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Reactions of Carboxylic Acids on Oxides

2. Bimolecular Reaction of Aliphatic Acids to Ketones

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The reaction of aliphatic carboxylic acids over oxidic catalysts has been studied. Ketones are the main product in this reaction. Up to now there has been no agreement in the literature concerning the mechanism of this ketonization reaction. In the case of acetic acid, it appears that the ketone can be formed via two different routes. On oxides with a low lattice energy, bulk acetates are formed, decomposition of which leads to acetone. On oxides with a high lattice energy, the reaction to acetone takes place on the surface and leaves the bulk structure of the catalyst unaltered. The surface reaction to ketones probably proceeds via an intermediate that is oriented parallel to the surface and that has chemical interactions with the catalyst via both the carboxyl group and the α-carbon of the alkyl group. For the latter interaction abstraction of an α-hydrogen atom is required. The alkyl group of this intermediate can react with a neighboring carboxylate to give the ketone. The remaining carboxyl group forms CO_2. The intermediate is very likely to be in pseudo-equilibrium with the corresponding ketene. © 1997 Academic Press

INTRODUCTION

The formation of acetone from acetic acid with oxidic catalysts has been known for a long time. All kinds of catalysts are found to be active in this reaction: Al_2O_3 (1, 2), ThO_2 (2–5), UO_2 (3), CdO (2, 6), MgO (7), Bi_2O_3 (8), ZnO (2, 6), Fe_3O_4 (1, 9–12), TiO_2 (1, 13, 14), SnO_2 (1), and Cr_2O_3 (2, 15). The formation of acetone from two molecules of acetic acid, i.e., so-called ketonization, is accompanied by water and carbon dioxide production and is therefore sometimes, undeservedly, called decarboxylation:

$$2RCOOH \rightarrow RCOR + CO_2 + H_2O. \qquad [1]$$

When a basic oxide is used as catalyst, carbonates can be formed by reaction of the acidic carbon dioxide with the oxide. These carbonates are active catalysts in the ketonization reaction, too. This is the oldest method known to produce ketones (16). Thermal decomposition of metal acetates also leads to the formation of acetone. Examples are the acetates of Ba (16), Ca (17), Cu (2), and Mg (7).

Other aliphatic acids also react to their symmetric ketones (by reaction [1]) over a large variety of oxidic catalysts. The most studied aliphatic acids are the unbranched acids, ranging from propionic acid to fatty acids, and some branched acids, such as isobutyric acid and trimethylacetic acid. Some old literature mentions use of such catalysts as ThO_2 (5, 18, 19), ZnO (6, 20), Cr_2O_3 (2), and NiO (6) for ketone production from carboxylic acids. The same papers also report that when a mixture of acids is led over the catalyst, the mixed ketones are formed together with the symmetric ketones. Decomposition of mixed metal carboxylates yields mixed ketones, too (21, 22). Some recent publications show the continuing interest in the production of ketones from carboxylic acids (23–25).

Although ketonization of carboxylic acids occurs very often and has been studied extensively, no agreement has yet been reached concerning the mechanism. Good overviews on this subject are given by Rajadurai (26) and Kwart and King (27). Some suggestions concerning the mechanism are mentioned briefly below.

Bamberger (28) and Koch and Leibnitz (29) suggested that acetic anhydride might be the reaction intermediate during bimolecular ketonization of acetic acid; however, Kuriacose and Jungers (4) and Neunhoeffer and Paschke (30) suggest that any similarity observed between acid and anhydride is caused by the presence of water, which decomposes the anhydride to give two molecules of acid. On α-Fe_2O_3 it was found that, at room temperature, acetic anhydride is very unstable in the presence of surface hydroxyl groups and formed adsorbed acetates (31). Thus, anhydride is not likely to be an intermediate in the ketonization reaction.

Neunhoeffer and Paschke proposed a mechanism with a β-keto acid as an intermediate (30). An α-hydrogen atom has to be abstracted first to form this intermediate. The β-keto acid intermediate can be formed via a concerted mechanism (27) or via a reaction between an acyl carbonium ion and a carboxylate (29). Kwart and King also

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suggest a concerted reaction in which CO_2 is lost instead of α-hydrogen (27).

The above-mentioned mechanisms are based on salt decomposition experiments. The following models have been proposed to describe the reaction mechanism of ketonization over catalyst surfaces.

Swaminathan and Kuriacose propose that ketonization of acetic acid and propionic acid on Cr_2O_3 proceeds via interaction between a carboxylate ion and an acyl group formed on the surface (15). Imanaka *et al.* have carried out investigations on the reaction of acetic acid on ZnO, MnO, CaO, and MgO (32). They suggest that the ketene produced by acetic acid dehydration reacts with surface acetate ions on the basic oxides of Ca and Mg, whereas on MnO and ZnO the reaction intermediates are acetate ion and acyl carbenium ion. González *et al.* suggest that, even on the acidic TiO_2 surface, ketene formation precedes ketonization (14).

An entirely different mechanism operates in synthesis gas reactions, where acetone is also found as a product. Formation of acetone is explained here by a reaction between a surface acetyl group and a methyl group (33–35).

The aim of this paper is to suggest a plausible mechanism for the ketonization reaction that would explain all results now available.

METHODS

The acids used were obtained from J. T. Baker, Holland (acetic acid, 99–100%); Aldrich, Germany (propionic acid, 99+%); Janssen, Belgium (isobutyric acid, 99.5%, and pivalic acid, 99%); and Isotec Matheson USA ([1-^{13}C]acetic acid, 99.3%). Other compounds, which were used for calibrations, were always p.A. grade. Ketene was made *in situ* by pyrolysis of acetone in a quartz reactor at 520°C. The reaction products were collected in a liquid nitrogen trap. After a short increase in temperature to remove contaminants, ketene was slowly evaporated at acetone/dry ice temperature.

The catalysts were pure oxides, which were used as purchased, i.e., as powders. Details are given in Part 1 (36). In some experiments titanium oxide was pretreated in a deuterium flow (Messer–Griesheim, 99.7%) at 350°C prior to the reaction.

The catalytic experiments were performed in a hydrogen flow, which was saturated with acid at such a temperature that the saturation pressure was 25 mbar (i.e., 22, 44, 56, and 67°C for acetic, propionic, isobutyric, and pivalic acids, respectively).

All experiments with acetic acid were performed in a system equipped with a mass spectrometer. Details of the setup and data analysis are given in Part 1 (36). The recorded values were corrected for overlapping fragmentation peaks and mass spectrometer sensitivity. During the reaction, the temperature was raised from room temperature to 450°C at the rate of 7°C/min, and subsequently lowered to 200°C at the rate of 10°C/min.

The reactions of the other acids were carried out in a similar flow system equipped with a gas chromatograph. This flow system was heated with a heating wire to at least 100°C, to avoid condensation of both reactants and products. During the temperature-programmed reaction, the reactor temperature was raised from room temperature to 450°C at the rate of 0.5°C/min. Samples were taken every 30 min and analyzed by an on-line gas chromatograph (Packard 433, packed column: Tenax G.C.) equipped with a flame ionization detector. The recorded values of the peak areas were converted into gas concentrations by using sensitivity factors determined by calibration. In the case of the ^{13}C-labeling experiments the products were collected in a cold trap, which was cooled with acetone/dry ice. Analysis of these products was done by GC–MS.

The selectivities were calculated as the molecular percentage of all organic products.

RESULTS

Figures 1–6 illustrate the reaction behavior of acetic acid over different catalysts. The partial pressures of acetic acid and its most important products are plotted as a function of temperature. Arrowheads are added to the graphs to distinguish between the programs of increasing and subsequent decreasing temperature, respectively.

It can be concluded from Fig. 1 that γ-alumina is a good catalyst for the ketonization. The ratios found coincide approximately with the reaction of two molecules of acetic acid to form one molecule each of acetone, carbon dioxide, and water (reaction [1]). The reaction runs above 300°C, and no other products are detected. TiO_2, Cr_2O_3, and ZrO_2 behave similarly; however, chromia and zirconia are slightly

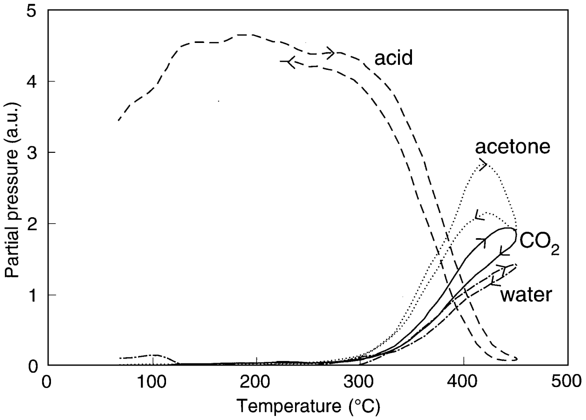


FIG. 1. Partial pressures in the reaction of acetic acid over γ-Al_2O_3.

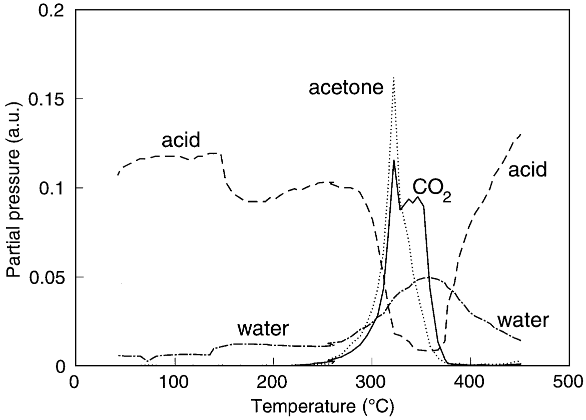


FIG. 2. Partial pressures in the reaction of acetic acid over Bi_2O_3. Only the increasing temperature range is shown.

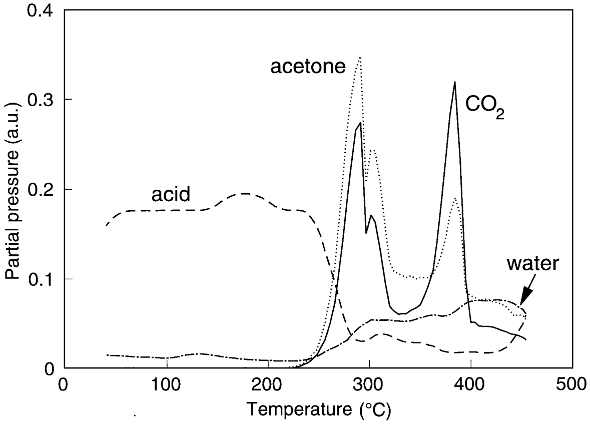


FIG. 4. Partial pressures in the reaction of acetic acid over $Pb(CH_3COO)_2$. Only the increasing temperature range is shown.

less active. The reaction starts on these catalysts at a higher temperature (approximately 400°C).

Bismuth oxide (Fig. 2) also catalyzed exclusively the ketonization reaction; however, it behaved clearly differently than alumina. At about 150°C, a sudden drop in the acetic acid signal was seen, accompanied by a small increase in the water signal. Just above 300°C, sharp peaks in the formation of acetone and carbon dioxide appeared. Probably, acetic acid was first consumed in a reaction with the oxide to give an intermediate, the sudden decomposition of which gave rise to the formation of acetone and CO_2. When the reaction mixture was led over bismuth oxide at a constant temperature of 200°C (i.e., below the temperature of acetone formation), the yellow oxide turned into a white compound within 4 h. The X-ray diffraction (XRD) pattern of this white compound was very similar to that of bismuth(III) acetate.

Reaction of acetic acid on lead oxide as a catalyst yielded a complicated product pattern (Fig. 3). Like bismuth oxide, lead oxide consumed acetic acid from the gas phase before any product formation started. When the reaction mixture was led over the lead oxide at a constant temperature of 175°C, lead(II) acetate formed, as evidenced by XRD analysis. Comparison of Fig. 3 (lead oxide) with Fig. 4 (lead acetate) shows many common features.

Magnesium oxide and zinc oxide showed behavior comparable to that of Bi_2O_3: the acetic acid signal decreased at 200°C, accompanied by an increase in the water signal, and sharp peaks in the production of CO_2 and acetone were observed at about 350°C.

Manganese(IV) oxide appeared to be a good ketonization catalyst, too (Fig. 5). The peak at 300°C in CO_2 production was, surprisingly, not accompanied by acetone formation. Mn_3O_4 (obtained by prereduction of MnO_2) showed the same CO_2 peak, but in this case, in contrast to MnO_2, CO_2 evolution was accompanied by acetone formation (Fig. 6). Water is omitted from the figures as it reached its saturation pressure at ambient temperature as soon as the reaction started, i.e., at 300°C. It subsequently

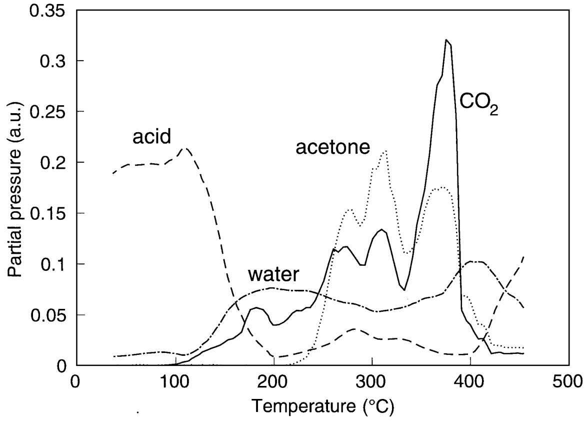


FIG. 3. Partial pressures in the reaction of acetic acid over PbO_2. Only the increasing temperature range is shown.

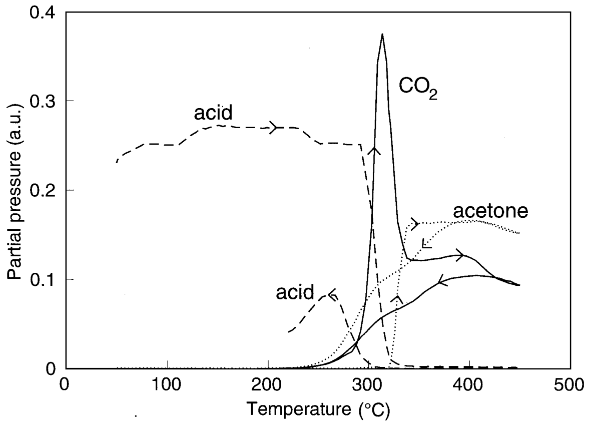


FIG. 5. Partial pressures in the reaction of acetic acid over MnO_2.

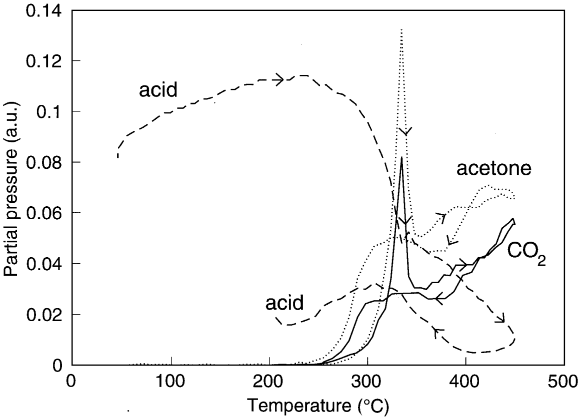


FIG. 6. Partial pressures in the reaction of acetic acid over Mn_3O_4.

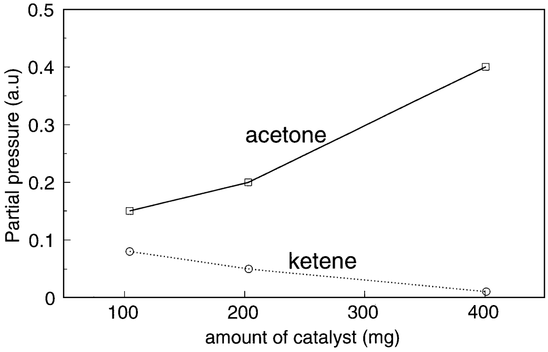


FIG. 8. For the reaction of acetic acid over zirconia (at 450°C, during a temperature-programmed reaction), the partial pressures of the products using different amounts of catalyst (i.e., with varying contact times).

condensed in the flow system, and a constant water signal, corresponding to its saturation pressure, was recorded by the mass spectrometer. Because acetic acid dissolved in this condensed water, no acetic acid signal was observed at decreasing temperatures. Both catalysts were still active at decreasing temperatures. XRD analysis showed that the used catalysts consisted mainly of MnO.

Figures 1 to 6 show results concerning the reaction of acetic acid. The selectivity to ketone in the reactions of other acids with a different number of α-hydrogen atoms is shown in Fig. 7 for the catalysis on iron oxide, vanadia, and titania. Ketone production is obviously suppressed on all three catalysts by decreasing the number of α-hydrogen atoms in the acid. Propionic acid on titania seems to be the only exception. This is probably related to an extensive polymerization reaction scavenging reaction products and causing the formation of a yellowish oil, which condensed after the reaction. The selectivity in this particular reaction is thus not determined at a complete mass balance, which explains the deviating result.

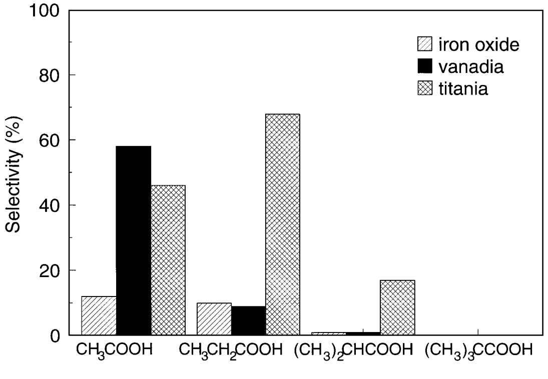


FIG. 7. Selectivities to the various ketones in the reaction of four acids in which the number of α-hydrogen atoms varies from 3 to 0. The catalysts used are the oxides of iron, vanadium, and titanium. The selectivities are determined during a temperature-programmed reaction at 350°C for iron oxide, at 440°C for vanadia, and at 430°C for titania.

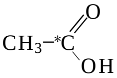
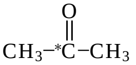
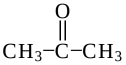
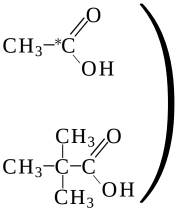
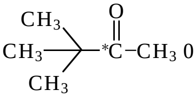
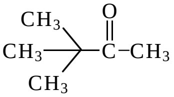
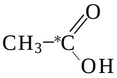
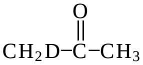
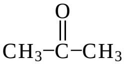
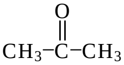
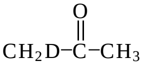
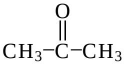
As mentioned in the Introduction, it has been suggested that ketene could be an intermediate in the production of ketones (26, 37). This possibility was checked by changing the contact time of the reactants during the reaction of acetic acid over a zirconia catalyst. The contact time was altered by changing the amount of catalyst used. The partial pressures of the products are shown in Fig. 8. At shorter contact times, ketene is found in larger concentrations; the reverse holds for acetone.

To examine the mechanism of ketonization more closely, a mixture of acetic [^{13}C] acid and trimethylacetic acid (pivalic acid) was led over a titania catalyst in the temperature range 370 to 450°C. Apart from small amounts of hydrocarbons originating from the decomposition of pivalic acid, only ketonization products were observed. These were acetone and 2,2-dimethyl-3-butanone (pinacoline), which are products of the reaction between two acetic acid molecules and between acetic acid and pivalic acid, respectively. Pivalic acid did not react to its corresponding ketone. The results are summarized in Table 1. No label was found in the pinacoline in the case of a combined labeled acetic acid and unlabeled pivalic acid feed, indicating that its carbonyl group originated from the pivalic acid, which cannot form ketene, and not from the acetic acid.

The results of the exchange reaction between acetic acid and surface-bound deuterium are also shown in Table 1. In this experiment, the surface of a titania catalyst was pretreated in a deuterium flow at 350°C. This treatment supposedly led to a surface on which the hydroxyl groups are partially exchanged with deuterium. The deuterated titania obtained in this way was used in a reaction with acetic acid in helium at 350°C. The only product found was acetone, of which initially the undeuterated and monodeuterated species were found in equal quantities. When the product itself (acetone) was led at 350°C over titania pretreated with deuterium in the same way, it did not exchange its hydrogen atoms with the deuterated surface.

TABLE 1

Occurrence of the Labeled and Unlabeled Forms of Some Products in the Reaction over Titania

Reactants	Products	
	Labeled	Unlabeled
 $CH_3{-}^{*}C(=O)OH$	 $CH_3{-}^{*}CO{-}CH_3$ 100%	 $CH_3{-}CO{-}CH_3$ 0%
 $CH_3{-}^{*}C(=O)OH$ $(CH_3)_3C{-}C(=O)OH$	 $(CH_3)_3C{-}^{*}CO{-}CH_3$ 0%	 $(CH_3)_3C{-}CO{-}CH_3$ 100%
 $CH_3{-}^{*}C(=O)OH$ $+ D_{surface}$	 $CH_2D{-}CO{-}CH_3$ 38%[a]	 $CH_3{-}CO{-}CH_3$ 40%[a]
 $CH_3{-}CO{-}CH_3 + D_{surface}$	 $CH_2D{-}CO{-}CH_3$ 0%	 $CH_3{-}CO{-}CH_3$ 100%

[a] Product distribution after reaction time of 20 s.

DISCUSSION

Reaction Type

The most frequently observed product in the reaction of acetic acid over oxides is acetone, together with carbon dioxide and water (reaction [1]). As is explained in the Introduction, there is no agreement in the literature on the way acetone is formed. The above-described results demonstrate that the reaction proceeds via two different pathways.

With the oxides of lead, bismuth, magnesium, and zinc, a sharp peak in acetone formation is seen, accompanied by a peak in carbon dioxide production. The sudden onset of this reaction can be explained by the decomposition of bulk acetate, formed at the beginning of the experiment. Such formation of bulk acetates is possible since the oxides in question are basic and have a low lattice energy. The salt formation is particularly distinct in the experiment performed with the bismuth oxide (Fig. 2). At 150°C the acetic acid signal suddenly decreased, while the water signal increased. This can be explained by the following acetate formation reaction:

$$2CH_3COOH + MO \rightarrow M(CH_3COO)_2 + H_2O. \quad [2]$$

The salt decomposes thereafter at higher temperatures, resulting in sharp peaks of acetone and carbon dioxide. This well-documented decomposition reaction can proceed either via

$$M(CH_3COO)_2 \rightarrow CH_3COCH_3 + CO_2 + MO \quad [3]$$

or via

$$M(CH_3COO)_2 \rightarrow CH_3COCH_3 + MCO_3. \quad [4]$$

(2, 7, 16). Two facts confirm these ideas. These are the similarity between the reaction of acetic acid over lead oxide and the decomposition of lead acetate and the fact that bismuth oxide and lead oxide react to acetates at temperatures lower than the temperature at which the reaction to acetone starts.

During this decomposition reaction, there is also a parallel continuous reaction of acetic acid to acetone. This can be deduced from the low signal of acetic acid at the temperatures at which acetone and CO_2 are formed. Hence the acetone is formed not only from acetic acid, which reacted previously with the oxide, but also from acid led over the catalyst during the decomposition reaction. Probably, surface acetates are continuously regenerated; however, this regeneration (via reaction [2]) always makes a minor contribution to the total reaction, since the signal of water expected from reaction [2] is always lower than the acetone and CO_2 signals.

It should be stressed that when using oxides with a low lattice energy, not the oxide but the acetate forms the actual working catalyst.

Reactions of acetic acid on oxides having a high lattice energy; e.g., alumina, chromia, titania, and zirconia do not show a sharp decomposition peak. In addition these catalysts remain macroscopically unaltered during the reaction. This is confirmed by the unchanged XRD pattern after reaction and by the fact that the product patterns at increasing and decreasing temperature programs are very similar (Fig. 1). Probably, the reaction runs on the surface without any formation of bulk acetates.

The existence of two different reaction routes to acetone has already been suggested by Yakerson *et al.* (38, 39). These authors propose a reaction via bulk acetates for oxides with a low lattice energy and a surface reaction for oxides with a high lattice energy. This idea can now be formulated in a slightly different way: on oxides with low metal–oxygen bond strength, the ketonization reaction proceeds via bulk acetates, whereas on oxides with high metal–oxygen bond strength, a surface reaction is responsible for acetone formation.

The just-mentioned findings can be rationalized as follows. Schuit *et al.* (40) proposed a correlation between the heats of formation (Q_f^0) of metal oxide MO and metal formate $M(HCOO)_2$:

$$Q_f^0(M(HCOO)_2) = 1.25 \cdot Q_f^0(MO).$$

According to the same authors, it is possible to extrapolate this correlation to acetates. This leads to the conclusion that the formation of an acetate is always thermodynamically favored to oxide formation; however, the catalysts are originally in the oxidic form. To form acetates, the metal ions must be extracted from the oxidic lattice. When the heat of formation, and thus the metal–oxygen bond strength, is too high, extraction of the metal ion is too slow and no salt formation is observed, even though the salt is thermodynamically more stable.

Magnesium oxide, which has a high metal–oxygen bond strength, forms bulk acetates, too. Probably not only low metal–oxygen bond strength, but also high basicity (ionicity) can facilitate the formation of bulk acetates.

The peak in CO_2 production in the absence of acetone, which is seen on manganese oxide (Fig. 5), is probably caused by complete stoichiometric oxidation of the acetic acid by lattice oxygen. This reaction can reasonably be expected, since the manganese oxide is a well-known oxidation agent and catalyst:

$$CH_3COOH + 4O_{\text{lattice}} \rightarrow 2CO_2 + 2H_2O. \qquad [5]$$

Reaction Mechanism

Knowing now that there are two routes to form ketones, we focus on solving the yet undetermined reaction steps in the catalytic surface reaction to ketones.

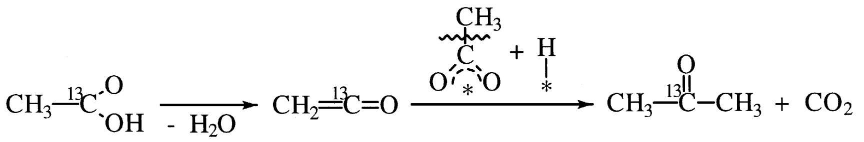
Figure 7 demonstrates that, to form a ketone, the acid has to contain α-hydrogen atoms. When going from acetic acid, via propionic acid and isobutyric acid, to pivalic acid, i.e., when decreasing the number of α-hydrogen atoms from 3 to 0, ketone formation gradually disappears on all three catalysts. This may occur either because steric hindrance impedes the reaction of two intermediates to give the ketone or because α-hydrogen is needed in some way during the reaction to ketone. Two facts support the latter possibility. First, benzoic acid hardly forms any ketone (benzophenone) by a catalytic surface reaction (41). The carboxyl group of this molecule is not hindered sterically, but the molecule lacks α-hydrogen atoms. Second, by reducing the contact time, the extent of acetone formation decreases while ketene is found in larger concentrations (see Fig. 8). This suggests the intermediacy of the latter in the reaction to the former. To form ketene or a ketene-like intermediate, the abstraction of an α-hydrogen atom is required.

Ketene or a ketene-like intermediate (e.g., $RR'C{=}COO_{ads}$) can, in principle, react to ketones in two different ways. The first way is by attacking an adsorbed carboxylate species and subsequently abstracting the alkyl group of the carboxylate to form a ketone: (reaction [6] represents this mechanism for acetic acid). This mechanism and variations of it are described by several authors (12, 14, 15, 32). They all have in common that the carboxyl group in the ketone originates from the ketene and not from the carboxylate. As can be seen in Table 1, this is not what happens. In the experiment shown in this table, acetic acid is the only molecule able to form a ketene; pivalic acid has no α-hydrogen and, therefore, is not able to form a ketene. However, no labeled pinacoline is found, meaning that the carbonyl group originates from the carboxylate (i.e., pivalic acid) and not from the ketene (i.e., acetic acid). Reaction [6] can therefore be disregarded.

A reaction route via a β-keto acid as an intermediate or transition state (27, 29, 30, 42) would explain the results found in the labeling experiment; however, it cannot explain the intermediacy of ketene as described above and in the literature (12, 14, 15, 32).

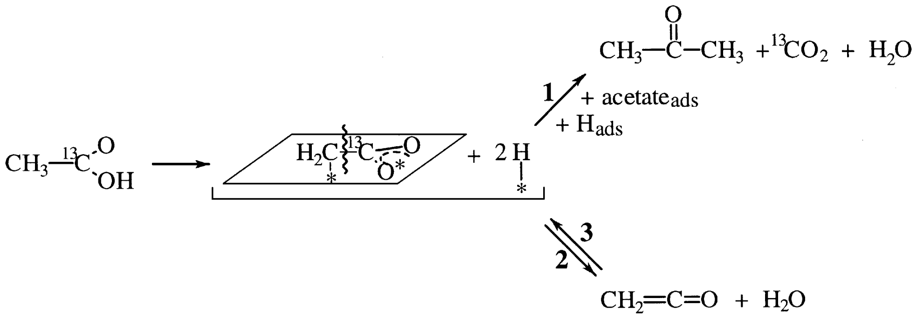
Therefore, we must focus on the second way in which ketene, or a ketene-like intermediate, can react to acetone. The possibility exists that not the complete ketene (carbonyl plus methylene group) is donated but only the methylene group, which reacts with a carboxylate and a hydrogen atom to a ketone. The question then arises as to exactly what this methylene-donating intermediate can be. To answer this, it is enough to list all the data collected. First, as can be concluded from Fig. 7, α-hydrogen is needed. Second, acetic acid, or an intermediate leading to acetone, can exchange α-hydrogen with the surface. This can be deduced from the fact that α-deuterium is found in acetone when the reaction proceeds on a deuterated surface (Table 1). Thus, the intermediate to acetone interacts with the catalyst surface through the methyl group; this interaction leads to α-hydrogen abstraction and exchange. This is remarkable, as no exchange of hydrogen seems to be needed to form acetone from two acetic acid molecules, and acetone itself does not exchange its hydrogen atoms. Reactions between the α-hydrogen and the surface, which can even result in complete oxidation of the α-carbon, have been described (43–46). This interaction is reasonable as the dissociation energy of the C–H bond in acetic acid is much lower (94 kcal/mol) than the ΔH characterizing the gas-phase acidity (349 kcal/mol), i.e., deprotonation (47).

If the methylene-donating intermediate is indeed ketene, CO would be the fragment remaining after C–C bond scission. As CO_2 is always found, and CO is never found, the intermediate involved probably still has both its oxygen atoms.



$$CH_3{-}{}^{13}C(O)OH \xrightarrow[-\,H_2O]{} CH_2{=}{}^{13}C{=}O \xrightarrow{CH_3COO^{*} \;+\; H^{*}} CH_3{-}{}^{13}C(O){-}CH_3 + CO_2 \qquad [6]$$

All results can be explained by assuming that the intermediate to acetone is not ketene, but something related to, and in equilibrium with, ketene. This intermediate should have both oxygen atoms, and interact simultaneously with the surface via the α-carbon. For the latter interaction abstraction of an α-hydrogen atom is required. Summarizing, we suggest the following picture:



[7]

The readsorption step 3 causes the dependence found for acetone and ketene formation on apparent contact time. This mechanism explains not only the results presented in this paper but also those presented in the literature (14, 15, 26, 32). C–C bond scission, which is needed for the ketonization reaction, should now not be difficult, as the intermediate, which is oriented parallel to the surface, is bound to the surface by both its ends and can thus split into CO_2 and a reactive methylene group.

As methane or larger hydrocarbons are never found as a by-product of the ketonization reaction, the formation of methylene is probably immediately followed by a reaction with a neighboring carboxylate. Otherwise, methylene would react to methane or even larger hydrocarbons.

A possible reaction site for the ketonization is proposed by Barteau *et al.* (13, 48, 49). They found that for ketonization doubly unsaturated titanium ions have to be present at the surface. González *et al.* (14) suggested that to achieve ketonization, ketene and acetic acid must be brought together on one cation. It seems reasonable that the ketene-like intermediate shown in reaction [7] reacts with a carboxylate on one doubly unsaturated cation.

The reaction mechanism presented by reaction [7] is based on the results obtained only with oxidic catalysts with a high lattice energy, and it is thus applicable only to ketonization by surface reactions.

CONCLUSIONS

Acetone is the main product in the reaction of acetic acid over most oxidic catalysts. Its formation can proceed via two different routes. On oxides with a low lattice energy, bulk acetates are formed, decomposition of which leads to acetone. On oxides with a high lattice energy, the reaction to acetone takes place on the surface and leaves the bulk structure of the catalyst unaltered.

The surface reaction of aliphatic acids to ketones probably proceeds via an intermediate that is oriented parallel to the surface and chemically interacts with the catalyst via both the carboxyl group and the α-carbon of the alkyl group. For the latter interaction, abstraction of an α-hydrogen atom is required. The so-formed alkylidene group of this intermediate can react with a neighboring carboxylate and a hydrogen atom to give the ketone. The remaining carboxyl group forms CO_2. The intermediate is very likely in pseudoequilibrium with the corresponding ketene.

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