

Studies on the Surface Interaction of Acetic Acid on Iron Oxide

J. C. KURIACOSE AND S. S. JEWUR

Department of Chemistry, Indian Institute of Technology, Madras 600036, India

Received July 7, 1976; revised July 19, 1977

Acetic acid undergoes ketonization on iron oxide. The activation energy of the reaction depends on the region of temperature in which the reaction is carried out, indicating the dependence of the mechanism of the reaction on temperature. The nature of the primary activities of the catalyst effective in the ketonization, as well as the mechanistic model for ketonization, have been deduced from the study of the reaction in the presence of alcohols using the technique of competitive reactions. Below 400°C, the ketonization reaction is a surface phenomenon involving the interaction of two adsorbed molecules of acetic acid, one of them forming ketene as an intermediate. At higher temperatures, the reaction takes place through the formation of a salt.

INTRODUCTION

The ketonization of aliphatic acids has been considered to proceed through the intermediacy of acid anhydrides (1) or β -keto acids (2). Decarboxylative cyclization of dicarboxylic acids can be conveniently explained by the former mechanism and the decarboxylations of carboxylic acids having an α -hydrogen atom, by the latter. However, these mechanisms are inadequate to explain the formation of benzophenone from benzoic acid (3). A concerted mechanism (4) therefore has been suggested for the ketonization of benzoic acid. It has been observed that when vapors of acetic acid are passed over several metal oxides, metal salts are formed which subsequently decompose to give acetone (5-7). Yakerson *et al.* (8) concluded from their studies on the ketonization of acetic acid on oxides that the reaction takes place through the intermediacy of the salt, only when the lattice energy of the oxide is low (<2500 kcal mole⁻¹). When the lattice energy of

the oxide is high some other surface species is responsible for the reaction (9).

While there is much information available on the study of the reactions of alcohols on semiconductor oxides, relatively little is known about the ketonization reaction of acids on oxides. The present investigation has been undertaken with a view to understand the nature of the primary catalytic activities of iron oxide and to elucidate the mechanism of the ketonization reaction.

EXPERIMENTAL

Acetic acid (BDH, LR) used in this investigation was purified by distillation according to the method suggested by Orton and Bradfield (10), and its purity was checked by the freezing point. Tertiary butanol (BDH, LR) was dried and distilled over pure sodium metal. Methanol (BDH, AR), isopropanol (BDH, AR), deuterated acetic acid (E. Merck, spectroscopically pure), and heavy water (isotopic purity: 99.4%, Bhabha Atomic Research Centre,

Trombay) were used without further purification. All alcohols used for the study were chromatographically pure.

α -Fe₂O₃ was prepared starting from FeCl₃·6H₂O (SM, LR; purity: 99.3%) by the procedure described by Skarchenko *et. al.* (11). The oxide was heated at 500°C for 5 hr and was crushed into a uniform granular form. After a preliminary study to determine the particle size and the volume that would eliminate the diffusion effects, a volume of 1.25 ml of catalyst with a grain size of 1.4 mm (mesh size 8) was chosen for the experiments. Catalysts containing different proportions of ferrous and ferric iron were prepared by controlled reduction of the ferric oxide by hydrogen at 450°C. The difference in volume of the same weight of the catalyst reduced to different extents was negligible and so a constant weight of 1 g of the catalyst was used for the experiments. Surface areas of the samples were determined by the BET method. A separate sample of catalyst was used for each run because of the difficulty in restoring the original composition by regeneration.

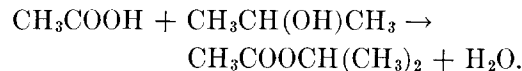
The chemical composition of the reduced catalyst was determined by conventional volumetric procedures (12). Weighed quantities of the samples were dissolved in concentrated hydrochloric acid in the cold. The Fe³⁺ was quantitatively reduced to Fe²⁺ by SnCl₂, excess SnCl₂ was destroyed by HgCl₂, and the total iron which is now in the form of Fe²⁺ was estimated by titration against standard 0.05 N K₂Cr₂O₇ using *N*-phenylanthranilic acid as indicator. The Fe²⁺ was also determined in a sample that was not subjected to reduction by SnCl₂. The difference between the total iron and the ferrous iron permitted the computation of the ferric iron present in the sample. On the basis of this, the Fe₂O₃, Fe₃O₄, and free Fe present in catalysts reduced to various extents was calculated. Ferric acetate was prepared by leaching

ferric oxide with a sufficient amount of glacial acetic acid. Excess acetic acid was removed by evaporation under a dehumidified atmosphere to obtain a rose-colored fine powder which was analyzed as (CH₃COO)₃Fe.

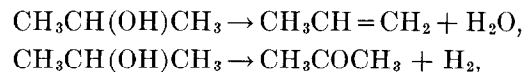
The reactions were studied at a total pressure of 1 atm using a flow reactor (13). Liquid products were analyzed by vapor-phase chromatography making use of a Carbowax column maintained 10–15°C above the boiling point of the highest boiling liquid in the mixture to be analyzed. Hydrogen was used as a carrier gas. With pure acetic acid, the only reaction is the formation of acetone:



The acetic acid reacted was computed from the acetone formed as determined by vapor-phase chromatography and also by direct titration with standard sodium hydroxide. When acetic acid is reacted in mixture with isopropanol, in addition to the ketonization of acetic acid, isopropanol reacts with acetic acid to form an ester:

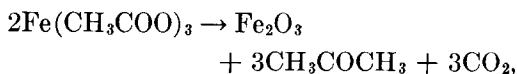


The isopropanol itself reacts to form propylene, water, acetone, and hydrogen. The amount of ester is determined,



by first titrating a known weight of the liquid product with standard sodium hydroxide to determine the unreacted acid, then refluxing a known weight of the product with excess alkali to hydrolyze the ester, and back titrating the excess alkali. From these two titer values the ester formed was calculated. The gaseous products were analyzed for carbon dioxide with potassium hydroxide solution and for olefins with bromine in saturated potassium bromide, using an Orsat apparatus. The

remaining gas was identified as hydrogen. When mixtures of acetic acid and isopropanol were used, the hydrogen formed was equivalent to the acetone formed from isopropanol. Therefore, this was subtracted from the total acetone determined by vapor-phase chromatography to obtain the acetic acid converted to acetone. The polythermal decomposition of ferric acetate was studied by thermogravimetry using 100 mg of the salt with a constant,



heating rate of 6°C/min. The ir absorption of the used catalyst was recorded in the region of 4000–600 cm^{-1} using KBr as a diluent. The acetone obtained in the tracer studies was separated using the method of preparative vapor-phase chromatography and was analyzed by mass spectrometry.

RESULTS

Figure 1 represents the Arrhenius plot for the ketonization of acetic acid on ferric oxide in the temperature range of 330–

450°C. The initial rates are expressed in millimoles of acetic acid reacted per hour. The activation energy of the reaction below 400°C is 33.5 kcal mole^{-1} of acetone, whereas it has a value of 15.7 kcal mole^{-1} above 400°C. Figure 2 represents the Arrhenius plot for the thermal decomposition of ferric acetate making use of the expressions reported by Coats and Redfern (14). These equations are used on the assumption that the order is constant throughout the reaction. The thermal decomposition of the salt was found to follow first-order kinetics, giving rise to an activation energy of 17.6 kcal mole^{-1} of acetone formed. The ir absorption spectrum of the catalyst, used for ketonization for about 15 min at 440°C and then removed from the reaction system, showed absorption at 1590, 1430, 1020, and 657 cm^{-1} , indicating the presence of small amounts of metal-acetate (Fig. 3).

The partial pressure of acetic acid was varied by mixing it with nitrogen, an inert diluent, to study the effect of the partial pressure of acetic acid on the

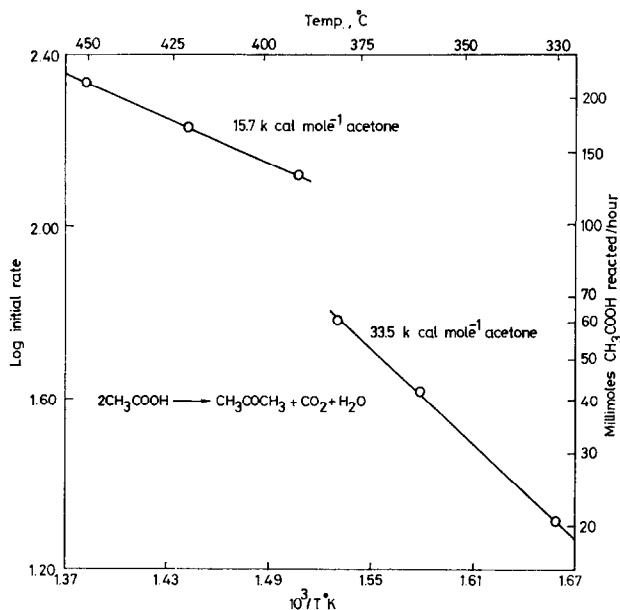


FIG. 1. Arrhenius plot for the ketonization of acetic acid.

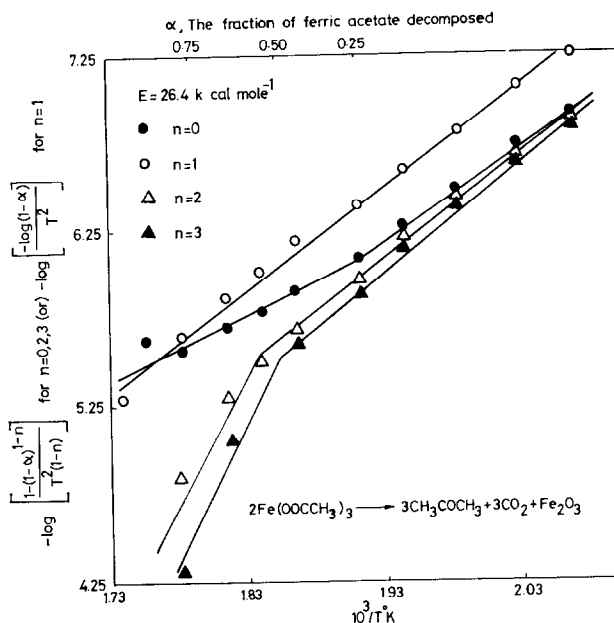


FIG. 2. Arrhenius plot for the decomposition of ferric acetate by thermogravimetric analysis.

reaction. Similarly, the effect of partial pressure on the reactions of isopropanol was also studied. Then, mixtures of acetic acid and isopropanol of various compositions, but at a total pressure of 1 atm, were reacted on the catalyst to determine the

influence of isopropanol on the reactions of acetic acid and the influence of acetic acid on the reactions of isopropanol. This could be done in the case of acetic acid by comparing the extent of conversion at the same partial pressure of reactant when the diluent is nitrogen which is inert, with the extent of conversion when isopropanol is the diluent. Similarly, the influence of acetic acid on the reactions of isopropanol can be determined. Figures 4 and 5 represent the mutual effect of isopropanol and acetic acid on each others' reaction at 375 and 440°C, respectively. When isopropanol and acetic acid were mixed and reacted over iron oxide, mutual inhibition of their reactions was observed at 375°C, whereas the ketonization of acetic acid was found to be enhanced at 440°C.

The mole percentages of free iron, α -Fe₂O₃, and Fe₃O₄ in the reduced catalyst obtained in different batches, along with the phases detected by XRD, are presented in Table 1. The results of studies of the reactions of acetic acid, isopropanol, and

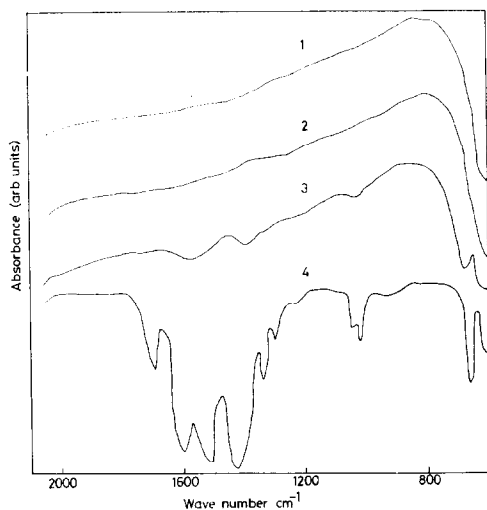


FIG. 3. Infrared absorption spectra of (1) α -Fe₂O₃; (2) α -Fe₂O₃ treated with CH₃COOH at 375°C; (3) α -Fe₂O₃ treated with CH₃COOH at 440°C; (4) ferric acetate.

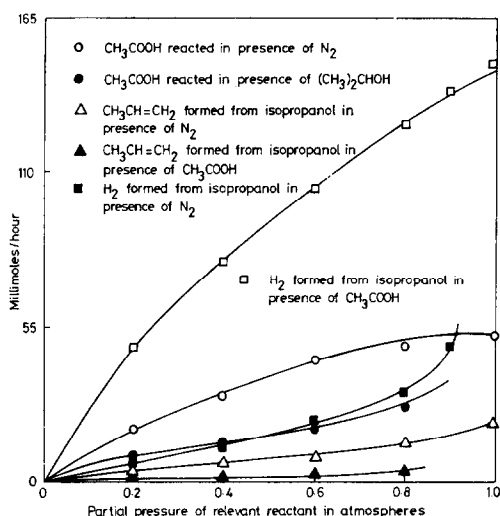
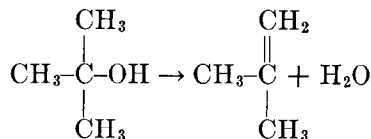


Fig. 4. Mutual effect of acetic acid and isopropanol on their respective reactions at 375°C.

tertiary butanol on reduced catalysts are presented in Fig. 6. These results are for 1 g of catalyst. The results are obtained at 375°C and hence no further reduction of the catalyst takes place during the reaction. The reduction of the catalyst during the

reaction takes place only at reaction temperatures above 390°C, as can be seen from the results in Table 2. The dehydrogenation of isopropyl alcohol and the ketonization of acetic acid show maxima for a composition corresponding to the Fe_3O_4 phase, whereas, for this composition, the dehydration of tertiary butyl alcohol falls to about



half the value on an unreduced catalyst.

A plot of the logarithm of the initial rate against the logarithm of partial pressure for typical runs for reactions of acetic acid at 375 and 440°C is given in Fig. 7. The slopes of the lines suggest that the reaction at both temperatures, though less than first order, is closer to first order. The orders seem to suggest a common mechanism in the two temperature regions even though the energies of activation do not.

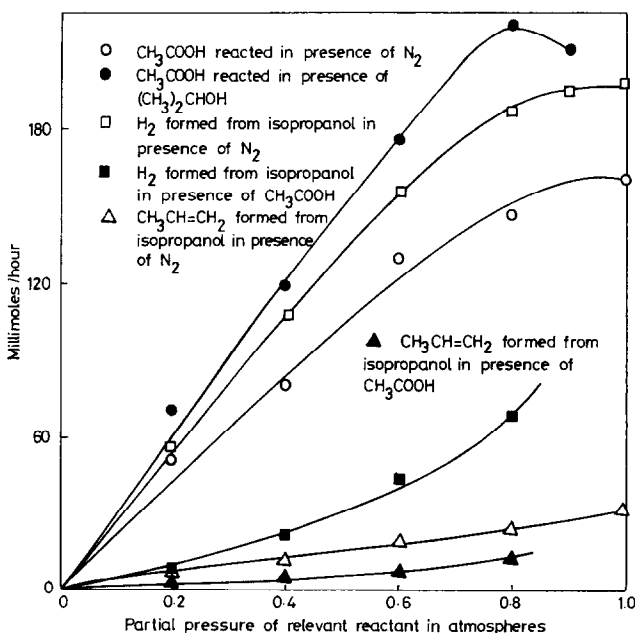


Fig. 5. Mutual effect of acetic acid and isopropanol on their respective reactions at 440°C.

TABLE 1
Chemical Compositions of the Different Phases Present in Various Batches of the Catalyst^a

Catalyst batch	Time of reduction (hr)	Surface area (m ² /g)	Chemical composition (mole%)			Phases detected by XRD
			Fe	Fe ₃ O ₄	Fe ₂ O ₃	
A	0.0	44	—	—	100	α -Fe ₂ O ₃
B	0.5	39	—	27.36	72.68	α -Fe ₂ O ₃ , Fe ₃ O ₄
C	1.5	41	—	55.12	44.88	α -Fe ₂ O ₃ , Fe ₃ O ₄
D	2.5	38	—	79.72	20.28	α -Fe ₂ O ₃ , Fe ₃ O ₄
E	3.5	40	1.86	96.27	1.87	—, Fe ₃ O ₄
F	4.5	42	13.65	86.35	—	—, Fe ₃ O ₄ α -Fe

^a Temperature of reduction: 450°C; 50 ml of H₂ per minute.

The data in Fig. 7 reveal that, at higher partial pressures, the experimental points deviate greatly from the straight lines. This could be because the reaction is tending toward zero-order conditions at higher partial pressures. The determination of order by this method is therefore not quite reliable. Further, assuming the Langmuir expression for surface coverage, the rate of the reaction if first order is given by

$$V = k\theta = k[bp/(1 + bp)].$$

The experimental observation of an apparent relationship,

$$V = kbp,$$

requires that $bp \ll 1$. This cannot be true because, as the partial pressure of acetic acid approaches 1 atm, the rate tends to become constant, indicating that $bp \gg 1$ at 1 atm of acetic acid. Since the reactions are not carried out at very low pressures, bp cannot be negligible compared to 1. During the study of the ketonization of

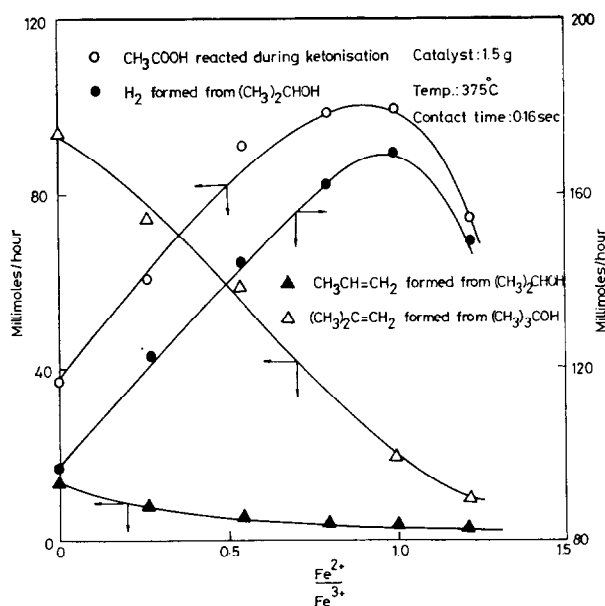


Fig. 6. Activity of the reduced catalyst for various reactions.

TABLE 2
Temperature Dependence of the Reduction
of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 ^a

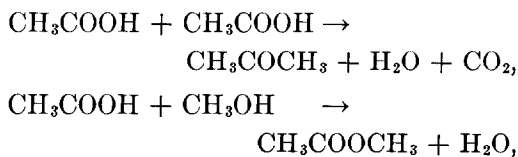
Temperature of keton- ization (°C)	Percentage conversion of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4	Phases detected by XRD
360	0.000	$\alpha\text{-Fe}_2\text{O}_3$
375	0.000	$\alpha\text{-Fe}_2\text{O}_3$
390	0.825	$\alpha\text{-Fe}_2\text{O}_3$
400	3.185	$\alpha\text{-Fe}_2\text{O}_3$
420	6.925	$\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4
440	17.270	$\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4

^a Feed rate, 0.525 mole/hr. Duration of reaction: 15 min.

acetic acid on thoria, it was pointed out that, unless one works with extremely low partial pressures of reactant, the determination of order in this manner can lead to ambiguous results (6, 15). Hence the method of competitive reactions (16) was used to get a more certain idea of the order of the surface reaction.

Mixtures of acetic acid and alcohols were reacted on iron oxide, whereby the ketonization and esterification formed the competi-

ing reactions. In Fig. 8, the relative velocities of the ketonization and esterification are plotted as a function of the composition of acetic acid and methanol in the feed. The relative adsorption coefficients,



of acid and alcohol (b_{ac}/b_{al}) are calculated from the partial pressures at which the rate of esterification is at a maximum (16, 17). It was established earlier that, when the sum of the partial pressures of acid and alcohol is 1 atm, the catalyst surface could be considered to be completely covered. If the Langmuir-Hinshelwood (L-H) mechanism is operative for the esterification, the rate of esterification is given by

$$V_E = k_e \frac{b_{ac}p_{ac}b_{al}p_{al}}{(b_{ac}p_{ac} + b_{al}p_{al})^2}.$$

Differentiating this expression to obtain

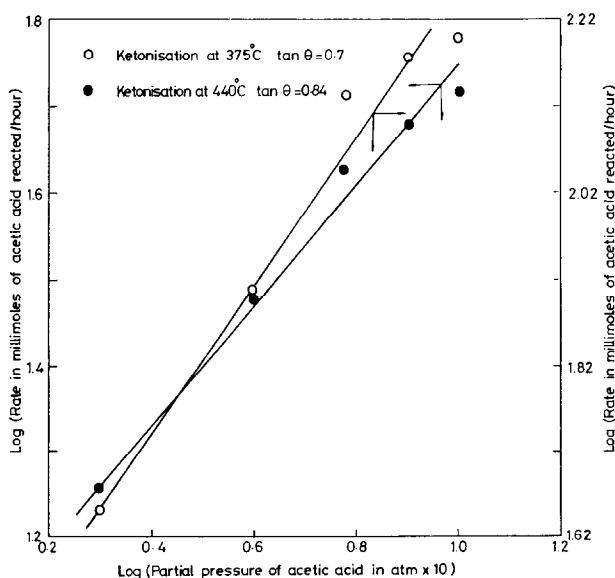


FIG. 7. Evaluation of the order for the ketonization of acetic acid on ferric oxide at 375 and 440°C.

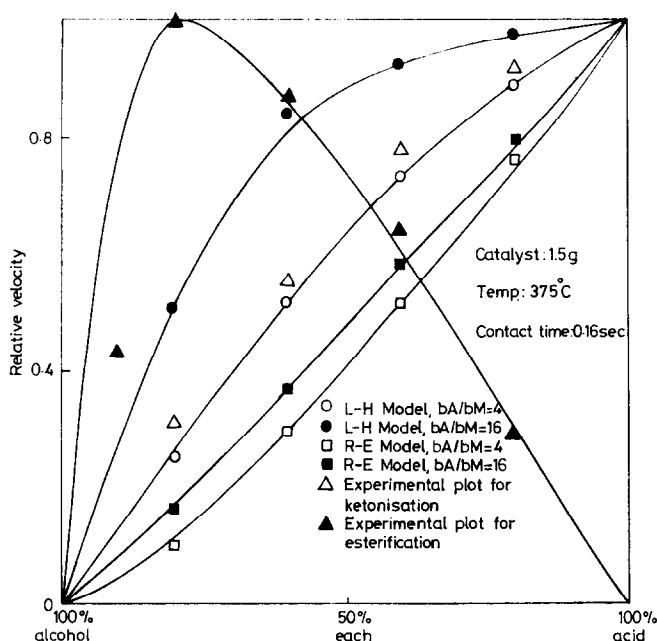


FIG. 8. Relative rates of formation of methyl acetate and ketone at 375°C for reaction mixtures containing different proportions of methanol and acetic acid.

the condition for maximum rate of esterification, one finds that, at V_E (maximum),

$$b_{ac}/b_{al} = p_{al}/p_{ac} = x.$$

Similarly, if the Rideal-Eley (R-E) mechanism is operative,

$$V_E = k_e \frac{b_{ac}p_{ac}p_{al}}{b_{ac}p_{ac} + b_{al}p_{al}}$$

or

$$k_e \frac{b_{al}p_{al}p_{ac}}{b_{ac}p_{ac} + b_{al}p_{al}},$$

and, at V_E (maximum),

$$b_{ac}/b_{al} = [p_{al}/p_{ac}]^2 = y.$$

Thus, two values are obtained for b_{ac}/b_{al} , depending on the reaction model for esterification. Using these values of x and y for b_{ac}/b_{al} , one can calculate theoretical curves for the ketonization using the L-H model where the rate expression is

$$V_K = k_k [(b_{ac}p_{ac})/(b_{ac}p_{ac} + b_{al}p_{al})]^2,$$

TABLE 3

Isotopic Distribution of Acetone during Tracer Studies at 375°C

<i>m/e</i>	Isotopic acetones	50% CD ₃ COOD + 50% CH ₃ COOH	10% D ₂ O + 90% CH ₃ COOH	10% D ₂ O + 90% CH ₃ COCH ₃	25% D ₂ O + 75% CH ₃ COOH	25% D ₂ O + 75% CH ₃ COCH ₃
58	CH ₃ COCH ₃	4.6	74.0	78.7	46.5	52.5
59	CH ₂ DCOCH ₃	13.9	17.3	14.3	34.6	30.8
60	CHD ₂ COCH ₃ CH ₂ DCOCH ₂ D	24.3	7.2	5.6	14.7	12.9
61	CD ₂ COCH ₃ CHD ₂ COCH ₂ D	27.4	1.5	1.7	3.7	3.4
62	CD ₃ COCH ₂ D CD ₂ HCOCHD ₂	19.2	—	—	0.5	0.4
63	CD ₃ COCHD ₂	8.8	—	—	—	—
64	CD ₃ COCD ₃	1.8	—	—	—	—

or the R-E model where the rate expression is

$$V_K = k_k [b_{ac} p_{ac}^2 / (b_{ac} p_{ac} + b_{al} p_{al})].$$

In each of these expressions, x or y can be substituted for b_{ac}/b_{al} . Therefore, four theoretical curves can be constructed (18-20). One can now find to which of these theoretical curves the experimental points correspond and determine which model is applicable to the ketonization reaction.

The experimental results are found to fall on the theoretical curve drawn on the assumption that esterification and ketonization both follow an L-H mechanism. This suggests that the ketonization is a second-order reaction on the surface.

The technique of competitive reactions could not be used at 440°C because the relative adsorption coefficients of alcohols and acids were not of a suitable magnitude to permit a clear distinction between the two mechanisms. The method can be used only if the ratio of adsorption coefficients of the reactants is 3 or more (16). This condition appeared to be satisfied by isopropanol. But isopropyl acetate decomposes at 440°C, making it impossible to study the competitive reaction.

Tracer studies were carried out by passing mixtures of CD_3COOD and CH_3COOH , CH_3COCH_3 and D_2O , and CH_3COOH and D_2O separately over ferric oxide. The results of the analysis of the products are tabulated in Table 3.

DISCUSSION

The discontinuity in the Arrhenius plot around 400°C indicates that the mechanism of the ketonization is not the same below and above this temperature (21, 22). The discontinuity in the Arrhenius plot may be attributed to surface unsaturation of the catalyst at higher temperatures. In such cases, when one extends the two straight lines obtained by joining the

points at the higher temperatures, with those at the lower temperatures, one observes that the two lines intersect and that all experimental points lie to the left-hand side of the area formed by these two lines (17). In the present case, it is found that there are at least two points to the right-hand side of this area. Hence, surface unsaturation is unlikely to be the reason for the discontinuity in the Arrhenius plot. The comparable values of the activation energies obtained for the ketonization of acetic acid (15.7 kcal mole⁻¹) above 400°C and the thermal decomposition of ferric acetate (17.6 kcal mole⁻¹) lead one to believe that the ketonization above 400°C takes place through formation of a salt (8). The ir spectrum which shows the presence of acetate groups on the catalyst used at 440°C supports this view. The ir spectrum of a catalyst used below 400°C does not indicate the formation of acetate on the catalyst surface. The mutual inhibition of the ketonization of acetic acid and dehydrogenation, as well as of the dehydration of isopropanol, when the two compounds are mixed and reacted below 400°C, brings out the importance of both dehydration and dehydrogenation sites of the catalyst for the ketonization. In contrast to this, above 400°C the presence of isopropanol enhances the ketonization, although its own decomposition is suppressed by acetic acid. This further points to the difference in the behavior of the catalyst in the two temperature regions.

Above 400°C, the catalyst is found to undergo transformation from $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 during the course of the reaction. The studies with catalysts reduced to different extents show that the Fe_3O_4 phase has the highest activity for ketonization. The reducing atmosphere of hydrogen that is made available by the dehydrogenation of isopropanol may be facilitating the

conversion of Fe_2O_3 to Fe_3O_4 . However, since the enhancement in activity in the presence of isopropanol is with respect to the steady-state activity of the catalyst when it is in the form of Fe_3O_4 , the beneficial effect of isopropanol cannot be due to the facilitation of the reduction of the oxide. There must be a beneficial surface modification brought about by the isopropanol and hydrogen. The analysis of the results obtained employing the technique of competitive reactions suggests a second-order surface reaction corresponding to the L-H model for the ketonization.

The experiments with the mixtures of CD_3COOD and CH_3COOH which were carried out below 400°C have given all possible ratios of hydrogen to deuterium in the acetone molecule. When CH_3COCH_3 exchanges with D_2O , the ratio of monodeuterated acetone to undeuterated acetone is always smaller than that obtained when the acetone is formed from a reaction carried out with CH_3COOH to which D_2O is added. The monodeuterated acetone in the latter case, therefore, could not have arisen only by an exchange after the ketone is formed. CH_3COOH exchanges with D_2O to a much smaller extent than is necessary to account for the deuterated acetone formed when acetic acid and D_2O are passed through the reactor at the reaction temperature without a catalyst. Therefore, it is likely that ketene might have been formed as an intermediate prior to ketone formation, enabling the formation of multi-deuterated acetone.

A few experiments were carried out with mixtures of 25% D_2O and 75% CH_3COOH and 25% D_2O and 75% CH_3COCH_3 at 375 and 440°C . The ratio of monodeuterated acetone to undeuterated acetone is given in Table 4. It is observed that, when D_2O and acetic acid are used, the ratio of $\text{CH}_3\text{COCH}_2\text{D}/\text{CH}_3\text{COCH}_3$ is almost the same at both temperatures, while, with D_2O and CH_3COCH_3 , the

TABLE 4

Extent of Monodeuteration in Acetone When Acetic Acid or Acetone Is Passed with D_2O over the Catalyst

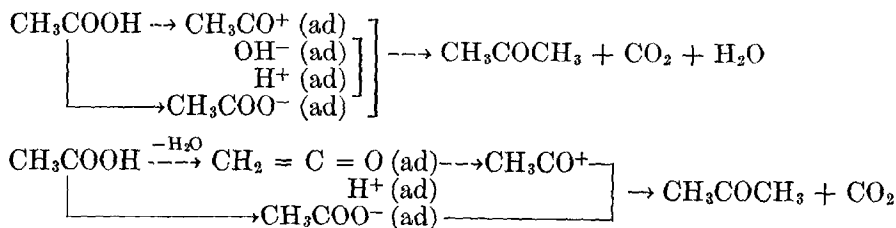
Reaction mixture	Moles of $\text{CH}_3\text{COCH}_2\text{D}/$ moles of CH_3COCH_3	
	375°C	440°C
25% D_2O + 75% CH_3COOH	0.75	0.72
25% D_2O + 75% CH_3COCH_3	0.58	1.36
10% D_2O + 90% CH_3COOH	0.23	—
10% D_2O + 90% CH_3COCH_3	0.18	—

ratio is greater at 440°C . If the exchange is taking place after the formation of the ketone, then one would expect the ratio to be higher at 440 compared to 375°C , when D_2O and CH_3COOH are reacted. Further, the higher ratio at 375°C for $\text{D}_2\text{O} + \text{CH}_3\text{COOH}$ compared to $\text{D}_2\text{O} + \text{CH}_3\text{COCH}_3$ shows that exchange after ketone formation cannot account for the $\text{CH}_3\text{COCH}_2\text{D}$, supporting the possible intermediacy of ketene. At 440°C the ratio for $\text{D}_2\text{O} + \text{CH}_3\text{COOH}$ is even less than that for $\text{D}_2\text{O} + \text{CH}_3\text{COCH}_3$, suggesting that the exchange is less facile than with the ketone. From the suggested explanation for the result at 375°C a ketene intermediate cannot be responsible for this result at 440°C . It is therefore not in contradiction with the suggestion that at 440°C the mechanism is different and the reaction is taking place through the formation of a salt.

The spectral studies on catalysts on which reactions have been carried out show evidence of acetate formation when the reaction temperature is above 400°C and no evidence at all for it when the temperature is below 400°C . It is unlikely that a common mechanism, with the formation of acetate being rate determining at lower temperatures and its decomposition being rate determining at higher temperatures, is operative. This result further justified the consideration of two different mechanisms

in the two temperature ranges. Since dehydration and dehydrogenation sites are important for the ketonization and since

the L-H model is applicable to the reaction, one can envisage the following mechanisms for the reaction below 400°C.



Tracer studies lend some support for the mechanism involving ketene as an intermediate. The dehydration of acetic acid produces ketene which takes up an adsorbed hydrogen to form an acyl carbonium ion. The interaction of the acyl carbonium ion with the acetate anion produces acetone and carbon dioxide. This would permit the easy incorporation of D₂ into the acetone molecule.

CONCLUSION

The mechanistic route of a reaction is largely dependent upon the reaction conditions since the intrinsic properties of metal oxides are temperature dependent. The surface substrate interaction is as important as the intrinsic nature of the catalyst. The ketonization of acetic acid below 400°C is a surface phenomenon involving the adsorption and interaction of two molecules of acetic acid, utilizing the dehydration and dehydrogenation activities of the catalyst. Apparently, the surface interaction does not amount to salt formation. At higher temperatures the reaction takes place through the formation of a salt. Above 400°C, the Fe₂O₃ is converted in the initial stages to Fe₃O₄, and the real catalyst is Fe₃O₄, while, at temperatures below 400°C, the catalyst is Fe₂O₃.

ACKNOWLEDGMENT

S.S.J. is grateful to the C.S.I.R. India for a research fellowship.

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