JOURNAL OF CATALYSIS 16, 357–362 (1970)

Studies on the Ketonization of Acetic Acid on Chromia

II. The Surface Reaction

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Received July 10, 1969

The conversion of acetic acid to acetone on chromia and the decomposition of chromium acetate to give acetone were studied at various temperatures. Based on a comparison of the energies of activation and the previously established fact that both the dehydration and dehydrogenation activity of chromia are required for the ketonization reaction, a mechanism for the surface reaction of acetic acid on chromia is suggested and discussed. The observed break in the Arrhenius plot for the reaction of acetic acid on chromia is attributed to the ability of chromia to change its electronic character with change in temperature.

INTRODUCTION

The results discussed in the previous paper (*1*) indicated that the ketonization of acetic acid on chromia involves the interaction between two acetic acid molecules adsorbed on the surface of chromia, one of them being adsorbed utilizing the dehydration activity and the other utilizing the dehydrogenation activity. It was further suggested that of the two, the adsorption that involves the dehydrogenation activity controls the reaction. The activation energies for the ketonization of acetic acid on chromia and for the thermal decomposition of chromium acetate which may be a likely intermediate in the ketonization of acetic acid on chromia have been determined. On the basis of these results a mechanism for the surface reaction is proposed and discussed.

METHODS

The experimental setup used and the preparation of the catalyst have been described previously (*1*). Studies on the decomposition of acetic acid on chromia using nitrogen as a diluent, discussed in an earlier paper (*2*), showed that the rate tended to attain a constant value as the partial pressure of the acid was increased to 1 atm. These results indicated that the surface of the catalyst gets completely covered with acid molecules at atmospheric pressure. Therefore, for the purpose of determining the activation energy for the ketonization of acetic acid on chromia, experiments were carried out with pure acetic acid at atmospheric pressure to ensure complete coverage. At a given temperature, studies were performed at various contact times. The initial rates were estimated at various temperatures in the region of 360–480°C from a plot of percentage of acid converted versus contact time in seconds (Fig. 1).

For the thermal decomposition of chromium acetate, a specially designed reactor, one end of which was closed, was used. The temperature could be measured with a thermocouple inserted into the thermocouple well provided in the reactor. Chromium acetate was prepared by extracting chromia with acetic acid at 60°C and filtering the clear green liquid which was then evaporated in a vacuum to drive out any acetic acid present. The residue left behind was chromium acetate. The purity

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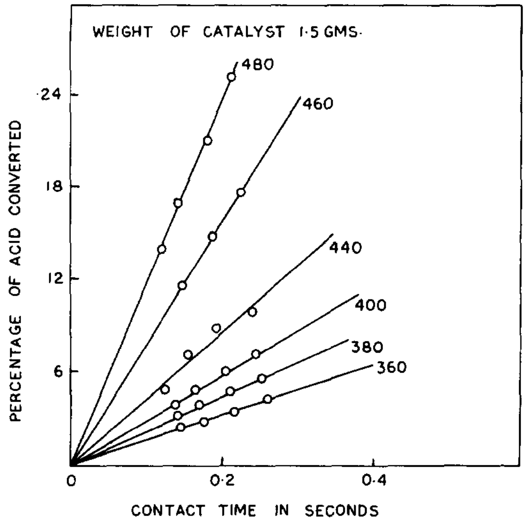


FIG. 1. Effect of variation of contact time on the ketonization of acetic acid.

of the sample was tested by estimating the chromium content in it. The sample was treated with sodium peroxide and converted into sodium chromate. The solution was then boiled to decompose the excess peroxide completely. The resulting solution was acidified and made up to a known volume and its strength was estimated by titration with a standard solution of thiosulfate. The sample thus estimated was 99% pure chromium acetate.

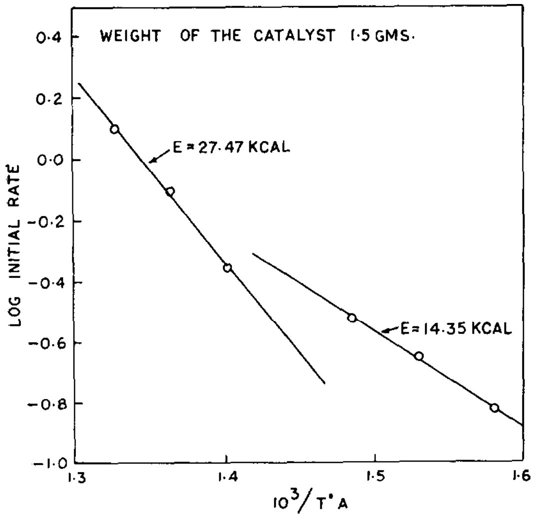


FIG. 2. Arrhenius plot for the ketonization of acetic acid.

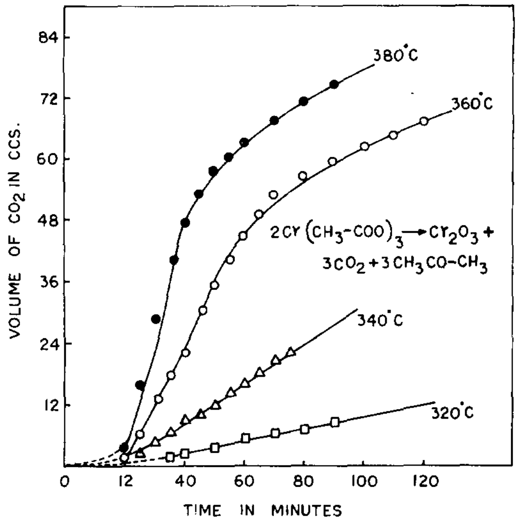


FIG. 3. Thermal decomposition of chromium acetate.

The results for the thermal decomposition of chromium acetate are represented in Fig. 3 which shows the volume of carbon dioxide, in milliliters, evolved plotted against time, in minutes, for various temperatures between 320 and 380°C. There is an initial period of induction at every temperature which decreases slightly with increase of temperature. The induction period is followed by a steep rise in the volume of carbon dioxide evolved. The slope, measured in milliliters of carbon dioxide evolved per unit time at the initial portion of the steep rise, is taken as the initial rate for that temperature. This is converted into moles of carbon dioxide per unit time for the Arrhenius plot to calculate the energy of activation (Fig. 4).

RESULTS

The Arrhenius plot for the ketonization of acetic acid on chromia at various temperatures in the region of 360–480° (Fig. 2) gives, instead of a single line, two lines with two different slopes. The change in the slope seems to occur in the region of 400–440°C. The activation energy for the ketonization of acetic acid in the region of 360–400°C has a value of 14.35 kcal/mole whereas it has a value of 27.47 kcal/mole in the region of 440–480°C. These values correspond to the energy of activ-

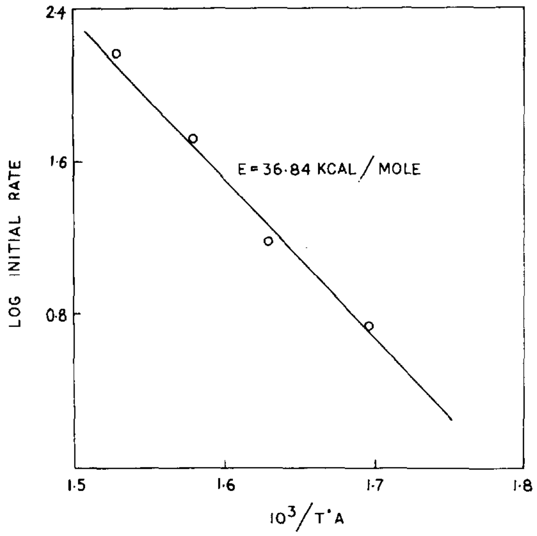


FIG. 4. Arrhenius plot for the decomposition of chromium acetate.

ation needed for the decomposition of one molecule of acetic acid. Since two molecules of acetic acid decompose according to the equation,

$$2CH_3\cdot COOH = H_2O + CO_2 + CH_3\cdot CO\cdot CH_3,$$

to give one molecule of acetone, the activation energy values obtained on the basis of the acid reacted, are multiplied by 2, to get the energy of activation needed for the formation of one molecule of acetone. Thus $2 \times 14.35 = 28.70$ kcal/mole of acetone is required in the region of 360–440°C and 54.94 kcal/mole of acetone in the region of 440–480°C.

The Arrhenius plot for the thermal decomposition of chromium acetate in the temperature range 320–380°C gives a value of 36.83 kcal/mole for the activation energy for the formation of acetone.

DISCUSSION

The fact that there is a break in the Arrhenius plot for the ketonization of acetic acid on chromia in the region of 400°C, resulting in the formation of two lines with two different slopes instead of a single line, indicates that the rate determining step in the mechanism of ketonization may be different in the two temperature regions. Since chromia is known to change its electronic character around 400°C (*3–6*), the change in the electronic nature of the catalyst may be responsible for the change in the rate-determining step.

It has been shown that in a number of cases, the ketone formation on oxides and carbonates is accompanied by side reactions, leading to the formation of compounds like methane, ketene, etc. (*7*). But the extent of these reactions depends on the temperature and nature of the catalyst employed, since the energy of activation needed for these reactions to occur is very great, of the order of 70 kcal/mole. Hence, according to Rubinshtein and Yakerson (*8*), for a good ketonization catalyst, the value of the activation energy must not exceed 60 kcals/mole. On the basis of this criterion the present studies show that chromia is a good ketonization catalyst.

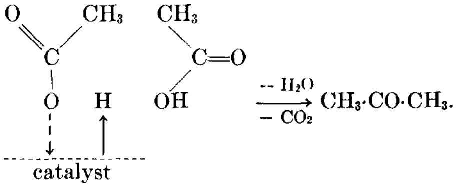
The mechanism of ketonization of acetic acid on a number of oxides and carbonates has been shown to involve the formation of an acetate intermediate (*8–14*). In all these cases, the fact that the activation energies for the ketonization of acetic acid on these catalysts and the decomposition of the acetate are the same, has been used as an evidence for the formation of the acetate intermediate. According to Yakerson (*15*), if the ketonization of the acid proceeds through the formation of the acetate intermediate, the crystalline lattice of the oxide or the carbonate as the case may be, is first destroyed and the lattice of the acetate is formed. The acetate lattice then gets destroyed with the formation of acetone and the re-formation of a new lattice of the original oxide or carbonate. Thermodynamic calculations on the ketonization of acetic acid on the carbonates and oxides of calcium, barium, and strontium show that this process is not only possible, but also advantageous as the lattice energies of these compounds are of the order of only 600 kcals/mole (*16*). The ketonization of acetic acid on catalysts of this type is termed by Yakerson as a "volume reaction" as it involves the whole lattice of the oxide or the carbonate. However, the same group of workers showed that the ketonization of acetic acid on the oxides of quadrivalent metals like zirconium, titanium, etc. occur without the formation of the salt intermediate. This is probably due to the fact that the lattice energies of these oxides are of the order of 3600 kcal/mole and, hence, too high to permit any alteration of the lattice. Accordingly, the ketonization of acids on these compounds has been termed as a "surface reaction."

To try the applicability of these conclusions to the ketonization of acetic acid on chromia, the thermal decomposition of chromium acetate was studied. Our studies show that the activation energy for the formation of acetone from chromium acetate (36.83 kcal) is different from the values obtained for the ketonization of acetic acid on chromia. Hence, it is reasonable to assume that the decomposition of acetic acid on chromia and decomposition of chromium acetate do not involve the same intermediate. Chromia probably behaves like zirconia, titania, and ceria in promoting the ketonization of acetic acid without involving the formation of the acetate as an intermediate. This view is supported by the fact that the lattice energy of chromia is very high, of the order of 4600 kcal/mole (*16*) so that any destruction of the oxide lattice, with the formation of the acetate lattice followed by the subsequent reformation of the new lattice of the original oxide would be energetically difficult. Hence, the ketonization of acetic acid on chromia may be considered to be a "surface reaction."

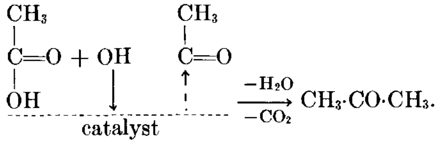
Probable Mechanism of Ketonization of Acetic Acid on Chromia

There can be only three species that can interact among themselves, leading to the ketonization of acetic acid. They are the acetate ion CH_3-COO^-, the acylcarbonium ion, CH_3-CO^+, and the gas-phase acid molecule. Of these, the first mentioned species can be assumed to be formed by the adsorption of the acetic acid, in a manner similar to the adsorption of an alcohol as RO^- and H^+, the species involved in the dehydrogenation mechanism as suggested by Volkenstein (*17*). The acylcarbonium ion CH_3-CO^+ can be considered to be formed during the adsorption of acetic acid, in a manner similar to the adsorption of alcohol as R^+ and OH^-, the species involved in the dehydration reaction. In other words, acetic acid interacts with both dehydration and dehydrogenation activities of chromia during chemisorption. The following five modes of interaction leading to ketonization of acetic acid may be considered.

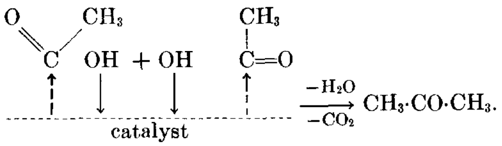
I. The interaction between a gas-phase molecule and an adsorbed acetate ion.



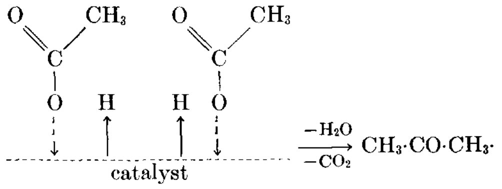
II. The interaction between a gas-phase acid molecule and an adsorbed acylcarbonium ion.



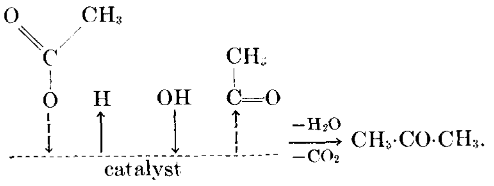
III. The interaction between two adsorbed acylcarbonium ions.



IV. The interaction between two adsorbed acetate ions.



V. The interaction between an acetate ion and an acylcarbonium ion.



Of the five modes, the first two involve the interaction between a gas-phase molecule and an adsorbed species. Experiments with mixtures of acetic acid and isopropyl alcohol, cyclohexanol, benzyl alcohol and cyclohexane show that even the presence of a very small amount of alcohol is able to considerably suppress the ketonization of acetic acid. This shows that the surface concentration of acetic acid is an important factor in the rate of ketonization of acetic acid. Hence this type of mechanism is unlikely to be operative.

The three modes III–V involve the interaction between two adsorbed species. Mechanism (III) involves the interaction between two adsorbed acylcarbonium ions. This means that acetic acid must utilize the dehydration activity alone for ketonization purposes, which is quite unlikely in the light of evidences obtained in support of the importance of dehydrogenation activity for ketonization (*1*). One has, therefore, to choose between (IV) which involves the interaction between two adsorbed acetate ions and (V), which involves an adsorbed acetate ion and an adsorbed acyl carbonium ion. Mechanism (IV) would be similar to the decomposition of an acetate and from the evidences presented earlier, this may be ruled out. Comparative studies on the reaction of isopropyl alcohol in presence of acetic acid and propionic acid reported in the previous paper (*1*), suggest that utilization of both dehydration and dehydrogenation activities are important for ketonization of the acid. The results obtained from studies on mixtures of acetic acid and cyclohexane which competes for the dehydrogenation activity alone show that the ketonization of acetic acid, although suppressed by the presence of cyclohexane does not fall to the same extent as it does in presence of alcohols like isopropyl alcohol and cyclohexanol which compete for both dehydration and dehydrogenation activities. These results indicate that the acylcarbonium ion formed by the interaction of acetic acid with the dehydration activity is also important for the formation of acetone. The relative importance of the dehydrogenation activity for the ketonization of acetic acid may be greater as seen from the results obtained in the studies of acetic acid and benzyl alcohol. These studies with mixtures show that the ketonization activity is greatly inhibited in presence of benzyl alcohol which competes for the dehydrogenation activity alone. All these evidences suggest that the scheme (V) involving the interaction between an adsorbed acetate ion and an adsorbed acylcarbonium ion is the most likely mechanism for the ketonization of acetic acid on chromia.

As stated above, the break in the Arrhenius plot for the ketonization of acetic acid on chromia could be attributed to a change in the rate-determining step in the ketonization mechanism, consequent on chromia's ability to change its electronic nature from predominantly *p* type to *n* type in the region of 400°C. In other words, the cause for the break in the Arrhenius plot for the ketonization of acetic acid could be the same as that reported for the dehydrogenation of isopropyl alcohol in the same regions of temperature (*18*, *19*). This agrees with the suggestion that utilization of dehydrogenation activity is important for acid ketonization purposes.

The mechanism of ketonization of acetic acid on chromia can be envisaged as follows:

The adsorption of two acetic acid molecules, one as CH_3COO^- and H^+ and the other as CH_3CO^+ and OH^- followed by the surface reaction between CH_3COO^- and CH_3CO^+ leading to the formation of acetone, water, and carbon dioxide. In the adsorbed acetate ion an electron shift from the oxygen through which the acetate ion is adsorbed on the surface towards the carbon atom will facilitate the departure of the methyl group from this ion as a carbanion leaving behind adsorbed carbon dioxide. As is usual in reactions involving molecules containing a carbonyl group, a nucleophilic attack by the carbanion at the acyl carbon of the CH_3CO^+ will lead to the formation of acetone. The adsorbed hydrogen and hydroxyl can combine to form water.

The formation of CH_3COO^- is favored

by an electron-rich surface (*n* type) which facilitates the adsorption of the acid as CH_3COO^- and H^+. The formation of CH_3CO^+ is favored by the *p* character of the catalyst, which facilitates the removal of electrons from acetic acid during adsorption to form CH_3CO^+ and OH^-. The surface reaction does not depend very much on the electronic character of the catalyst.

Accordingly, depending upon the electronic character of the catalyst, CH_3COO^- formation or CH_3CO^+ formation may be rate-determining in the mechanism of ketonization of acetic acid. It is likely that below 400°C, CH_3COO^- formation is rate-determining because the catalyst is mainly *p* type under these conditions and does not favor the adsorption of acetic acid as $CH_3 \cdot COO^-$ and H^+. Above 400°C, CH_3CO^+ formation can be the slowest because it does not occur easily on an electron-rich surface.

CONCLUSION

The present results show that the ketonization of acetic acid on chromia is a surface reaction involving the interaction between an adsorbed acetate ion and an adsorbed acylcarbonium ion. The formation of these species depend upon the utilization of both dehydration and dehydrogenation activities of chromia. The fact that the activation energies for the ketonization of acetic acid and the thermal decomposition of chromium acetate are not the same, shows that these two processes do not involve the same intermediate. The break in the Arrhenius plot observed in the region of 400°C is probably due to a change in the rate-determining step, consequent on the ability of chromia to change its electronic character in this temperature range.

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