this question of diesel fuels, that, although naphthenes are not high cetane number components, they are better than aromatics; thus, complete saturation of catalytic cycle stocks by operating at pressures of the order of 3000 psig and with active catalysts will result in cetaine number increases of about 10 to 15. Similar hydrogenation of Fischer-Tropsch synthesis gas oil obtained using an iron catalyst produces an excellent diesel fuel[262]. Diesel fuels obtained from products derived by destructively hydrogenating crude scale wax, petrolatum or foots oil are excellent[262]. Destructive hydrogenation can also be used to produce good diesel fuels from a variety of petroleum fractions.

Catalytic Cracking Charge Stocks

Hydrodesulfurization may also be applied to light and heavy distillates for upgrading them as catalytic cracking charge stocks. Examples are available on the improvement of light and heavy catalytic cycle stocks[86, 259, 263, 264], heavy coker gas oil[86] and heavy virgin gas oil[230].

In general, the reaction conditions required are more severe in the case of the cracked stocks and should be such that olefinic unsaturation is reduced and aromatics partially hydrogenated. To effect this most advantageously along with desulfurization, denitrogenation, and demetallization, reaction pressures should usually be in the range 750 to 1000 psig. For substantial aromatic hydrogenation, pressures of 3000 psig may be employed[264]. Temperatures will usually be in the range 700 to 800°F, volume space velocities may range up to 8, and hydrogen to oil ratios of up to 4000 or higher scf/bbl may be employed. In the lower pressure operation, adequate improvements in cracked cycle charges are obtained to make them essentially equivalent in crackability to the virgin stocks from which they were derived[259, 263]. The higher pressure operation gives products which have considerably better catalytic cracking characteristics than the virgin charges[264]. As is usual for the type of processing being considered, yields of liquid products are essentially 100 volume per cent; however, particularly with heavier cracked stocks, up to a few per cent of lower boiling products including naphtha may be obtained[86, 230] This is due to the occurrence of some hydrocracking under the severe conditions employed to effect the desired upgrading and to formation of lower boiling hydrocarbons from heterocyclics by hydrogenation.

At constant conversion by catalytic cracking, hydrogenated stocks give higher yields of gasoline and light catalytic cycle stock or furnace oil and lower yields of dry gas, coke, and heavy recycle stock. When comparing the catalytic cracking of hydrogenated and unhydrogenated stocks at constant coke formation, hydrogenated stocks give considerably more gasoline and less heavy cycle stock. Gasolines from hydrogenated stocks usually have clear Research and Motor ratings of 1 to 3 octane numbers higher than those from unhydrogenated stocks. Leaded (+3 ml TEL) Research and

Motor ratings are usually 2 to 5 octane numbers higher. As an exception to these generalizations, clear Motor octane number may sometimes be lower[264].

It should be emphasized that only partial saturation of aromatics is necessary to obtain improved cracking results. With virgin West Texas gas oil, reducing the aromatic concentration from 12.5 to 9.9 weight per cent is sufficient[230]. With catalytic cycle stock, reducing the aromatic ring content from 27 to 24 weight per cent is adequate to make this charge as susceptible to cracking as the stock from which it was derived[263]. It may also be mentioned that the amount of desulfurization accompanying such a degree of aromatic saturation results in the formation of low sulfur catalytic gasolines[263].

Miscellaneous Stocks

Miscellaneous distillates which may be hydrodesulfurized using cobalt molybdate type catalysts include coker distillate from oil from Athabasca tar sand[7] and coker distillates or fractions thereof from shale oil[7, 265, 266, 267, 268, 269]. Shale oil itself has also been processed over cobalt molybdate type catalysts[179, 221, 268] as well as with an unsupported mixed nickel sulfide-tungsten sulfide composition[270]. In processing these stocks to obtain low sulfur and low nitrogen products, it is usually necessary to operate in the hydrocracking temperature range and at pressures above 1000 psig.

Lubricating Oil Stock Processing

Lubricating oil stocks are selected petroleum fractions and may be refined or semirefined distillate or residual products. Thus they are considered apart from the sections on distillates and residues. Mild hydrogenation with negligible loss is applicable for finishing such oil bases[229, 261]. Temperatures suitable for this type of operation are in the range used for mild hydrodesulfurization, and pressures may be 1000 psig or lower or may range up to 3000 or 4000 psig, depending on the degree of improvement desired and on the stock being treated. Nonextracted and heavy stocks require more severe processing. Space velocity may also be varied to alter severity; a satisfactory hydrogen to oil ratio is 4000 scf/bbl. Long cycle lengths (e.g., over 6 months) are possible[228].

Table 31 shows some results obtained[261] upon mild processing of good quality unfiltered neutral distillate and unfiltered bright stock. In such operation, inappreciable ring saturation occurs, but marked improvement in color and significant reduction in carbon residue is possible. Decreased neutralization numbers indicate substantial elimination of oxygen compounds, and decreased iodine numbers show a reduction in olefinic bonds. A minor amount of hydrocracking occurs and viscosity is reduced somewhat. A slight increase in viscosity index is usually observed. This results from a combination of the hydrogenation reactions which take place, including opening of heterocyclic rings which should be highly desirable from the standpoint of increasing viscosity index. In general, oxidation stability is improved.

Hydrogenated motor oils processed to low sulfur contents and containing additives perform somewhat more satisfactorily in engines than products from conventional finishing. Furthermore, hydrogenated oils generally respond better to inhibitors[229]. Thus, good base stocks can be obtained for use by themselves or for blending for motor and commercial lubricant production. Turbine oils may be reduced in sulfur and improved in inhibited oxidation stability and other properties[229]. Sulfur reduction to the required low level and low power factors can be obtained with transformer oils[229].

TABLE 31. HYDROGEN TREATING OF LUBRICATING OIL STOCKS

	Unfiltered Neutral Distillate		Unfiltered Bright Stock	
	Charge	Product	Charge	Product
Inspection Data:				
Viscosity, SUS at				
100°F	471	451	2768	2070
210°F	61.9	61.0	161	137
Viscosity index	97	98	96	98
Pour point, °F	−5	+5	−5	−5
Carbon residue, Conradson, %	0.03	0.01	1.05	0.25
Color, ASTM Union	3.25	0.75	4.25[a]	4.25
Iodine No.	4.7	2.8	11.5	8.6
Sulfur, %	0.19	0.11	0.33	0.09
Neutralization No.	—	—	0.09	0.01

[a] Dilute.

WHOLE CRUDE AND RESIDUAL OIL PROCESSING

In the application of hydrodesulfurization to whole crudes and residues, objectives have ranged from processing with minor hydrocracking to obtain a salable product or one more amenable to subsequent refining to processing to obtain virtually complete elimination of higher boiling components with the production of a major amount of gasoline. The mild type of processing is potentially important commercially and operations effecting substantial formation of lighter components are being practiced or have been proposed. These latter type of processes are of considerable interest because high yields of more valuable, lower boiling products which are low in sulfur are obtained. In contrast, in mild hydrodesulfurization the production of more valuable lower boiling products is smaller; however, such processing may be necessary in the future to produce marketable heavy oils.

In the hydrogenation of whole crudes and residues, the cobalt molybdate or other type catalysts have been employed. As usual, mild processing involves the use of temperatures under 800°F and pressures of under about 1000 psig. Processing with attendant hydrocracking is carried out at temperatures over 800°F and at low and high pressures. The low-pressure operation at 1000 psig and lower with hydrocracking has the advantage that equipment costs are relatively low but the disadvantage that coke formation is high necessitating frequent catalyst regenerations and the use of a rugged catalyst. In the higher pressure process, at about 3000 psig or higher, plant investments are more substantial but long process periods are possible.

Actually, even in the mild operation considerable viscosity reduction occurs, especially when high-sulfur oils are treated, because of the hydrocracking involved in the elimination of sulfur and other heteroatoms from molecules. The relatively greater ease of sulfur removal as compared with hydrogenative scission of carbon-carbon bonds makes high-sulfur stocks more susceptible to upgrading in the higher temperature-hydrocracking type of processing.

Mild Processing

Low temperature and pressure fixed-bed hydrodesulfurization of whole crudes and residues presents more problems than are encountered in the case of distillate hydrodesulfurization. High contents of sodium, nickel, vanadium, and other metals may be present in a stock and deposit in the catalyst bed to affect its efficiency and to decrease the selectivity of the catalyst. Certain stocks, such as those containing high contents of resins and asphalts, may also be difficult to process because of their refractory nature. In spite of these difficulties, throughputs of several hundred volumes of oil/volume of catalyst are possible in some operations with adequate desulfurization.

Whole Crudes. Most recent information on whole crude processing describes the use of cobalt molybdate type catalysts. However, Horne and Junge[271] found that the sulfur in West Texas Crude could be reduced from 1.46 to 0.28 per cent when processing downflow over a fixed-bed of 75 per cent nickel oxide—25 per cent kieselguhr catalyst at 750°F, 250 psig, 1.0 volume space velocity and a hydrogen to oil ratio of 2000 scf/bbl. Liquid yield was 99 volume per cent and no more than slight hydrocracking occurred as evidenced by a small increase in gravity from 34.2 to 38.2° API.

Porter and Northcott[272] have described the processing of whole crudes over cobalt molybdate type catalysts under correlated conditions of temperature and pressure which confined the reaction substantially to desulfurization only with concomitant reduction in viscosity due to the formation of lighter products from the sulfur compounds. Specific conditions which they applied to Iranian Crude and Kuwait Crude were 780°F, 1000 psig, 1 volume space velocity, and a hydrogen to oil ratio of 4000 scf/bbl. In a 2000-hour upflow, fixed-bed operation, consisting of ten equal length periods with regeneration after each, the sulfur removal from Kuwait Crude was 72 per cent based on the entire product. The residue over 700°F was reduced in viscosity from 9750 to 1200 seconds Redwood I at 100°F. The fairly small change in volatility and the excellent desulfurization of the charge upon processing are shown by the comparison of fractions of the charge and the 2000-hour product given in Table 32.

TABLE 32. COMPARISON OF FRACTIONS OF THE KUWAIT CRUDE CHARGE AND PRODUCT FROM MILD HYDRODESULFURIZATION OVER COBALT MOLYBDATE TYPE CATALYST

	Yield on Feedstock, Wt. %		Sulfur Content, Wt. %	
	Feed	Product	Feed	Product
Fraction				
H_2S	Nil	1.8	—	—
Dry gas	0.4	1.0	—	—
Gasoline, C_4—300°F	14.9	14.9	0.021	0.009
Kerosene, 300-450°F	12.4	14.8	0.175	0.037
Gas oil, 450-649°F	16.8	20.4	1.23	0.34
Heavy gas oil, 649-700°F	3.9	4.8	2.37	0.71
Cracking stock, 662-1022°F	26.6	28.9	2.91	0.74
Residue above 700°F	51.6	42.3	4.22	1.31
Residue above 1022°F	28.2	16.7	5.12	1.96

When processing Kuwait Crude as described above, it has been shown[273] that a bauxite guard chamber, operating under the same conditions as the cobalt molybdate type catalyst, removes a considerable amount of the sodium and vanadium from the charge and thus reduces the rate of metal deactivation of the catalyst. It is estimated that a catalyst life of 10,000 hours would be possible before the operation became uneconomic with the use of such a guard chamber as compared with 2800 hours without a guard chamber.

With respect to guard chamber operation, sodium is more easily removed from petroleum feedstocks than vanadium, and for sodium removal the presence of hydrogen is unnecessary[273, 274], although elevated pressures help[275]. In fact, it appears that sodium removal is a physical process and that the competition of hydrogen for the bauxite surface may actually hinder sodium removal. On the other hand, vanadium removal is apparently a hydrogenation process, thus requires the presence of hydrogen. Accordingly, a method of guard chamber operation is to treat the charge over bauxite under optimum conditions in the absence of hydrogen for sodium removal and then over bauxite under optimum conditions in the presence of hydrogen for vanadium removal[273, 274]. Iron oxide on alumina[276] and fuller's earth[277] have both been mentioned as alternates for bauxite in the guard chamber operation. These alternate contacts, however, appear to be inferior.

Residual Oils. Hughes, Stine and Faris[78] give results for fixed-bed cobalt molybdate type processing of 500°F West Texas reduced crude. As shown in Figure 16, appreciable desulfurization can be obtained in 750°F and 300 to 400 psi operation at a volume space velocity of either 0.5 or 1.0. Particularly excellent desulfurization is obtainable at 0.5 volume space velocity for about 100 hours, with the product having the same sulfur content (0.4 to 0.5 per cent) as a similarly reduced sweet crude.

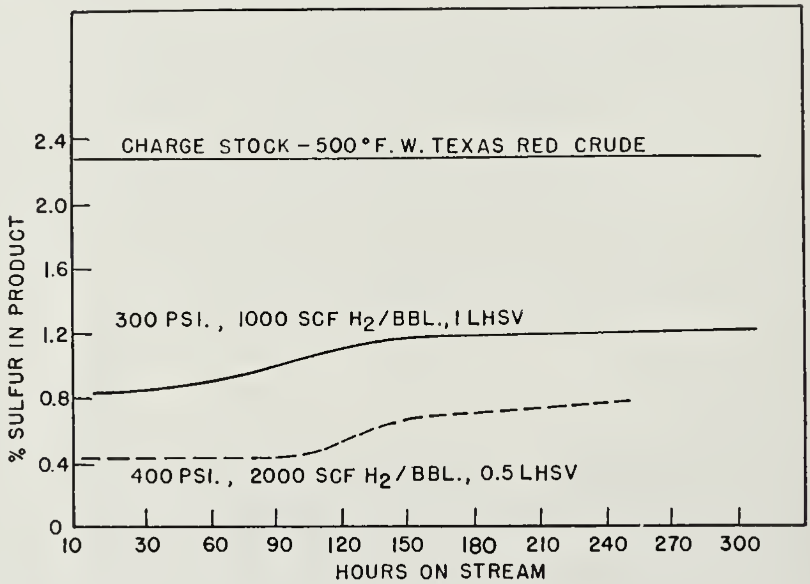


Figure 16. Hydrodesulfurization of West Texas reduced crude at 750°F. (Derived from Ref. 78 by permission of the authors and the Editor of the *Industrial and Engineering Chemistry*).

Hughes, Stine and Faris[78] also present data for fixed-bed cobalt molybdate type processing of thermal tars under conditions similar to those which they employed for reduced crude operation. In the case of a 4.0°API Mississippi thermal tar (Sample A, Figure 17), sulfur could be reduced from about 2.0 per cent for the charge to about 1.0 to 1.1 per cent for product representing an extended throughput over the catalyst. A high resin content, 10.4° API Mississippi-Louisiana thermal tar (Sample B, Figure 17) was not as susceptible to processing presumably because of inordinate fouling of the catalyst by the resins.

Processing with Hydrocracking

Low-Pressure Operation. Processing whole crudes and residual oils at temperatures above about 800°F and at pressures of 1000 psig or lower is not being practiced commercially. However, the recently announced Gulf HDS Process[278] indicates the feasibility of such a procedure.

Actually, the work which culminated in the Gulf HDS Process was preceded by study of the use of supported nickel oxide catalysts. An operable fixed-bed process using such catalysts was developed[271, 278], which was novel in that operation for useful cycle lengths was possible with substantially complete retention of the hydrogen sulfide by the catalyst. This retention of hydrogen sulfide was accomplished by terminating the cycle when about 50 to 60 per cent of the available nickel had been converted to nickel sulfide. At higher conversions to sulfide, hydrogen sulfide appeared in the reaction product. Additional features of the process included the use of a rugged catalyst[132, 133, 149] and employment of the catalyst initially in the oxide state to reduce uncontrolled hydrocracking activity which tended to result in excessive coke formation.

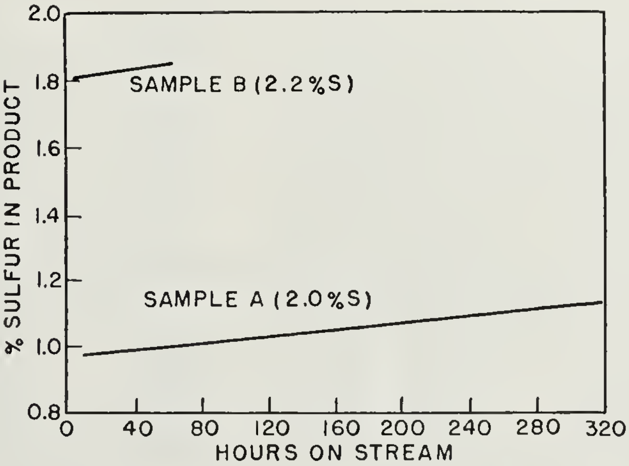


Figure 17. Hydrodesulfurization of thermal cracking tars at 750°F., 300-400 psi., 0.75 LHSV. and a hydrogen to tar ratio of 1000 scf./bbl. (Derived from Ref. 78 by permission of the authors and the Editor of the *Industrial and Engineering Chemistry*).

In the Gulf HDS Process, undisclosed compound supported metallic catalysts, which have higher hydrocracking activity than supported nickel oxide catalysts, are employed. These new catalysts are rugged, resist poisoning and are capable of being regenerated repeatedly. Reaction conditions are 800 to 850°F, 500 to 1000 psig, 0.5 to 2.0 volume space velocity, a recycle hydrogen gas to feed ratio of 2500 to 10,000 scf/bbl and 4 to 24-hour process period lengths[278].

Results which are obtainable by the Gulf Process when hydrogenating West Texas Crude, Kuwait Crude, Kuwait reduced crude, and a blend of Kuwait reduced crude and Kuwait light catalytic cycle stock have been reported[261, 278]. Partial typical data for whole Kuwait Crude are shown in Table 33 and similar results for Kuwait reduced crude are given in Table 34.

TABLE 33. COMPARISON OF KUWAIT CRUDE CHARGE AND PRODUCT FROM GULF HDS PROCESSING

	Fractionation of Charge and Product, Vol. %		Sulfur Content, Wt. %	
	Feed	Product	Feed	Product
C_3 and C_4 gas	2.4	3.2	—	—
Gasoline, C_5—300°F	16.4	25.8	0.04	0.03
Naphtha, 300–410°F	9.2	14.9	0.16	0.05
Furnace oil, 410–670°F	22.6	35.7	1.21	0.47
Residue above 670°F	49.4	20.4	4.11	0.84

TABLE 34. COMPARISON OF PRODUCTS FROM GULF HDS PROCESSING KUWAIT REDUCED CRUDE AT TWO SEVERITIES

	Fractionation of Products, Vol. %		Sulfur Content, Wt. %	
	Severity I	Severity II	Severity I	Severity II
C_3 and C_4 gas	0.5	1.3	—	—
Gasoline, C_5—300°F	6.5	14.9	0.17	0.10
Naphtha, 300–410°F	5.2	11.0	0.11	0.03
Furnace oil, 410–670°F	19.3	41.4	0.54	0.16
Cracking stock, 670–925°F	21.1	—	0.93	—
Cracking stock, 670–950°F	—	27.3	—	0.42
Bottoms above cracking stock[a]	47.4	4.1	2.40	3.72

[a] The charge represented bottoms above 1030°F or about 17 volume per cent of the crude.

With the whole crude (Table 33), which contained 2.61 per cent sulfur, a 96.0 volume per cent yield of product and 82.5 per cent desulfurization were obtained. The amounts of gasoline, naphtha, and furnace oil fractions increased at the expense of the bottoms fraction and all fractions were desulfurized to a considerable extent. The reductions of carbon residue and sulfur for the bottoms fraction were of sufficient magnitude to make it an acceptable catalytic cracking charge stock. The plot given in Figure 18 of the distillation data for charge and product presents a clear picture of the extent of formation of lighter products.

Gulf HDS processing data for the Kuwait reduced crude (Table 34) were obtained at severity levels I and II which gave conversions of the 5.8°API charge into lighter products of 53 and 96 volume per cent, respectively. The degrees of upgrading this charge into lower-boiling components is shown by Figure 18. Distillate fractions of acceptable sulfur contents were obtained from the residual oil charge, with the sulfur contents being lower when the severity was higher. Also, fairly low sulfur content bottoms fractions were obtained when the 5.45 per cent sulfur content of the charge is considered.

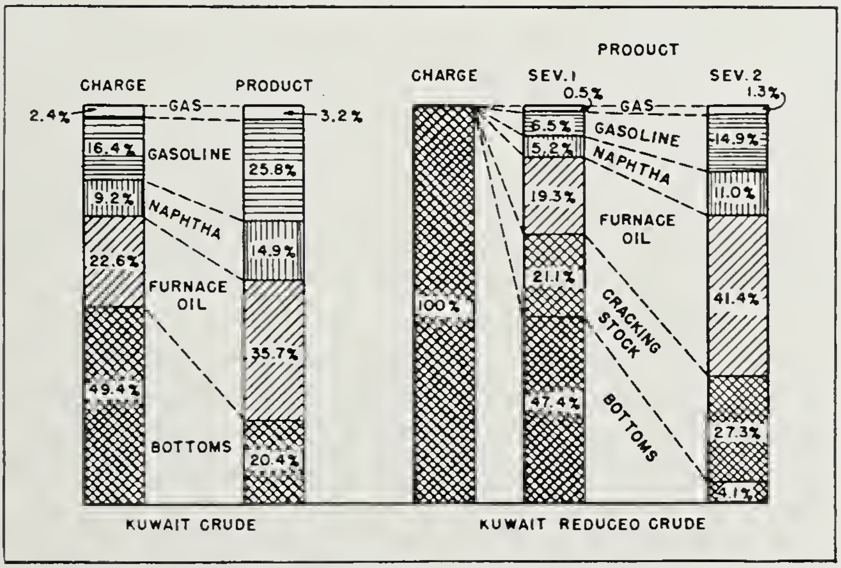


Figure 18. Typical results for Gulf HDS processing of whole Kuwait Crude and Kuwait reduced crude. (Reproduced from Ref. 261 with permission of the authors).

High-Pressure Operation. Processing of whole crudes and residues at about 3000 to 10,000 psig may be carried out in fixed-bed[279, 280, 281, 282] or suspended catalyst (slurry) operation[279, 280, 283, 284, 285]. Slow catalyst deactivation results in long cycles in the case of a fixed-bed operation and low rates of fresh catalyst addition in the slurry process. Probably the fixed-bed type of operation is more desirable where it is applicable because of the higher catalyst to oil ratios which are possible. In the suspended catalyst process, maximum catalyst concentration is limited by the necessity of maintaining fluidity of the reaction mixture and generally cannot exceed 25 to 30 per cent. On the other hand, a more degraded stock may be handled because of the provisions for continuously adding and removing catalyst.

Likewise this feature makes slurry operation applicable at pressures even below 3000 psig but with higher rates of catalyst addition and with greater equipment capacity for recovering oil from spent catalyst. In either operation, increasing the pressure increases the allowable charge rate to a specific volume of reaction space for a given extent of conversion and permits operation on a more degraded stock[280]. Whole crudes and straight-run and cracked residues may be processed.

Actually, there is no commercial operation at the present time which involves the use of fixed-bed operation at high pressures. As with the low-pressure corresponding method, one of the main problems involves the ash-forming components of charge stocks which tend to deposit on the catalyst and alter or decrease its activity as well as plug the bed so that operation with a guard chamber is usually necessary. The most desirable charge stocks include low-asphalt, low-ash crudes and their straight-run residues. Certain high sulfur crudes crack easily, thus are also quite suitable[279, 282]. Cracked stocks are less desirable and even residue of product from hydrogenating a topped crude in high-pressure slurry operation is a poorer charge stock than the topped crude itself, because hydrogenation when carried out by the slurry method is accompanied by thermal cracking and thermal alterations of the residue occur[280].

In contrast to the fixed-bed process, the high-pressure type of processing involving slurry operation has been used extensively in Germany in recent years as a step in the production of gasoline and some diesel oils from residues[280, 283, 285]. Although the original process[286, 287] underwent considerable improvement[280, 283, 285], its combination with thermal cracking or catalytic cracking was necessary to permit greater crude capacity and to meet the requirements for higher octane number gasoline[285]. Finally, demand for even higher quality product has made necessary plans for catalytic hydroreforming of the gasoline or portions thereof[288].

Although pressures as high as 10,300 psig were employed in the basic German process[283], operation at 5900 to 7300 psig was found to be adequate for the first-stage processing of straight-run residues[285], such as those from the available paraffinic, hydrogen-rich Near East (viz., Arabian and Kuwait) and German crudes which are processed in Germany[280, 283]. In this first stage, the catalyst which was employed was grude, an activated lignite semicoke, saturated with ferrous sulfate and an equivalent amount of caustic soda. A slurry of crude topped to about 662 to 680°F. and one weight per cent of this catalyst, calculated on fresh feed, was contacted with hydrogen in liquid phase operation at about 896°F. Product from this operation was separated in a hot separator into a small amount of bottoms containing catalyst and an overhead. Part of the bottoms plus catalyst were recycled and part were carbonized, with the oil from carbonization also being returned to the liquid phase operation. The overhead was cooled and depressured and distilled to separate gasoline, middle oil (from gasoline end point to 680°F) and residual oil, which latter was recycled to the liquid phase reactor. In a second stage, the middle oil was presaturated over catalyst 5058 (tungsten disulfide) or tungsten disulfide-alumina in fixed-bed operation, and finally, in a third stage, the prehydrogenated stock was hydrocracked over a fixed-bed of catalyst 6434 (10 per cent tungsten disulfide on hydrofluoric acid treated Terrana clay) completely to gasoline by recycling the material boiling over 374°F. Both of these latter operations were at 4400 psig and a temperature of about 752°F.

The product from the liquid phase or slurry operation, contained about 15 to 20 parts of gasoline, 40 to 45 parts of middle oil, and 40 parts of heavy cycle oil. The yields of end products were 80 to 82 weight per cent gasoline and 10 per cent liquid petroleum gas. This gasoline included the gasoline from the liquid phase operation which was refined together with the middle oil in the presaturation stage or by acid and caustic washing. The Research octane number of the gasoline from the vapor phase hydrocracking or splitting stage was about 70 clear or about 82 leaded (+1.9 ml TEL). Mixing with the lower quality liquid phase gasoline and that obtained by topping the original crude resulted in a lower quality total gasoline.

In further development of the process, it was found that vacuum bottoms and cracked residues could be handled in the liquid phase in the same manner as topped crude if the catalyst concentration, calculated on fresh feed, was increased from 1 to 2–3 weight per cent and if the reaction temperature was raised slightly. It was also established that crude liquid phase product, containing about 50 weight per cent of components boiling above 662°F and which was produced in about 8800 psig once-through operation[280], could be freed of gasoline and hydrocracked directly over fixed-bed catalysts at 7350 to 8800 psig. A 50 weight per cent yield of gasoline could be obtained in once-through operation or complete conversion into gasoline and lighter components could be obtained by recycling the fraction heavier than gasoline[280, 285].

A similar process which was found to be feasible involved processing the entire liquid phase product, stripped of tar and catalyst, without condensation or decompression over a fixed-bed of hydrocracking catalyst according to the general procedure suggested by Skinner, Donath, Schappert and Frese[289]. This was found possible with both stages operating at 4400 psig and is being practiced commercially[285]. In once-through operation of this so-called combined hydrogenation, yields of 35 volume per cent gasoline, 45 volume per cent 56–57 cetane number diesel oil and 20 volume per cent heavy oil are obtained. The heavy oil can either be recycled or further processed by itself by catalytic cracking or processed together with the diesel oil in a separate vapor-phase hydrogenation plant. The gasoline produced by the combination process itself is of poorer quality (68 Research octane number with 1.9 ml of TEL) than that produced by the conventional three-stage procedure, but plant capacity is increased by not operating the liquid phase reactor separately with recycle of heavy oil as is done in the three-stage operation.

As already indicated, hydrogenation has been integrated with thermal or catalytic cracking at the hydrogenation plants in Western Germany[280, 283, 285, 290, 291]. At the Wesseling (Union Rheinische Braunkohlen Kraftstoff A.-G.) plant, one of the three in operation, the topped crude is subjected to thermal cracking, and the cracked residue is subjected to liquid phase hydrogenation to produce light oil for vapor phase hydrogenation and heavy oil for recycle to the thermal cracking stage. The cracked gasoline is hydrofined, and the cracked light gas oil is subjected to vapor phase hydrogenation over metal aluminum silicate catalysts. Substantially the same yield of gasoline results as obtained by hydrogenation alone, but the octane number of the gasoline is at least three units higher.

At the Gelsenberg (Gelsenberg Benzin A.-G.) plant, the topped residue is vacuum distilled to produce a vacuum bottoms and a catalytic cracking charge stock which is catalytically cracked in a TCC unit. The residue from catalytic cracking and the vacuum bottoms are subjected to liquid phase and vapor phase hydrogenation, and, in addition, the light catalytic cycle stock is subjected to vapor phase hydrogenation. The motor fuel yield is substantially the same as could be obtained from hydrogenation alone, but the gasoline octane number is increased several points.

At the Scholven (Scholven-Chemie A.-G.) plant, which is the only one that employs the 3700 to 4400 psig combined hydrogenation procedure, the topped residue is subjected to vacuum distillation. The vacuum residue is processed by the combined liquid phase-vapor phase procedure and the heavy oil from this operation together with the vacuum distillate is catalytically cracked in an Orthoflow-Fluid unit. The light catalytic cycle stock is employed as a diesel oil blending component, and the heavy catalytic cycle oil is subjected to once-through vapor phase hydrogenation to produce gasoline, diesel oil and heavier oil which latter is recycled to the catalytic cracking unit. Gasoline octane number is considerably improved over that obtained by hydrogenation alone.

The combined hydrogenation procedure was made feasible by newly developed catalysts which are composed of synthetic aluminum silicates and oxides or sulfides of molybdenum, tungsten or other heavy metals[280, 292]. These catalysts are less sensitive to poisoning by nitrogen compounds than the activated Terrana clay based 6434 catalyst and are effective for the fixed-bed hydrocracking stage at pressures of 4400 psig and below[292]. In heavy oil operations at pressures above 5900 psig, the clay based catalyst[292], as well as natural or synthetic silicate supported compositions, may be employed[285].

The new catalysts have isomerization activities at least equivalent to that of 6434 and are weaker for hydrogenation. This latter characteristic results in the formation of a more highly aromatic, thus higher octane number gasoline when they are employed. An example of this is given in Figure 19 which compares aniline point, a measure of aromaticity, as a function of boiling point of the respective gasolines produced from Aramco straight-run gas oil with the 6434 and a new silicate type catalyst[292].

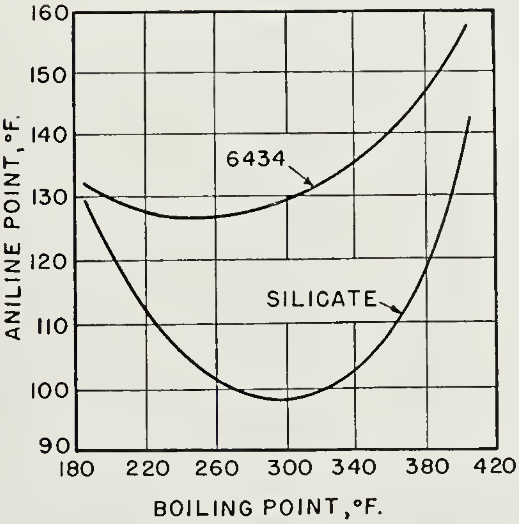


Figure 19. Aromatic content as indicated by aniline point for gasolines produced from gas oil over different type catalysts. (Derived from Ref. 292 by permission of the Editor of the *Petroleum Refiner*).

TABLE 35. HYDROCRACKING CRACKED LIGHT GAS OILS[a]

	Thermal	Catalytic		
Feed stock				
aniline point, °F	+68	+70	+90	+126
Product gasoline inspection				
Aromatics, Wt. %	45	46	43	29
Octane No.				
Motor clear	78	79	79	77
+1.5 ml TEL	85	85	85	86
Research clear	88	88	88	82
+1.5 ml TEL	94	95	94	90

[a] Processing conditions 716–788°F and 2900–4400 psig; space-time-yield of gasoline about 1.3 vol./vol./hr.

Inasmuch as the new catalysts are less sensitive to poisons, they may be applied for the hydrocracking of middle oil from the liquid phase operation

Table 36. Supplemental Hydrodesulfurization (HDS) Information

Catalyst	Process	Author	Reference
Gasoline Processing			
Cd or Cu chromite	HDS of straight-run gasoline	Smith, M.	U.S. 1,889,388
Active carbon containing 10% K as KOH	HDS of gasoline containing alkali insoluble S compounds at 662°F.	Engel, W. F.	Dutch 61,745
MoS_2, CoS or CoS and Al_2O_3	HDS of 302–347°F fraction of gasoline (10.6 wt. % S) from Kashpiriskii shale oil at 662°F and 1175–1790 psi to obtain almost complete sulfur removal with 10% of MoS_2. Other catalysts not as efficient.	Nametkin, S. S., Sanin, P. I., Makover, S. V., and Tzuiba, A. N.	*J. Appl. Chem.* (*U.S.S.R.*), **6,** 494 (1933).
Mo oxides, reduced Co, W oxides, V oxides, Al_2O_3, Cr_2O_3, metallic Cr, reduced Fe, reduced iron ore, Cr_2O_3 + Mo oxides, Cr_2O_3 + Co, Cr_2O_3 + Al_2O_3, Cr_2O_3 + 2Fe, Cr_2O_3 + Fe, Cr_2O_3 + 4Fe and Cr_2O_3 + CaS	Cr_2O_3 and reduced iron ore best for atmospheric pressure HDS of shale oil gasoline at 752°F.	Nametkin, S. S., Sanin, P. I., and Tzuiba, A. N.	*Goryuchie Slantzui,* **4,** No. 2, 40 (1934).
18–30 mole % Cr oxide-70–82 mole % alumina	HDS of naphtha with catalyst spent for aromatization. Product aromatized with fresh catalyst.	Burk, R. E., and Hughes, E. C.	U.S. 2,401,334
Sulfur insensitive catalysts	HDS and hydroprocessing of cracked gasolines	Cole, R. M.	U.S. 2,413,312 U.S. 2,392,579
Sulfur sensitive catalysts, e.g., Ni, Co or Cu type	HDS of light hydrocarbon distillates in a series of stages at about 167–572°F and 15 to 1500 psi.	Gwynn, M. H.	U.S. 2,073,578 U.S. 2,106,735 U.S. 2,174,510 U.S. 2,587,149

Partially sulfided supported Ni, Co or Fe	HDS of hydrocarbons at temperatures above about 700°F.	Szayna, A.	U.S. 2,273,297
Partially sulfided supported Ni, Co or Fe and active supported Ni, Co or Fe	HDS of hydrocarbon oils with sulfided catalyst at above about 700°F then with active catalyst at below 650°F.	Szayna, A.	U.S. 2,337,358
Alumina	Fluid selective hydrotreating of cracked gasoline to remove diolefins and cyclic sulfur compounds at 900–1025°F and 100 to 400 psi H_2 pressure.	Johnson, C. A., and Schuman, S. C.	U.S. 2,707,698
Pt-alumina or Pd-alumina	Hydroprocessing of light naphtha at 200–400°F to selectively remove diolefins and of heavy naphtha at 400–700°F for S removal and to saturate unsaturates. Blend of products has improved stability and quality.	Jones, M. C. K.	U.S. 2,542,970
V oxide	HDS of cracked gasoline at 896°F and 200 psig without monoolefin saturation.	Komarewsky, V. I., Knaggs, E. A., and Bragg, C. J.	*IEC*, **46**, 1689 (1954).
Ni sulfide–W sulfide	Cracked naphtha selectively hydrotreated to obtain maximum conjugated diolefin saturation with low monoolefin saturation by maintaining an equimolar ratio of H_2-containing gas to cracked naphtha.	Baumgarten, P. K., Hoffman, E. J., and Wadley, E. F.	U.S. 2,717,861 U.S. 2,694,671
Sulfur insensitive catalyst	The degree of selective hydrogenation of diolefins in cracked naphtha is increased by adding alkali soluble alkanethiols or benzenethiols to the feed. Product alkali washed to remove soluble S-compounds.	Hoffmann, E. J., and Wadley, E. F.	U.S. 2,638,438
Co molybdate type	Autofining cracked naphthas	Porter, F. W. B., and Northcott, R. P.	U.S. 2,640,802
Co molybdate type containing F	Autofining cracked naphthas with added H_2 to maintain hydrogen to oil ratio at 4000 scf/ bbl.	British Petroleum Co., Ltd., and Porter, F. W. B.	British 728,505

TABLE 36—*continued*

Catalyst	Process	Author	Reference
	Gasoline Processing—continued		
Co molybdate type	Autofining gasoline—commercial benzene mixtures	British Petroleum Co., Ltd., Porter, F. W. B., and Hyde, J. W.	British 728,755
Co and Mo oxides on alumina	Autofining cracked naphtha in presence of kerosene and heavy naphthas as H_2 donors to improve operation.	Anglo-Iranian Oil Co., Ltd., Porter, F. W. B., and Richardson, A. H.	British 716,786
HF	Straight-run gasolines, gas oils, kerosenes or naphthas extracted with HF to obtain S-free raffinate and a S-containing extract. Extract phase hydrogenated to H_2S-containing gas and to S-free liquid which still contains HF and is returned to extraction step.	Gerald, C. F.	U.S. 2,689,207
	Olefinic and Aromatic Stocks Processing		
Ni and Cu on alumina	HDS and partial saturation of olefinic stocks in presence of 125% of stoichiometric amount of H_2 to effect saturation.	Reid, J. A.	U.S. 2,376,086
Ferrous sulfide	HDS of olefin polymer fraction (2.0% S) at 725°F and 400 psig using an amount of H_2 sufficient to convert the thiol and disulfide sulfur to H_2S but insufficient to saturate monoolefins which are unchanged.	Lyman, A. L., Mithoff, R. C., and Nichols, H. B.	U.S. 2,236,216
Pt or Pd on alumina	Simultaneous saturative hydrogenation and HDS of triisobutylene prepared by sulfuric acid polymerization of butenes.	Brandon, R. C.	U.S. 2,461,959

Coprecipitated Mo oxide-alumina or W-Ni sulfide	HDS of silica gel aromatic extract of thermally cracked gasoline to obtain good blending component.	Eagle, S., and Rudy, C. E., Jr.	*IEC*, **42,** 1294–9 (1954).
—	HDS of dialkyl formamide aromatic extract of cracked gasoline to obtain blending component.	Deters, J. F., Lien, A. P., and Shalit, H.	U.S. 2,608,519
W-Ni sulfide	HDS of sulfur contaminated aromatic compounds (e.g., crude toluol) in presence of added olefin to maintain 1 to 5 vol. % olefins in product to prevent hydrogenation of aromatics.	Cole, R. M.	U.S. 2,394,751
MoS_2	Selective hydrotreating of crude olefin and S-containing benzene at 662°F and 294 psi.	Carlile, J. H.	*J. Soc. Chem. Ind.*, **57,** 347 (1938).
Sulfided Ni, Co or Ag molybdate on activated carbon or sulfided Ni molybdate on F-10 alumina	HDS of crude benzene containing, e.g., thiophene and CS_2	Stiles, A. B.	U.S. 2,620,362
CoS on pumice	HDS of benzene containing thiophene and other S-compounds	Roberti, G.	*Mem. accad. Italia chim.*, **2,** No. 5, 5–15 (1931).
Equimolar mixture of MgO, ZnO and MoO_3	HDS of crude benzene at 752°F and atmospheric pressure.	Kamms, E. D., Taffs, B., and Imperial Chemical Industries, Ltd.	British 404,960
Ni sulfide on active charcoal or Ni sulfide and chromic oxide on active charcoal	HDS of crude benzene at 482°F.	Guthke, F. W., and I. G. Farbenind. A.-G.	British 315,439 U.S. 1,897,798
Mo sulfide on active charcoal	HDS of crude naphthalene at 572°F and 735 to 1470 psi H_2 pressure.	Guthke, F. W., and I. G. Farbenind, A.-G.	British 315,439 U.S. 1,897,798
Alumina	Fluid HDS of aromatics containing cyclic S-compounds at 900–1300°F and 100 to 750 psi H_2 pressure.	Johnson, C. A., and Schuman, S. C.	U.S. 2,707,699

TABLE 36—*continued*

Catalyst	Process	Author	Reference
	Middle, Heavy and Miscellaneous Distillate Processing		
H_2S pretreated Co and Mo oxides on alumina	Autofining naphtha-kerosene fraction with use of excess H_2 produced for wax distillate HDS.	Porter, F. W. B., Northcott, R. P., and Rowland, J.	U.S. 2,672,433
Co molybdate type, Cr oxide or W sulfide, pellets of 2 parts W sulfide and 1 part Ni sulfide.	Autofining a S- and naphthene-containing petroleum fraction boiling within the range of about 302–464°F.	Porter, F. W. B., and Green, F. R. G.	U.S. 2,574,445
Co molybdate type	Autofining of straight-run petroleum distillates (e.g., 70% kerosene and 30% gas oil) followed by hydrogenation of olefins formed over W and Ni sulfides to produce product stable to storage.	Anglo-Iranian Oil Co., Ltd., and Howes, D. A.	British 682,309
Co molybdate type	Autofining distillates boiling in the gas oil and kerosene ranges.	Docksey, P., and Porter, F. W. B.	U.S. 2,574,446
—	HDS and hydrogenation of gas oil at 295–735 psi.	Wissel, K.	*Erdöl u. Kohle*, **6**, 696–700 (1953).
MoO_3-alumina	HDS of diesel oils at 736–797°F and 735 psi to improve cetane number. Catalyst pretreated with H_2S less efficient.	Birthler, R., and Szkibik, Chr.	*Chem. Tech. (Berlin)*, **6**, 373–8 (1954).
Co molybdate type	HDS of gas oils at 750°F and 300 psi to obtain products having the same S content as similar fractions from a sweet crude.	Hughes, E. C., Stine, H. M., and Faris, R. B.	*IEC*, **42**, 1879–82 (1950).
Co molybdate type	HDS of 356–707°F catalytic feeds at 608–797°F and 295 to 2950 psi to produce aromatics from S-compounds and to obtain aromatic engine fuels.	N. V. deBataafsche Petroleum Maatschappij	British 675,620
MoO_3-alumina	HDS of gas oil to obtain up to 96% S removal at 720–800°F and 800–1000 psi.	Strang, L. C., and Owen, J.	British 588,765

Co molybdate type	Desulfurization of hydrocarbon feedstocks (e.g., Iranian gas oil) without addition of H_2 or H_2 recycle at 700–800°F and at 500–1000 psi to maintain feed as liquid. Naphthene dehydrogenation furnishes H_2 at sufficiently high partial pressure for reaction with S compounds.	Anglo-Iranian Oil Co., Ltd., and Porter, F. W. B.	British 690,806 U.S. 2,697,682
Promoted (F and P) Co molybdate type first stage; Co molybdate or W-Ni sulfide second stage	Ditto in first stage plus a second stage using excess hydrogen produced in the first stage on a recycle basis.	British Petroleum Co., Ltd., and Porter, F. W. B.	British 728,506 U.S. 2,719,108
Co molybdate type	HDS of gas oil with H_2 derived from naphtha reforming. H_2 purified by scrubbing with gas oil to be desulfurized.	Stine, H. M.	U.S. 2,580,478
Co molybdate type	Autofining thermal cracking charge stocks.	Anglo-Iranian Oil Co., Ltd., Doeksey, P., and Porter, F. W. B.	British 670,619
Mixed Mo sulfide, Fe sulfide, SiO_2, TiO_2, and Al_2O_3	HDS and hydroprocessing one-pass gas oil to improve crackability.	Johnson, H. L., and Stuart, A. P.	U.S. 2,649,419
Sulfur insensitive and sulfur sensitive compositions	Hydroprocessing cycle stocks in two stages to improve crackability. First stage at 700–900°F and 200–1000 psig using sulfur insensitive sulfide of Group VI or VIII; second stage at same pressure but at 500–700°F using same catalysts or sulfur sensitive composition such as Group VIII oxide.	Smith, W. M.	U.S. 2,459,465
Co molybdate-alumina type	Autofining cracking stocks to obtain feeds which catalytically crack to give substantially S-free products.	Lorne, H. T., and Porter, F. W. B.	U.S. 2,574,449
Co molybdate type	Autofining heavy feedstock (e.g., Iranian wax distillate) to obtain a 392–752°F gas oil fraction and a catalytic cracking stock.	Porter, F. W. B., and Haresnape, J. N.	U.S. 2,686,150

TABLE 36—*continued*

Catalyst	Process	Author	Reference
	Middle, Heavy and Miscellaneous Distillate Processing—continued		
Hydrogenation catalysts	HDS and hydroprocessing of heavy visbreaker gas oil at 600–800°F to obtain catalytic cracking stock.	Standard Oil Development Co.	British 593,496
Co molybdate type	Autofining flash distillates from petroleum feedstocks. Degree of vaporization of charge being flashed controlled by passing part or all of the Autofining reactor effluent hydrogen containing gas and/or liquid products to the flash chamber.	Anglo-Iranian Oil Co., Ltd., and Meyer, P.	British 669,551 U.S. 2,606,141
Co molybdate type	Autofining Iranian wax distillate to obtain S reduction from 1.5 to 0.3%.	Porter, F. W. B.	U.S. 2,574,447
Co and Mo oxides on special activated alumina	Desulfurization of heavy oil (e.g., gas oil with mid-boiling point above 482°F) at, e.g., 752°F and about 1500 psi in presence of naphtha added to lower critical temperature. No H_2 is added and desulfurization occurs by transfer of H_2 within oil itself. Substantially unchanged naphtha recycled.	Engel, W. F., and van't Spijker, P.	U.S. 2,591,525
Ni and W sulfides or Ni and Mo sulfides	HDS and hydrodenitrogenation of shale oil or fractions at 700–800°F and 2000–4000 psig.	Smith, W. M.	U.S. 2,692,226
	Lubricating Oil Stock Processing		
Mo sulfide on alumina	Improvement of color and color stability of lubricating oils by hydroprocessing in liquid phase operation at 450–575°F and about 150–515 psi.	La Porte, W. N.	U.S. 2,654,696

2 $NiS \cdot WS_2$	Improvement of lubricating oil stocks by hydroprocessing at 700–775°F and 2500 psig. The mixed sulfide catalyst gives better yields of products than MoS_2 .	Voorhies, A., Jr.	U.S. 2,554,282
Pt on alumina or silica gel	Hydroprocessing of virgin distillates at 600–700°F, 100–200 psig and 1–2 LHSV to improve color and reduce neutralization value.	Esso Research and Engineering Co.	British 737,020 U.S. 2,756,183
Ni on kieselguhr, Mo oxide or sulfide on alumina, Co molybdate on alumina, W-Ni sulfide and Pt on alumina	Hydroprocessing solvent extracted and dewaxed lubricating oil fractions from a crude oil at 500–650°F, 200–1000 psig and 0.5–1.0 LHSV.	Esso Research and Engineering Co.	British 748,154
Modified Mo on alumina	Hydroprocessing light, intermediate and heavy motor oils	Moreton, A. G.	*World Petroleum,* **27,** 44 (1956).
	Whole Crude and Residual Oil Processing		
Co molybdate type	HDS and vanadium removal from residual oils. E.g., at 750°F and 1000 psi 78% desulfurization of and 60% V removal (as catalyst deposit) from 35% Iranian residue (2.35% S; 45 ppm V) obtained.	Hyde, J. W., Porter, F. W. B., and Anglo-Iranian Oil Co., Ltd.	British 682,387
Co molybdate type and others	Treatment of petroleum residues at 700–900°F and 100–1000 psig in absence of H_2 to precipitate dissolved metalloorganic compounds, ash, and unstable high molecular weight constituents; product including suspended precipitated material subjected to liquid phase catalytic hydrogenation at 600–1000°F and 100–1000 psig to obtain improved catalyst life.	Nicholson, E. W. S.	U.S. 2,717,855

Table 36—*continued*

Catalyst	Process	Author	Reference
Whole Crude and Residual Oil Processing—continued			
Co molybdate type	HDS of vapor and liquid phases of crude oil and residues separately in parallel reactors so that each phase can be treated under optimum conditions.	British Petroleum Co., Ltd., Porter, F. W. B., and Northcott, R. P.	British 736,782
Hydrogenation catalyst	HDS and hydrogenation of asphaltic feedstocks first in suspended catalyst operation which transforms into fluid bed operation when most of the oil has been vaporized.	McAfee, J.	U.S. 2,723,943
Co-Mo-bauxite or Zn-Mo-bauxite	HDS of Slaughter Crude at 750°F and 225 psig. Co-Mo catalyst better for desulfurization; Zn-Mo composition better for hydrocracking.	Hale, J. H., Simmons, M. C., and Whisenhunt, F. P.	IEC, **41,** 2702 (1949).
Cr oxide-Mo oxide-alumina	HDS of heavy petroleum fractions (including topped crudes and cracking coil tars) containing 1.0–6.5% S at 725–800°F and 300–400 psi.	Stine, H. M.	U.S. 2,577,823
Fe, Ni or Co oxide on carrier	Crude oil fractionated and heavy fractions hydrogenated separately followed by blending the treated fractions with those of lower boiling point and treatment of blend under more severe conditions.	Franklin, L. U.	U.S. 2,587,987

Hydrogenation catalysts	HDS and hydrocracking of high-boiling hydrocarbon charge at 750–950°F and 500–1000 psig. Vaporized oil treated upflow. Nonvaporized oil treated downflow and partly recycled. A continuous liquid phase in the reactor is avoided.	Montgomery, C. W., and Horne, W. A.	U.S. 2,662,846
BF_3/H_2O, ratio 2:1	HDS with homogeneous catalyst of heavy petroleum fractions such as Kuwait reduced crude which was treated at 750°F and 2000 psig.	Mason, R. B.	U.S. 2,657,175
$Ni(CO)_4 + I_2$ promoter	Ditto	Mason, R. B.	U.S. 2,636,841
$SnCl_4$ or $TiCl_4$ each with HCl promoter	Ditto	Mason, R. B., and Rose, H. J.	U.S. 2,640,011

with less drastic prehydrogenation than required when using the 6434 catalyst[285]. Thus, with the new catalysts, a refining treatment which retains the aromatics is adequate and tungsten-nickel sulfide and cobalt molybdate type catalysts can be employed. When the 6434 catalyst is employed, the presaturation must remove substantially all nitrogen compounds, and a large part of the aromatics are simultaneously hydrogenated. The less saturated nature of the charge to the new catalysts as well as their weaker activity for hydrogenating aromatics during the vapor phase hydrocracking stage both contribute to the higher octane number of the resulting gasoline. Even with regular prehydrogenation of middle oil, their use in the vapor phase hydrocracking stage results in an increase of octane number for the gasoline of at least five units. Furthermore, they are especially adapted for the processing of thermal and catalytic light gas or middle oils as shown (Table 35) by the interestingly high octane numbers of gasolines obtained[285].

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