The formation of ketones and aldehydes from carboxylic acids, structure–activity relationship for two competitive reactions

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Abstract

Four carboxylic acids with a number of α-hydrogen atoms ranging from three to zero were tested in the selective hydrogenation to aldehyde. The acids used were acetic, propanoic, isobutyric, and pivalic acid. The oxides of iron, vanadium, zirconium, and titanium were used as catalysts. It was found that by decreasing the number of α-hydrogen atoms the selectivity to the aldehyde increased, while the formation of the main by-product, ketone, was suppressed. It is suggested that this is due to the fact that the ketonisation proceeds via a ketene-like intermediate, the formation of which needs the presence of α-hydrogen. Furthermore, the reactions to aldehyde and ketone seem to be in competition with each other.

1. Introduction

Aldehydes are not only widely used as fragrances and flavours, but also serve as intermediates in the production of agrochemicals, dyes, and other commonly used chemical compounds [1]. So there is a considerable demand for aldehydes. As most carboxylic acids are directly available from natural resources or easy to synthesize, there is incentive to use these acids for the production of aldehydes. The most common way to do this is the so-called *Rosenmund reduction* [2]. This two-step reaction, however, has the disadvantage of producing large quantities of waste. A cheaper and cleaner method to perform this reaction would be the direct catalytic reduction of carboxylic acids by hydrogen.

Until now there have been only a few patents that describe the possibility of this direct catalytic reduction (e.g. Refs. [3–6]). All these patents indicate that, in order to make the reaction possible, the acid must not contain more then one α-hydrogen atom. Examples are the production of the aldehydes from 2,2-dimethylpropionic acid [7] and from benzoic acid [8–10], which both have no α-hydrogen. The latter one is the only reaction already applied commercially.

However, in contradiction to what the patents claim, acetic acid can be reduced to acetaldehyde [11,12]. Even though this acid contains three α-hydrogen atoms. It has been established that the selective reduction occurs only when three conditions are fulfilled. First, hydrogen must be present in the gas phase. Second, the catalyst must consist of both a metallic and an oxidic phase. Third, the oxidic phase must be an oxide with a

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moderate metal–oxygen bond strength. If all these conditions are not fulfilled, acetone is the main product.

As it is known that acetic acid can be reduced, it is desirable to learn about the exact influence of the number of α-hydrogen atoms on the selective reduction. This question is especially interesting since the commonest side-reaction is the formation of ketone from two molecules of carboxylic acid. It has been suggested that this reaction needs the presence of α-hydrogen. But the literature does not agree on the reason for this [13]. A plausible explanation is that the reaction to the ketone proceeds via a ketene-like intermediate [12–15]. It is impossible to form this ketene when no α-hydrogen is present. Another possibility is that the ketone is formed via a β-ketoacid [16]. The formation of a β-ketoacid also needs the abstraction of an α-hydrogen atom. Thus, in addition to investigating the influence of α-hydrogen atoms on the aldehyde formation, we also addressed the problem of the mechanism of ketone formation.

Four carboxylic acids were tested, which have a number of α-hydrogen atoms ranging from zero to three (i.e. pivalic, isobutyric, propionic, and acetic acid). Four different oxides were used as catalysts: titanium and zirconium oxide, which have a strong metal–oxygen bond strength, vanadium oxide, which has an intermediate bond strength, and iron oxide, which has a low metal–oxygen bond strength. The influence of varying the contact time was tested on zirconia.

2. Experimental

The pure oxides were used as purchased, i.e. as powders (Fe_2O_3: Fluka, Switzerland; TiO_2: Tioxide, England; V_2O_5: BDH, England; ZrO_2: Merck, Germany). The acids were obtained from J.T. Baker, Holland (acetic acid, 99–100%), Aldrich, Germany (propionic acid, 99 + %), and Janssen, Belgium (isobutyric acid, 99.5%, and pivalic acid, 99%). The catalytic experiments were performed in a flow system at atmospheric pressure. A hydrogen flow (20 ml/min) was saturated with the car-
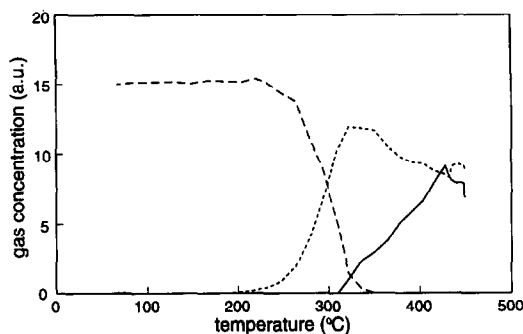

Fig. 1. The temperature-programmed reaction of acetic acid over titanium oxide. (– – –) acetic acid; (——) acetaldehyde; (- - - -) acetone.

boxylic acid at a temperature where the saturation pressure was about 25 mbar. The gas mixture was led over a microreactor containing 0.2 g of catalyst. The catalysts were not pretreated or activated in any way before starting the reaction. During the temperature-programmed reaction, temperature was raised from room temperature to 450°C at a 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 GC) equipped with an FID detector. The recorded values of the peak areas were converted into gas concentrations by using sensitivity factors determined by calibration.

The selectivities were calculated as the molecular percentage of all organic products. Since both pivalic acid and its products decomposed partly, only the undecomposed products were taken into account, when this acid was studied.

The experiments on zirconia were done in a similar flow system, but analysis was done with a mass spectrometer. Apparatus and data evaluation have been described earlier [11].

3. Results

At low temperatures, acetone is the only product formed on titanium oxide. At high temperatures acetaldehyde is formed, too (Fig. 1). Isobutyric acid leads to the same type of products, but with a relatively high amount of the aldehyde (isobutyraldehyde) and almost no ketone (2,4-
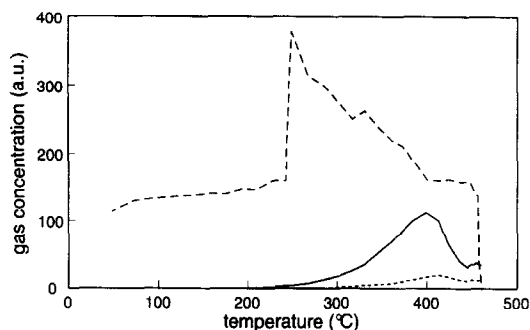
Fig. 2. The temperature-programmed reaction of isobutyric acid over titanium oxide. (– – –) isobutyric acid; (———) isobutyraldehyde; (- - - -) 2,4-dimethyl-3-pentanone.

dimethyl-3-pentanone) (Fig. 2). The steep rise in isobutyric acid around 240°C is caused by desorption of the acid from relatively cold spots near the reactor.

Other acids with a different number of α-hydrogen atoms were also tested. The selectivities to aldehyde and ketone are plotted in Fig. 3.

Aldehyde selectivity increases and ketone production is suppressed by diminishing the number of α-hydrogen atoms in the acid (propionic acid on titania is the only exception). In the literature it is suggested that ketene could be an intermediate in the production of ketones [12–15], and for the formation of ketene α-hydrogen is needed. Therefore, the possibility of ketene being an intermediate was more closely investigated here. This was done by changing the contact time of the reactants, during the acetic acid hydrogenation. Since it has a low activity and produces both ketene and ketone, zirconia was used as a catalyst. The partial pressures of the products are given in Table 1.

By increasing the contact time, two things happen. Ketone is produced more at longer contact times, while ketene is formed less.

In Fig. 4 the results are given for the hydrogenation of a reaction mixture containing both acetic and isobutyric acid. The formation of the aldehydes and symmetric ketones from the separate acids can be seen, as well as the production of the mixed ketone (3-methyl-2-butanone). It is noteworthy that, when acetic acid is present, the production of the aldehyde from isobutyric acid is low. This can be seen by comparing the reaction

in the presence of acetic acid (Fig. 4) with the reaction in the absence of acetic acid (Fig. 2).

The appearance of three compounds in the low temperature regime is most likely caused by dimerisation of the acid on the GC column. Notice that two acids can form three different dimers, and thus cause three distinct FID signals. An increase of column temperature indeed decreased the con-
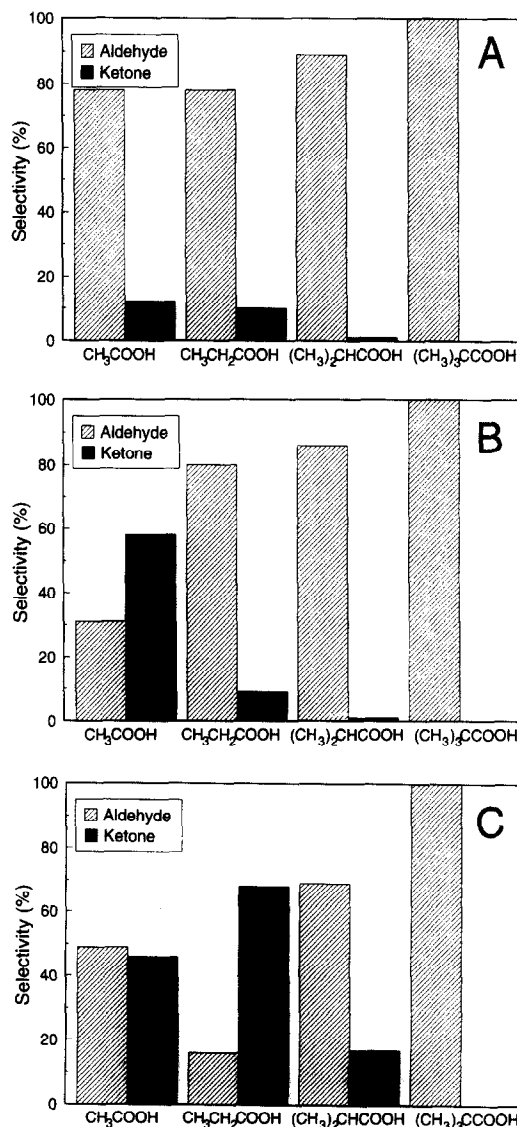

Fig. 3. The selectivities to the various aldehydes and ketones in the reaction of four acids, which have a number of α-hydrogen atoms ranging from three to zero. The catalysts used are the oxides of (A) iron, (B) vanadium, and (C) titanium. The selectivities are determined during a temperature-programmed reaction at 350°C for iron oxide, at 440°C for vanadia, and at 430°C for titania. These temperatures are in the range where the optimum aldehyde yield was found.

Table 1
The reaction of acetic acid over zirconia [a]

Amount of catalyst (mg)	Acetone, partial pressure (a.u.)	Ketene, partial pressure (a.u.)	Conversion (%)
104.5	0.15	0.08	40
203.4	0.20	0.05	47
401.2	0.40	0.01	93

[a] At 450°C, during temperature programmed reaction. The product partial pressures and conversion using different amounts of catalyst (i.e., with varying contact times.

tribution of the (mixed) dimers, resulting in only two detectable compounds, but also giving poorer resolution for the products.

Finally, an experiment has been done to test the stability of the iron oxide catalyst, by following the reaction of acetic acid at 380°C as a function of time. Although the total conversion decreases, the yield of acetaldehyde remains practically constant. Only the decrease in acetone formation is responsible for the drop in activity.
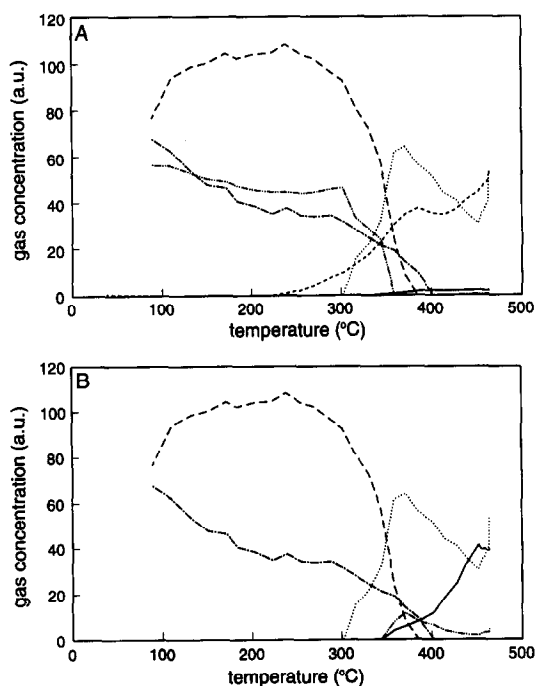

Fig. 4. The temperature-programmed reaction of acetic acid together with isobutyric acid over titanium oxide (mixed ketone: 3-methyl-2-butanone, large ketone: 2,4-dimethyl-3-pentanone). (A) (– – –) acetic acid; (· — · — ·) isobutyric acid; (· · — · · — · ·) dimer; (- - - -) acetone; (· · · · ·) mixed ketone; (———) large ketone. (B) (– – –) acetic acid; (· — · — ·) isobutyric acid; (———) acetaldehyde; (· · — · · — · ·) isobutyraldehyde; (· · · · ·) mixed ketone.

4. Discussion

As Fig. 2 and Fig. 3 show, it is possible to produce aliphatic aldehydes from acids other than acetic acid. So the selective reduction of acetic acid found earlier [11] is not an exception. By diminishing the number of α-hydrogen atoms, the selectivity to aldehydes is even increased, while the production of ketones is suppressed. This explains why the patent literature, in which aldehyde is the desired product [3–6], recommends the use of acids with no more than one α-hydrogen.

The ketone formation completely disappears when no α-hydrogen is present in the acid. Two explanations for this phenomenon can be put forward. First, the methyl groups can hinder sterically the reaction of two acids to ketone. When two intermediates are brought together to form the ketone, the reaction can in principle be hindered by bulky methyl groups. Second, the α-hydrogen atom can be important in the formation of an intermediate in the reaction to ketone.

Benzoic acid, just as pivalic acid, has no α-hydrogen. However, a smaller steric hindrance is expected from the phenyl group compared with the three methyl groups of pivalic acid. Surprisingly, also benzoic acid hardly ever forms its ketone, i.e. benzophenone, under comparable catalytic conditions [17]. Thus, the steric hindrance alone does not seem to be decisive for the formation of ketone from two intermediate species. The remaining possibility is that the presence of α-hydrogen is a prerequisite for the formation of the intermediate.

Table 1 shows that, by increasing the contact time, the production of ketene is suppressed, while the production of acetone is favoured. This indicates that ketene is a potential intermediate in the reaction to acetone. This has already been suggested earlier for acetone formation under low pressure conditions [12,13], but had not yet been found for reactions under higher (atmospheric) pressure. Ketene formation needs the abstraction of an α-hydrogen atom from the acid by the surface. Pivalic acid, of course, cannot form ketene, and in isobutyric acid the α-hydrogen is protected by two methyl groups. Furthermore, it is known for Pt(111) that there is a repulsive interaction between methyl groups and the catalyst surface. The methyl groups, therefore, force the adsorbed molecule into an orientation with the molecular axis perpendicular to the surface [18]. The same effect is expected with the catalysts described here. In this way the methyl groups hinder the abstraction of the α-hydrogen atom by the surface. Summarising, the formation of ketene is suppressed by replacing α-hydrogen atoms by methyl groups. As ketene is an intermediate, the ketone formation decreases as well. This explains the increase in selectivity to aldehyde when going from acetic acid, via propionic acid and isobutyric acid to pivalic acid.

If ketene or a ketene-like species is indeed an intermediate in the ketonisation, the reaction scheme as proposed earlier by us [12] is also applicable here. Scheme 1 illustrates the proposed mechanism for ketonisation in the case of acetic acid. Carboxylic acid adsorbs heterolytically on the catalyst surface to form a carboxylate. An α-hydrogen atom can subsequently be abstracted from the carboxylate. This is only possible when the intermediate is adsorbed horizontally (e.g. like intermediate I_1). In this orientation, a C_1 unit can
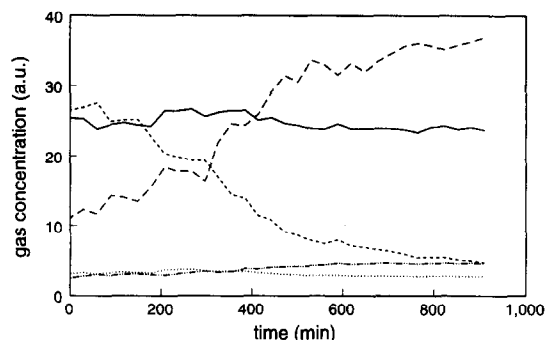

Fig. 5. The reaction of acetic acid over iron oxide at constant temperature (380°C). (– – –) acetic acid; (———) acetaldehyde; (· · · · ·) ethanol; (- - - -) acetone; (· · – · · – · ·) methane.

easily be split off, either from I_1 or I_2. In order to form acetone, this C_1 unit has to be coupled to a neighbouring carboxylate.

Probably the reaction to ketone is competing with the aldehyde production. As can be seen in Fig. 3, suppression of the ketone formation goes hand in hand with an increase in aldehyde production. Fig. 4 shows that the production of the mixed ketone is accompanied by a lower formation of the isobutyraldehyde compared with the reaction without acetic acid (Fig. 2). A possibility is that a ketene-like intermediate attacks the carboxylate of isobutyric acid before the latter can react to give aldehyde.

It is likely that the two competing reactions – i.e., aldehyde versus ketone formation – take place on different sites, with a different sensitivity to deactivation (Fig. 5). The site for the production of aldehyde hardly deactivates in time. We suggested that this site could be an oxygen vacancy [11], with, for example, an intermediate as proposed by Ding et al. [7]. Although these authors do not mention it explicitly, their suggested intermediate exchanges oxygen with the surface and it, therefore, reacts via a Mars and Van Krevelen mechanism. The site for the production of ketone,
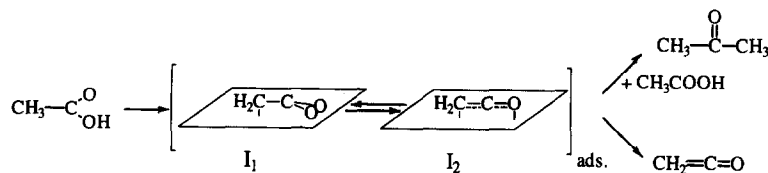
Scheme 1.

however, deactivates in time. According to the authors in Ref. [19,20] this site could be a doubly unsaturated cation. This would nicely fit in the picture as presented in Scheme 1, where a ketene-like intermediate has to react with a neighbouring carboxylate to form the ketone. For this reaction, the requirement of a doubly unsaturated reaction site would be very plausible.

5. Conclusions

It is possible catalytically to produce aldehydes from a range of simple aliphatic carboxylic acids. The main by-product is ketone. Its formation is suppressed by diminishing the number of α-hydrogen atoms. The reason for this is that probably ketene is an intermediate in the reaction to ketone.

The reactions to aldehydes and ketones are competitive, so the suppression of one reaction leads to an increase in selectivity for the other reaction.

Acknowledgements

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