

Studies on the Ketonization of Acetic Acid on Chromia I. The Adsorbate-Catalyst Interaction

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The ketonization of acetic acid has been studied on a chromia catalyst at 460°C and at a contact time of 0.7 sec at various partial pressures in presence of tertiary butyl alcohol and benzyl alcohol. There is no inhibition of the ketonization of acetic acid in presence of tertiary butyl alcohol which undergoes only dehydration giving isobutylene and water. Benzyl alcohol, which undergoes only dehydrogenation to give benzaldehyde and hydrogen, suppresses the ketonization of acetic acid. Comparative studies of the reaction of isopropyl alcohol in mixture with acetic acid and also with propionic acid, under identical conditions, confirm the conclusion that the ketonization is caused by the same activity of the catalyst that is responsible for dehydration and dehydrogenation. It is suggested that the ketonization occurs through the interaction of two acetic acid molecules adsorbed on the surface of chromia, one of them utilizing the dehydrogenation activity for adsorption and the other utilizing the dehydration activity.

INTRODUCTION

Earlier work (1, 2) has shown that acetic acid decomposes on chromia at 460°C to give acetone, water, and carbon dioxide and it has been suggested that acetic acid utilizes only the primary activities of chromia, viz., dehydration and dehydrogenation for ketonization purposes. Further studies have been conducted to determine the exact type of activity that promotes ketonization and to establish the mechanism of ketonization of acetic acid on chromia. The present paper deals with the results obtained in these studies.

METHODS

A flow type reaction unit as described in an earlier paper (1) was used in the present studies. The catalyst used was the same as the one used in the earlier studies. It was prepared by precipitating chromium hydroxide from an approximately normal ammonium hydroxide solution. The pre-

cipitate was washed free of nitrate ions, dried at 110°C in an air oven, ground to a fine powder of less than 240-mesh size and then pressed into pellets using about 2% stearic acid as a binding material. The pellets were heated to 500°C at first in a current of carbon dioxide-free dry air for 6 hr and then in hydrogen for 8 hr. About 2.5 ml of the catalyst weighing 1.5 g was used for the runs and after every run the catalyst was regenerated by heating to 500°C, first in carbon dioxide-free dry air for 4 hr and then in dry hydrogen for 6 hr.

Analar *tert*-butyl alcohol (BDH) was dried with sodium pellets and further purified by fractional distillation. The sample collected in the range of 80–81°C was used in the present study. Benzyl alcohol was fractionally distilled and the sample distilling at 205°C was used. Cyclohexane was also purified by fractional distillation. The acetic acid was purified by crystallization. All the reactants used were chromatographically analyzed to determine their purity.

All the experiments were carried out at

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460°C keeping the contact time constant at 0.7 sec except for energy of activation determinations. The liquid products collected in the trap, kept cool by ice, were analyzed by the vapor phase chromatographic method using a halcomid column at 70°C. Calibration factors were determined employing pure compounds, for the quantitative estimation. The gaseous products collected in a gas burette after passing through the cold trap were analyzed using a dimethyl sulfolan column at 30°C and sometimes by the Orsat method. Cyclohexene had a very short retention time and so it was estimated by a modification of the bromination method due to Kauffmann (3) employing a bromine-bromide mixture.

RESULTS

Experiments were carried out using mixtures of benzyl alcohol and isopropyl alcohol, as well as mixtures of isopropyl alcohol and nitrogen, and benzyl alcohol and nitrogen. The results of these runs are presented in Figs. 1 and 2. They show that benzyl alcohol and isopropyl alcohol suppress each other's dehydrogenation. Benzyl alcohol does not get dehydrated and it affects the dehydration of isopropyl alcohol only slightly. The results obtained for runs using mixtures of *tertiary* butyl alcohol and isopropyl alcohol and *tertiary* butyl alcohol and nitrogen are presented in Figs. 3 and 4. There is mutual suppression of

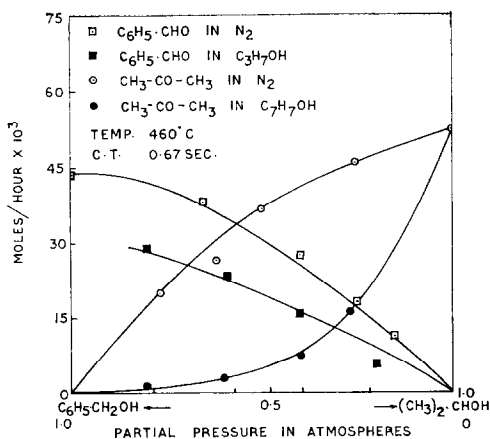


FIG. 1. Effect of benzyl alcohol and isopropyl alcohol on the dehydrogenation of each other.

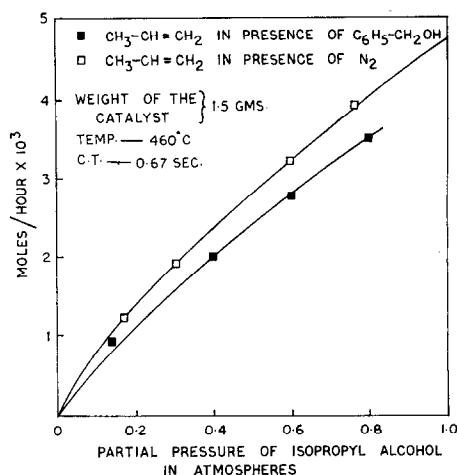


FIG. 2. Effect of benzyl alcohol on the dehydration of isopropyl alcohol.

dehydration and *tertiary* butyl alcohol which does not undergo dehydrogenation affects the dehydrogenation of isopropyl alcohol only slightly.

The results for the ketonization of acetic acid and the reactions of the alcohols for runs with mixtures of acetic acid and benzyl alcohol, acetic acid and *tertiary* butyl alcohol, and acetic acid and nitrogen in various proportions are presented in Figs. 5, 6, and 7. It is seen that in the presence of benzyl alcohol, the ketonization of acetic acid falls sharply as the partial pressure of the acid is decreased

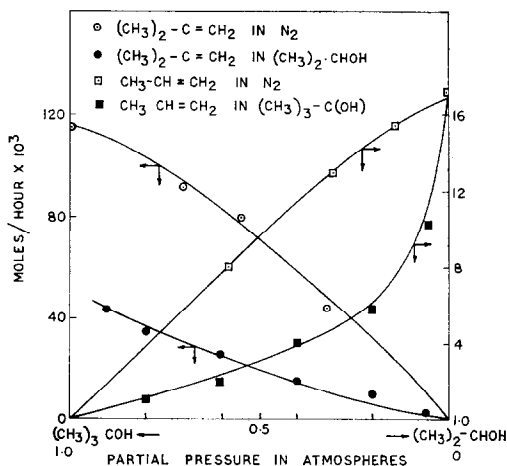


FIG. 3. Effect of *tertiary* butyl alcohol and isopropyl alcohol on the dehydration of each other.

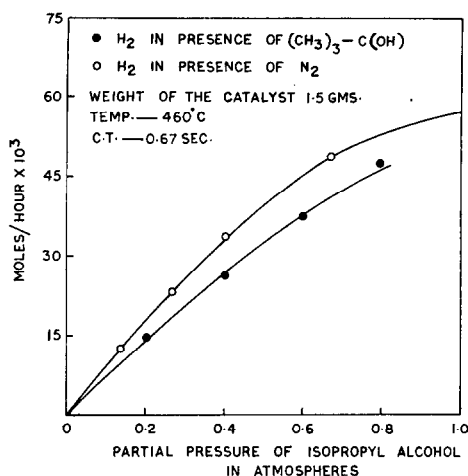


FIG. 4. Effect of *tertiary* butyl alcohol on the dehydrogenation of isopropyl alcohol.

from 1 atm. The dehydrogenation of benzyl alcohol is greatly suppressed by acetic acid at all partial pressures (Fig. 6). The ketonization of acetic acid proceeds in an almost uninhibited fashion in the presence of *tertiary* butyl alcohol, the dehydration of which is greatly affected by the acetic acid (Fig. 7).

Results obtained in the runs carried out with propionic acid in mixture with nitrogen or isopropanol are presented in Figs. 8, 9, and 10. The results for acetic acid are also given in the same figures for comparison. The results obtained in the few runs

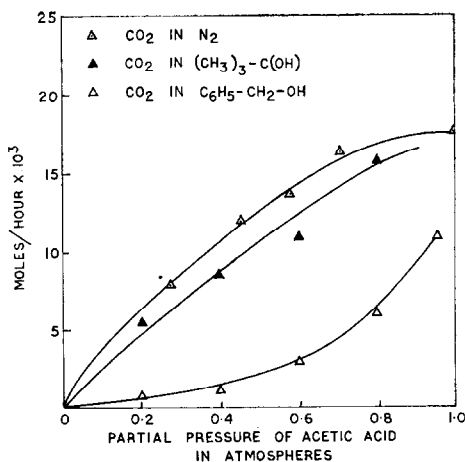


FIG. 5. Effect of *tertiary* butyl alcohol and benzyl alcohol on the ketonization of acetic acid.

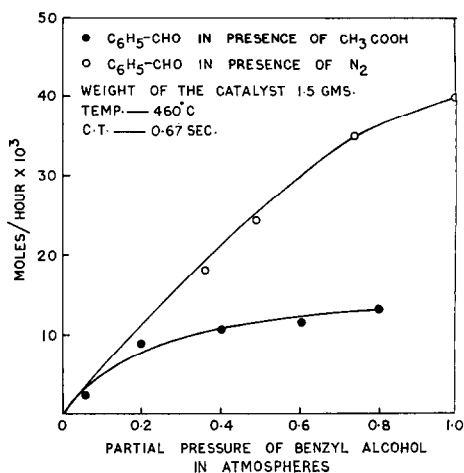


FIG. 6. Effect of acetic acid on the dehydrogenation of benzyl alcohol.

carried out with mixtures of acetic acid and cyclohexane and cyclohexane and nitrogen are presented in Fig. 11. The chromatographic analysis showed no indication of any ester formed in the runs using mixtures of acids and alcohols.

DISCUSSION

In the earlier studies (1), it was reported that acetic acid suppressed both the dehydration and dehydrogenation of alcohol, whether it was cyclohexanol or isopropyl alcohol. However, it was found that the ketonization of acetic acid fell sharply

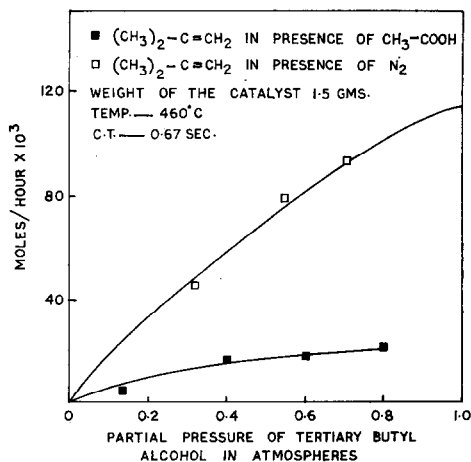


FIG. 7. Effect of acetic acid on the dehydration of *tertiary* butyl alcohol.

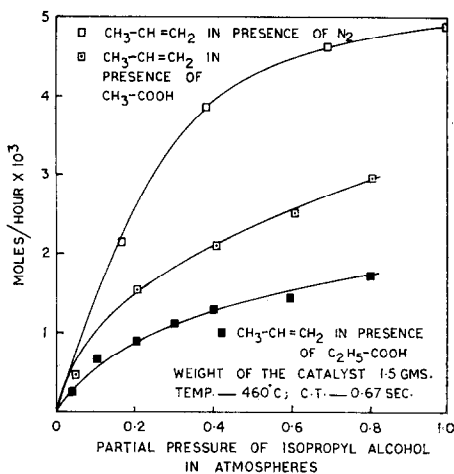


FIG. 8. Effect of (1) acetic acid and (2) propionic acid on the dehydration of isopropyl alcohol.

even at high partial pressures of the acid as the partial pressure of the acid was decreased from 1 atm. Hence, it was argued that the amount of acetic acid in the gas phase is not an important factor in determining the rate of ketonization of acetic acid. The acetic acid should get adsorbed utilizing the dehydration and dehydrogenation activities. Even if the acetic acid utilizes only one kind of activity, the two adsorbed species will have to be in sufficiently close proximity to lead to a reaction.

In order to find the exact nature of

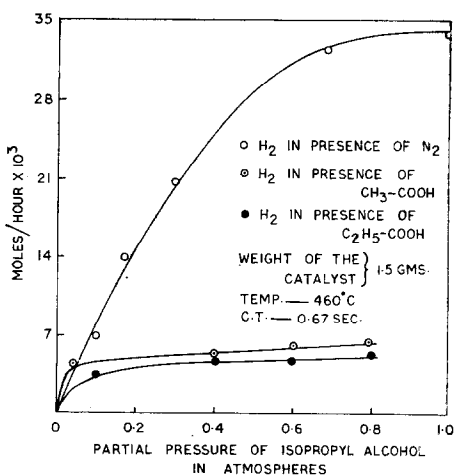


FIG. 9. Effect of acetic acid and propionic acid on the dehydrogenation of isopropyl alcohol.

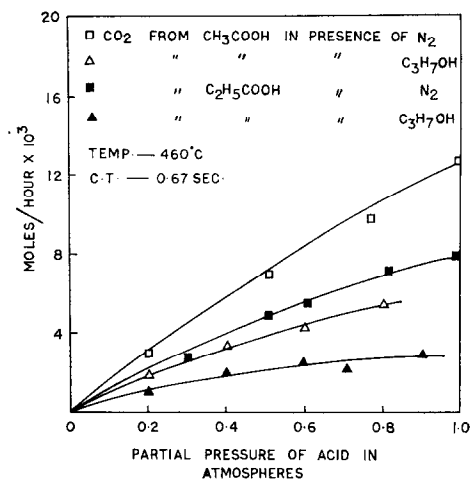


FIG. 10. Effect of isopropyl alcohol and nitrogen on the ketonization of (1) acetic acid and (2) propionic acid.

activity responsible for ketonization of acetic acid, it was thought desirable to carry out reactions with mixtures of acetic acid and an alcohol which utilized only one kind of activity for its adsorption, either dehydration or dehydrogenation. Such an alcohol would compete for only the type of activity it needs for its reaction, leaving the other free for acetic acid adsorption. If this "other" activity is the one that promotes ketonization, acetic acid could undergo uninhibited ketonization in presence of such an alcohol. In this

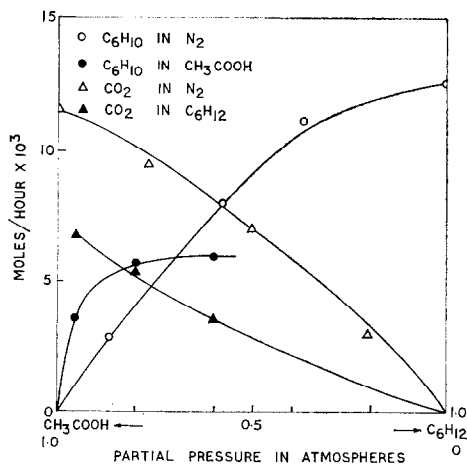


FIG. 11. Effect of cyclohexane and acetic acid on the reaction of each other.

manner one can make available to the acid, any one type of activity. For this purpose, *tertiary* butyl alcohol and benzyl alcohol were chosen for this study. It was found that the former underwent only dehydration giving isobutylene and water, and the latter only dehydrogenation giving benzaldehyde and hydrogen. Preliminary studies were made using mixtures of benzyl alcohol and isopropyl alcohol and also mixtures of *tertiary* butyl alcohol and isopropyl alcohol. These studies were conducted in order to make sure that benzyl alcohol affected only the dehydrogenation of isopropyl alcohol and so utilized only the dehydrogenation activity and not the dehydration activity; similarly, *tertiary* butyl alcohol affected only the dehydration activity and not the dehydrogenation activity. The results presented in Figs. 1-4 confirm that *tertiary* butyl alcohol competes only for the dehydration activity and benzyl alcohol only for the dehydrogenation activity.

The results for runs with mixtures of acetic acid and benzyl alcohol show that the type of activity needed for ketonization is competed for by benzyl alcohol. Since the suppression of dehydrogenation by acetic acid is a common feature in all the cases of alcohols which undergo dehydrogenation, it is quite likely that the dehydrogenation activity may be partially or wholly responsible for the ketonization. The results of the studies with *tertiary* butyl alcohol and acetic acid lend further support to the suggestion that the dehydrogenation function of chromia may be important for the ketonization of acetic acid. The dehydrogenation activity which is relatively free in the presence of *tertiary* butyl alcohol may be responsible for the uninhibited ketonization of acetic acid in its presence. This, however, does not mean that the dehydration activity is not necessary for the ketonization, as it is found that acetic acid at all partial pressures affects the dehydration of *tertiary* butyl alcohol or any alcohol that undergoes dehydration.

In order to obtain a more definite knowledge about the importance of dehydration

activity, it was thought useful to carry out studies with mixtures of isopropyl alcohol and propionic acid and compare the results with those obtained from studies on mixtures of isopropyl alcohol and acetic acid under similar conditions. These studies were made in order to discover to what extent propionic acid, a less acidic compound than acetic acid, affects the dehydration and dehydrogenation of isopropyl alcohol and also to find out whether it is possible to relate the velocities of ketonization of the two acids with the extents of suppression of dehydration and dehydrogenation of isopropyl alcohol. To determine the extent of suppression in each case, it was essential to know the activity of the catalyst for the two reactions in the presence of an inert diluent. For this reason partial pressure studies were carried out for the reaction of isopropyl alcohol in presence of nitrogen. Only the results obtained at intermediate partial pressures, i.e., between 0.2 and 0.8 atms where no saturation of the surface by any one compound alone took place, are compared.

A quantitative expression which relates the velocity of ketonization to both dehydration and dehydrogenation activities that are used by the acid can be worked out as follows.

The velocity of ketonization may be represented as:

$$V = k\theta_x\theta_y,$$

where k is the rate constant and θ_x and θ_y are the fractions of the dehydration and dehydrogenation activities that are used by the acid. As already stated, θ_x and θ_y are directly related to the extent of suppression of the corresponding reactions of isopropyl alcohol by the acid. If the subscripts A and P represent acetic acid and propionic acid, respectively, the ratio of the velocity of ketonization of acetic acid to that of propionic acid on the same catalyst can be represented as:

$$\frac{V_A}{V_P} = \frac{k_A(\theta_A)_y(\theta_A)_x}{k_P(\theta_P)_y(\theta_P)_x} = R$$

$$R = K \left(\frac{\theta_A}{\theta_P} \right)_y \left(\frac{\theta_A}{\theta_P} \right)_x,$$

TABLE I
THE VELOCITIES OF KETONIZATION OF ACETIC ACID AND PROPIONIC ACID AND THEIR RELATIONSHIP TO THE EXTENT TO WHICH THEY SUPPRESS THE DEHYDRATION AND DEHYDROGENATION OF ISOPROPANOL^a

Partial pressure of alcohol (atm.)	N-Nitrogen			A-Acetic acid			P-Propionic acid									
	Dehydrogenation deH ₂ moles/hr × 10 ³			Dehydration deH ₂ O moles/hr × 10 ³			Velocity of ketonization moles/hr 10 ³									
	N	A	P	N	A	P	N	A	P							
0.2	14.94	4.90	4.20	10.40	10.74	0.93	2.60	1.43	0.90	1.17	1.70	0.68	5.33	2.53	2.11	0.64
0.4	25.20	5.86	4.67	19.34	20.50	0.94	3.93	2.07	1.33	1.86	2.60	0.72	4.53	2.26	2.00	0.67
0.6	31.27	6.06	4.90	25.20	26.30	0.96	4.50	2.57	1.57	1.93	2.93	0.65	3.33	1.74	1.91	0.62
0.8	33.84	6.30	5.13	27.50	29.70	0.96	4.75	2.95	1.75	1.80	3.00	0.60	1.87	0.93	2.00	0.57

^a Temp. 460°C; Contact time = 0.68 sec.

$$\frac{V_A}{V_P} = V \left(\frac{S_A}{S_P} \right)_{\text{deH}_2} \times \left(\frac{S_A}{S_P} \right)_{\text{deH}_2\text{O}} = S K = V/S$$

where $K = k_A/k_P =$ a constant at a particular temperature. But θ_A and θ_P for the two reactions are proportional to the extents of suppression of the corresponding reactions of isopropyl alcohol by the two acids, S_A and S_P . Hence,

$$R = K \left(\frac{S_A}{S_P} \right)_y \left(\frac{S_A}{S_P} \right)_x = KS.$$

The data given in Table 1 have been computed from the results presented in Figs. 8 and 9. They show that the ratio of the velocities of ketonization of the two acids, R , is linear with S . Thus, the results of the comparative studies with isopropyl alcohol mixed with acetic acid or propionic acid support the idea that for ketonization to occur, acid molecules have to make use of both the dehydration and dehydrogenation activities, although the relative importance of the latter may be greater as revealed by the fact that the ketonization of the acid is greatly inhibited in the presence of alcohols that undergo dehydrogenation.

Studies with mixtures of cyclohexane and acetic acid were taken up in order to seek further confirmation regarding the utilization of the dehydrogenation activity for acid ketonization. In the initial runs, cyclohexane when passed over the catalyst used in our studies did not show any sign of reaction, but after two or three check runs alternately with acetic acid and cyclohexane, the latter showed a tendency to react even though only slightly. The products were cyclohexene and hydrogen. This indicated that it underwent only dehydrogenation.

The results in Fig. 11 show that the ketonization of acetic acid is considerably suppressed by the presence of cyclohexane. If it is assumed that a part of the dehydrogenation activity is semipermanently used by the acid, this can account for the suppression of the dehydrogenation of cyclohexane observed even at higher partial pressures of cyclohexane. The remaining dehydrogenation activity can be competitively utilized by both cyclohexane and acetic acid. Increased coverage of this re-

maining dehydrogenation activity by acetic acid as its partial pressure is increased can lead to increased ketonization which, however, still remains lower than the normal value obtained with nitrogen as the diluent due to the competition from cyclohexane. These results therefore support the suggestion regarding the importance of dehydrogenation activity for ketonization. The ketonization involves the interaction of two adsorbed acetic acid molecules, one utilizing the dehydrogenation activity and the other utilizing dehydration activity. The formation of the adsorbed species utilizing the dehydrogenation activity appears to control the reaction.

CONCLUSION

The results obtained in the present studies furnish further confirmation regarding the suggestion made in the earlier paper (1) that acetic acid utilizes only the primary activities of chromia, viz., dehydration and dehydrogenation, and no other kind of activity, for ketonization. The two molecules of acetic acid needed for the ketonization must be adsorbed on the surface of the catalyst. The two molecules that give rise to the ketone are adsorbed in different manners, one utilizing the dehydrogenation activity and the other, dehydration activity. The species adsorbed on the dehydrogenation centers appear to control the reaction.

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