

Reaction of Carboxylic Acids with Carbonyl Compounds over Alumina

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As part of a study to elucidate the mechanism of the ketonization of carboxylic acid, the reactions of carboxylic acids with carbonyl compounds over alumina at 350–400°C were studied. Products arising from the transfer of alkyl group of the carboxylic acid to the carbonyl compounds as well as those arising from a Perkin-type condensation of carboxylic acid with carbonyl compound were detected. Mechanisms of these reactions are discussed.

INTRODUCTION

Decarboxylative condensation of carboxylic acids to ketones either by heating metal carboxylates or by passing the carboxylic acids (as vapor) over heated metal oxides is a reaction of wide applicability. The mechanism of these reactions has been studied by several groups of workers (1), but the results have been inconclusive. Decarboxylation of the acid anhydride (2), Claisen condensation to form β -keto acid followed by decarboxylation (3), and decarboxylative alkyl anion transfer (4) have been proposed. Isotope-labeling studies (5) have supported the β -keto acid intermediate, but this route cannot account for the formation of benzophenone from benzoic acid (6) which does take place albeit to a minor extent. Isotope-effect studies (7, 8) have favored the alkyl transfer mechanism. In designing the present study it was expected that if carbanion-type intermediates are involved in the decomposition of acids, it should be possible to trap them by aldehydes or ketones.

EXPERIMENTAL

Catalyst Preparation

Alumina was prepared by controlled hydrolysis of aluminum isopropoxide by the

atmospheric moisture, as reported elsewhere (9).

Sodium-impregnated alumina. Weighed samples of alumina were shaken with sodium carbonate solution of known concentration for 6 hr, centrifuged, and the recovered supernatant solutions were titrated to estimate the amount of sodium carbonate adsorbed by the alumina. The residual damp solid was dried in an oven for 6 hr and calcined at 600°C for 6 hr.

Deuterated alumina. Aluminum isopropoxide was hydrolyzed slowly under D₂O atmosphere for 48 to 64 hr and the lumps formed were broken up and heated in an oven at 120°C for 6 hr and then calcined at 600°C for 6 hr.

Reagents

Acetic acid, propanoic acid, benzoic acid, phenylacetic acid, cinnamic acid, benzaldehyde, butanal, 2-butanol, 3-pentanone, 2-butanone, propanal, and 2-propanol used were of Analytical Grade.

Authentic 1,2-diphenylethene, phenyl-ethene, 1-phenylprop-1-enes, pentenes, and hexenes were prepared by passing the corresponding alcohols over alumina at 400°C. Deuterated propanoic acid (CH₃CH₂COOD) was prepared by treating propanoic anhydride with D₂O in the presence of a drop of pyridine.

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Apparatus and Experimental Techniques

The catalytic flow-reactor and the general experimental techniques had been described previously (10). Products were analyzed by gas chromatography using Carbowax (10% on 60–80 mesh Chromosorb, acid-washed, white, $\frac{1}{8}$ in. diam., 7 ft. length) and SE 30 (5% 60–80 mesh Chromosorb, acid-washed, white, $\frac{1}{8}$ in. diam., 6 ft. length) columns and FI-detector. After each reaction the catalyst was activated by passing a mixture of dry CO₂-free air and nitrogen (1:1 vol/vol). Then the catalyst was cooled to the required temperature under the flow of nitrogen.

Prior to the reactions of deuterated propanoic acid [CH₃CH₂COOD] alone and of deuterated propanoic acid with benzaldehyde over deuterated alumina, 3 ml of D₂O was passed over the alumina catalyst at 200°C and the catalyst was heated to 500°C under the flow of dry nitrogen for 2 hr and then cooled to the reaction temperature.

About 10 ml of deuterated propanoic acid was passed over 2 g of deuterated alumina at a 20 ml/hr rate at 400°C. The products were collected in a water-cooled receiver and dried over magnesium sulfate. Fractional distillation of this product using a short column gave diethyl ketone (2 g, bp 102°C) and unreacted propanoic acid (2.5 g, bp 141°C). NMR spectra of both the acid and the ketone showed extensive deuterium incorporation at the α -carbon atom.

Cinnamic acid was isolated from the reaction mixture of acetic acid and benzaldehyde. The cinnamic acid obtained was purified by crystallization from hot water, (mp 132°C). The *cis*- and *trans*-1,2-diphenylethenes and 1-phenylprop-1-enes were isolated from the corresponding reaction mixtures by column chromatography. Identification of the above samples was made by comparing the NMR spectra of these samples with those of authentic samples.

Reaction of carboxylic acids over alumina. A 5 M solution of phenylacetic acid

or cinnamic acid in benzene or of benzoic acid in toluene was passed individually over 1.5 g of alumina at 400°C at 20 ml/hr rate. Toluene, styrene, and benzene, respectively, were formed in 24, 15, and 12% yield, in addition to the ketones. Methane and ethane were detected in the reaction of acetic acid and propanoic acid, respectively.

RESULTS AND DISCUSSION

It was found that when a mixture of acetic acid and benzaldehyde was passed over an efficient ketonization catalyst like thoria, acetone was the main product along with products of condensation between acetone and benzaldehyde. Hence alumina, which is only a moderately active catalyst for ketonization was used for the present study.

Results of the reaction between carboxylic acids and carbonyl compounds over alumina at 400°C are given in Table 1. It can be seen that the major products of these reactions are olefins, as represented in the equation:



There is little doubt that carboxylic acids form surface carboxylate by dissociative adsorption (11–13)



The subsequent reaction of this surface species could be by one or more of several possible routes (Schemes I and II).

1. Decarboxylative Alkyl Transfer

The alcohol **3**, namely, 2-butanol, by the reaction between acetic acid and propanal could indeed be detected in trace quantities when the reaction was conducted at 350°C, at which temperature the overall reaction was negligible. At higher temperatures, where the conversion of acid was higher, only olefin **1** was formed and no alcohol

TABLE 1
Reaction of Carboxylic Acids with Carbonyl Compounds over Alumina

Sample No.	Reactants	Product distribution in mole % ^{a,b}	
		Products	Percentage
1	Benzaldehyde + acetic acid	Acetone	6
		Phenylethene	63
		Benzaldehyde	32
		Others ^c	5
2	Benzaldehyde + propanoic acid	3-Pentanone	3
		1-Phenylprop-1-enes	
		<i>cis</i>	31
		<i>trans</i>	22
		Benzaldehyde	40
		Others ^c	7
3	Butanal + acetic acid	Acetone	3
		Pentenes	75
		Butanal	12
		Others ^c	13
4	Butanal + propanoic acid	3-Pentanone	3
		Hexenes	60
		Butanal	25
		Others ^c	15
5	Benzaldehyde + benzoic acid	Benzophenone	3
		Benzaldehyde	90
		Diphenylmethane	2
		Others ^c	8
6	Benzaldehyde + phenylacetic acid	1,3-Diphenyl-2-propanone	10
		1,2-Diphenylethenes	
		<i>cis</i>	17
		<i>trans</i>	11
		Benzaldehyde	60
		Others ^c	12
7	Benzaldehyde + acetic acid (on 2.1% Na ⁺ /Al ₂ O ₃)	Acetone	60
		Phenylethene	2
		Benzaldehyde	92
		Others ^c	6
8	Butanal + acetic acid (on 2.1% Na ⁺ /Al ₂ O ₃)	Acetone	62
		Pentenes	0
		Butanal	90
		Others ^c	10

Note. Weight of alumina: 1.5 g; temperature: 420°C; flow rate: 10 ml/h; reactant: 1×10^{-2} each of carbonyl compound and carboxylic acid made up to 10 ml in benzene.

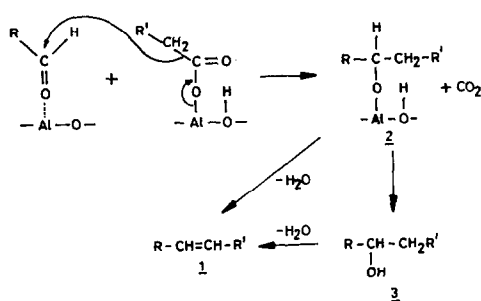
^a The product distribution refers to the composition of total product collected for entire period of reaction. Quantitative estimation of unreacted acids was not made.

^b Mole percentage of ketones are given w.r.t. carboxylic acid and all other products are given w.r.t. carbonyl compound.

^c Hydrocarbons arising from decarboxylation of acids were identified. In addition, trace quantities of unidentified products were also present.

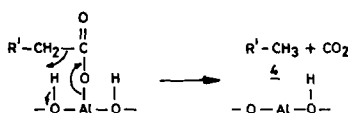
could be detected. Evidently the intermediate **2** decomposed to **1** rather than desorb to form **3**, at the working temperature. Detec-

tion of the alcohol **3**, even though in trace quantities, is in support of this mechanism. Further, the formation of small amounts of



SCHEME I

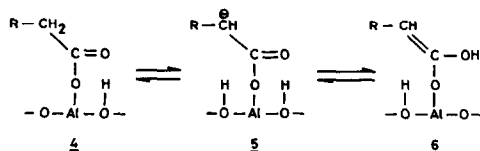
diphenylmethane and benzophenone in the reaction of benzaldehyde with benzoic acid (disproportionation products of diphenylcarbinol (14)) also supports this route. Besides, decarboxylation of carboxylic acid to alkane 4, evidently occurs through alkyl or aryl anion.



In an attempt to isolate the alcohol intermediate 3, Na⁺-impregnated alumina was employed. Incorporation of Na⁺ is known to suppress the dehydration activity of alumina (15–19). However, use of an alumina sample containing 2.1% Na⁺ led to practically no olefin, but to a very efficient ketonization of acid. The carbonyl compound was recovered unchanged. It was concluded that the reduction of the acidity of alumina by Na⁺ made the adsorption of the weakly basic carbonyl compound impossible, while surface carboxylate was readily formed, which yielded ketone.

2. Reaction through β -Hydroxy Acid Intermediate

The surface carboxylate 4 could dissociate and tautomerize on the surface as shown below

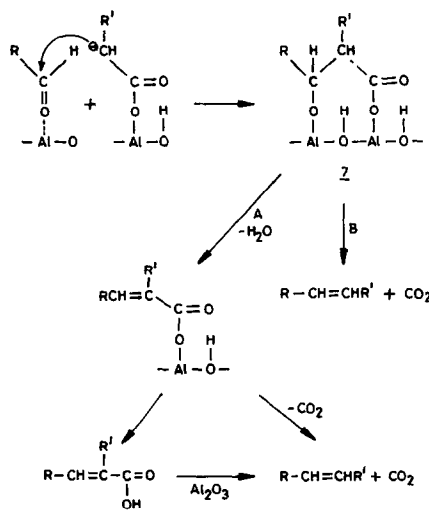


SCHEME II

Evidence for such an equilibration was obtained when it was shown that propanoic acid when passed over deuterated alumina at 400°C underwent extensive deuterium incorporation at the α -position. The 3-pentanone formed as a product in this reaction also had deuterium in the α -position. The intermediate 5 or 6 could react with a neighboring adsorbed carbonyl compound (for convenience only the reaction of 5 is shown) to form 7, which can react in two ways, A and B.

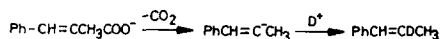
The occurrence of route A was demonstrated by the fact that in the reaction between benzaldehyde and acetic acid cinnamic acid was isolated in low yield. When cinnamic acid alone was passed over alumina, styrene was formed but only to the extent of 15%. This led to the conclusion that (i) part of the styrene formed in the benzaldehyde–acetic acid reaction arose through this route (ii) but this is not the major source of styrene since the amount of styrene formed is much more than could be obtained directly from cinnamic acid under the experimental conditions.

Route B, a direct decarboxylative elimination, should be quite facile, but there is no direct experimental evidence in the



present study for or against this mechanism.

To strengthen these mechanistic points, the reaction of deuterated propanoic acid [$\text{CH}_3\text{CH}_2\text{COOD}$] with benzaldehyde was carried out over deuterated alumina. The mass and NMR spectra of 1-phenylprop-1-enes formed in this reaction, showed $d_1 : d_0$ ratio of only 1 : 4 and that the d_1 species had the structure $\text{PhCH} = \text{CDCH}_3$. In this reaction if 1-phenylprop-1-enes were formed only through decarboxylative alkyl transfer, there might be partial deuterium incorporation (namely, less than one deuterium atom per molecule of olefin) due to partial H-D exchange at the α -carbon of propanoic acid, prior to the decarboxylative alkyl transfer. On the other hand, if they were formed through Scheme II route A, there should be one deuterium atom per molecule of olefin, due to the reaction:



Thus the present result suggests that 1-phenylprop-1-enes were formed mainly through Scheme I and only in part through Scheme II.

The present study definitely establishes that both the alkyl anion transfer and Perkin-type condensation of carboxylic acids with carbonyl compounds take place over alumina, the former route probably to a larger extent than the latter. By analogy it is to be surmised that ketonization of carboxylic acid takes place by more than one mechanism, namely, by alkyl anion transfer and through the β -keto acid intermediate.

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