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CATALYTIC AND STOICHIOMETRIC REDUCTION OF KETONES AND ALDEHYDES BY THE HYDRIDOTETRACARBONYL FERRATE ANION

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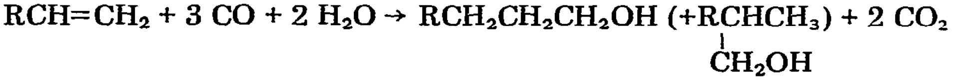
Summary

Acetone is catalytically reduced to isopropyl alcohol by carbon monoxide and water in the presence of iron carbonyls and triethylamine at 100°C and 100 bar. Use of NaOH in place of triethylamine gives a much less efficient catalyst system. The $Et_3NH \cdot HFe(CO)_4$ system also catalyses the reduction of n-butyraldehyde to n-butyl alcohol at room temperature in a fast stoichiometric reaction, whereas $NaHFe(CO)_4$ is inactive under the same conditions. The Et_3NH^+ cation is necessary for the transfer of a proton to the carbonyl group, while the $HFe(CO)_4^-$ anion carries out nucleophilic attack on carbonyl group and supplies the hydride ion.

Introduction

The hydroformylation of olefins with carbon monoxide and water (as the hydrogen source) in the presence of a base is catalysed by several metal carbonyls [1—12]. The first example of this reaction was the so called Reppe synthesis of alcohols, under the conditions used the aldehydes formed were hydrogenated in situ to the corresponding alcohols by the action of the $Fe(CO)_{53}$ + base catalyst system [1,3]:



$$RCH{=}CH_2 + 3\,CO + 2\,H_2O \rightarrow RCH_2CH_2CH_2OH\ (+R\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCH_3) + 2\,CO_2$$

Little is known about the factors influencing hydroformylation and related reactions catalyzed by metal carbonyls in basic water solution. Sternberg [2] and Pettit [8,9,11] have shown that the hydroformylation and the aldehyde hydrogenation step of the Reppe alcohol synthesis demand somewhat different reaction conditions. Sternberg observed, when sodium hydroxide was used as a

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base, aldehyde became the main product, while Pettit recognized that the hydrogenation reaction is favoured by increasing the pH of the medium. In the case of Ru, Rh, Os and Ir carbonyls, aldehyde formation was the main reaction [8,10], but no efforts were made to increase the amounts of alcohol.

To gain more insight into some of these problems a systematic study of the hydrogenation of ketones and aldehydes using iron carbonyls in basic solutions as catalysts or stoichiometric reagents was started.

Results and discussion

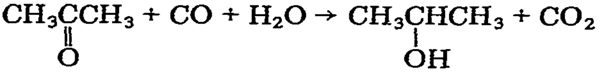
Acetone was chosen as the model substrate for the catalysis studies because preliminary experiments had shown that aldehydes undergo several side reactions under the reaction conditions. (In the case of n-butyraldehyde, for example, six organic products were detected by GLC.) $Fe_3(CO)_{12}$ was used as the catalyst precursor since it is easier to handle than $Fe(CO)_5$. The equivalence of the two iron carbonyls was proved by parallel experiments (Table 1). Reactions were always carried out at 100°C and 100 bar CO initial pressure (at 20°C).

With Et_3N as the base it was found that the extent of conversion of acetone into isopropyl alcohol increases with increasing concentration of the iron complex and the base (Figs. 1 and 2), and is only slightly affected by the CO pressure (Fig. 3).

The levelling off of the conversion/concentration curves at about 70% even when the catalyst concentration is increased is apparently due to several simultaneous inhibiting effects:

a) Lower aliphatic alcohols such as methanol (Fig. 4), ethanol (Table 1) and isopropyl alcohol (Fig. 5) inhibit the hydrogenation, for reasons which are not clear at present.

b) CO_2 is formed in equimolar amount (eq. 1) and strongly decreases the pH of the medium, and is therefore also an effective inhibitor (Table 1).



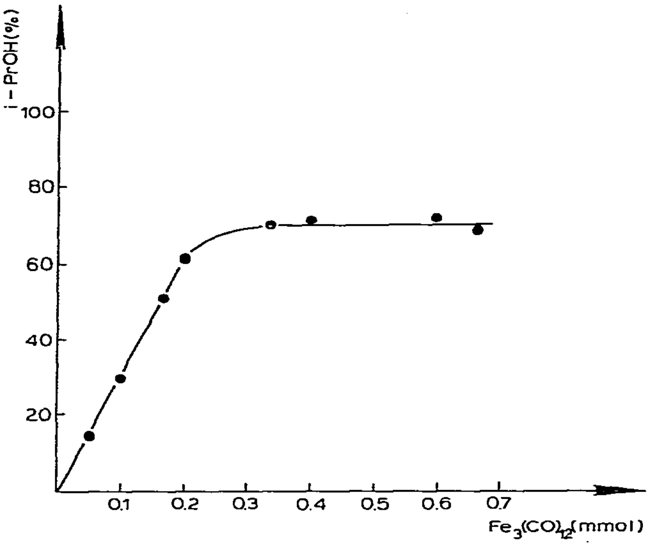
$$CH_3\underset{\overset{\|}{O}}{C}CH_3 + CO + H_2O \rightarrow CH_3\underset{\overset{|}{OH}}{C}HCH_3 + CO_2 \qquad (1)$$

TABLE 1

CATALYTIC HYDROGENATION OF ACETONE [a]

Catalyst	Base	Additive	Conversion, (%)
1 mmol $Fe(CO)_5$	10 mmol Et_3N	—	73.4; 73.1
0.33 mmol $Fe_3(CO)_{12}$	10 mmol Et_3N	—	69.9; 72.3
0.33 mmol $Fe_3(CO)_{12}$	10 mmol Et_3N	2.7 ml ethanol [b]	4.4
0.33 mmol $Fe_3(CO)_{12}$	10 mmol Et_3N	5 bar CO_2	4.3
0.33 mmol $Fe_3(CO)_{12}$	10 mmol Et_3N	5 mmol HCOOH	25.5
0.33 mmol $Fe_3(CO)_{12}$	10 mmol Et_3N	10 mmol HCOOH	7.6
0.33 mmol $Fe_3(CO)_{12}$	10 mmol NaOH	—	4.6
0.33 mmol $Fe_3(CO)_{12}$	5 mmol $Na_2(CO)_3$	—	4.6
0.33 mmol $Fe_3(CO)_{12}$	10 mmol HCOONa	—	1.3

[a] Reaction conditions: 10 mmol acetone (0.74 ml), 300 mmol water (5.4 ml), 100 bar CO, 100°C, 6 h.
[b] 2.7 ml water were used.



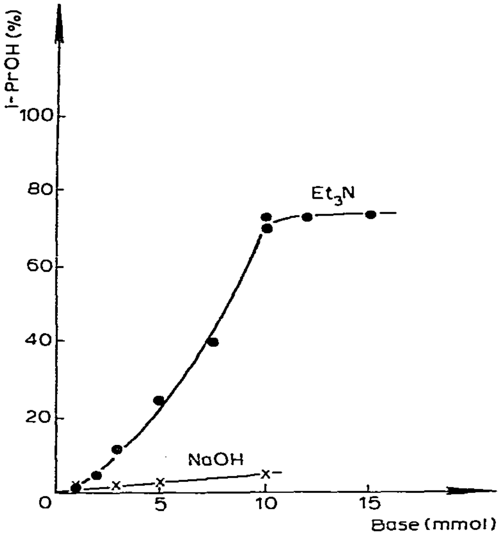


Fig. 1. Effect of base concentration on the catalytic hydrogenation of acetone. Reaction conditions: 10 mmol acetone, 0.33 mmol $Fe_3(CO)_{12}$, 5.4 ml water, 100 bar CO, 100°C, 6 h.

Fig. 2. Effect of catalyst concentration on the catalytic hydrogenation of acetone. Reaction conditions: 10 mmol acetone, 10 mmol Et_3N, 5.4 ml water, 100 bar CO, 100°C, 6 h.

c) The CO reacts with OH^- ions under the conditions to give formates [13], and this also causes a gradual decrease of the pH. The inhibiting effect of this reaction is shown by the decrease of acetone conversion on adding formic acid to the reaction mixture (Table 1).

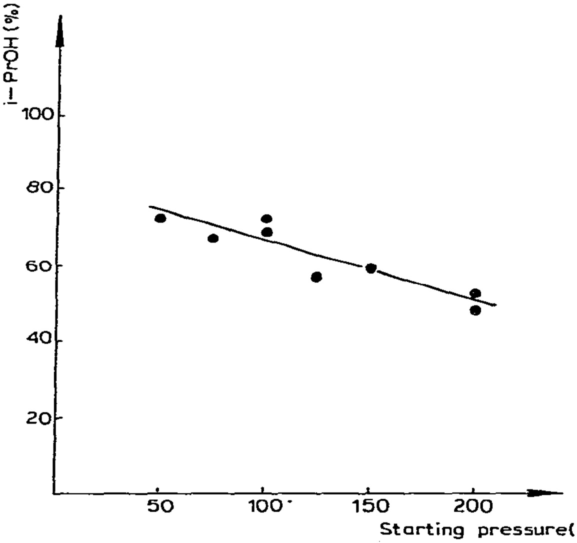


Fig. 3. Effect of carbon monoxide pressure on the catalytic hydrogenation of acetone. Reaction conditions: 10 mmol acetone, 10 mmol Et_3N, 0.33 mmol $Fe_3(CO)_{12}$, 5.4 ml water, 100°C, 6 h.

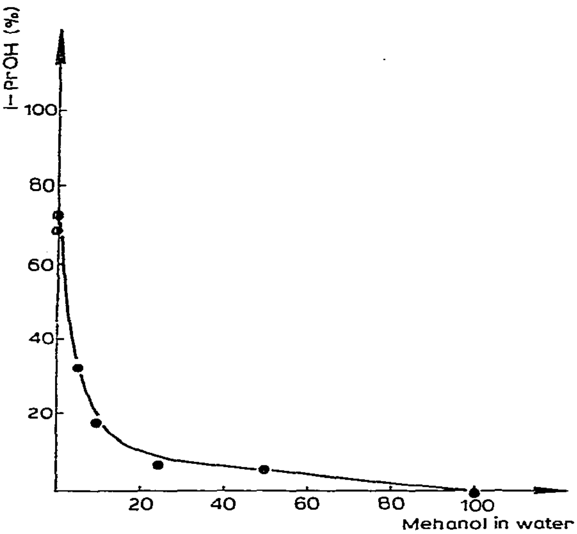


Fig. 4. Effect of methanol on the catalytic hydrogenation of acetone. Reaction conditions: 10 mmol acetone, 10 mmol Et_3N, 0.33 mmol $Fe_3(CO)_{12}$, 5.4 ml solvent (water + methanol), 100 bar CO, 100°C, 6 h.

The possibility that the retarding effect of isopropyl alcohol is due to the existence of an equilibrium cannot be ruled out on thermodynamic grounds since no reliable calculations can be made for the system investigated. However, equilibrium cannot provide the explanation for this phenomenon, because conversions up to 95% were observed in experiments with longer reaction times, and furthermore experiments to observe the reverse reaction starting from isopropyl alcohol and CO containing CO_2 failed; even at 150°C no formation of acetone was detected.

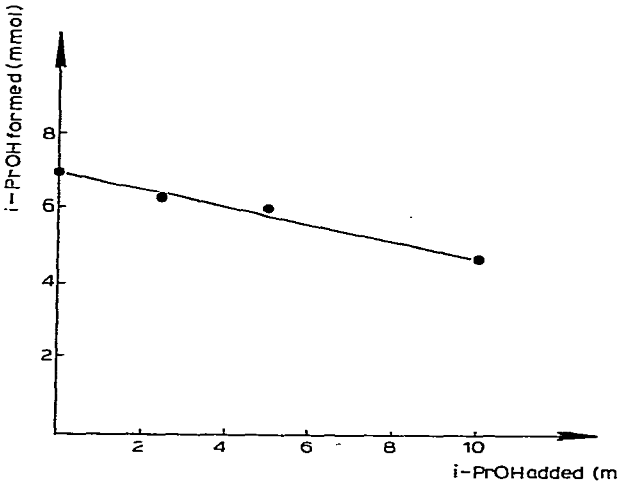


Fig. 5. Effect of isopropyl alcohol on the catalytic hydrogenation of acetone. Reaction conditions: 10 mmol acetone, 10 mmol Et_3N, 0.33 mmol $Fe_3(CO)_{12}$, 5.4 ml solvent (water + isopropyl alcohol), 100 bar CO, 100°C, 6 h.

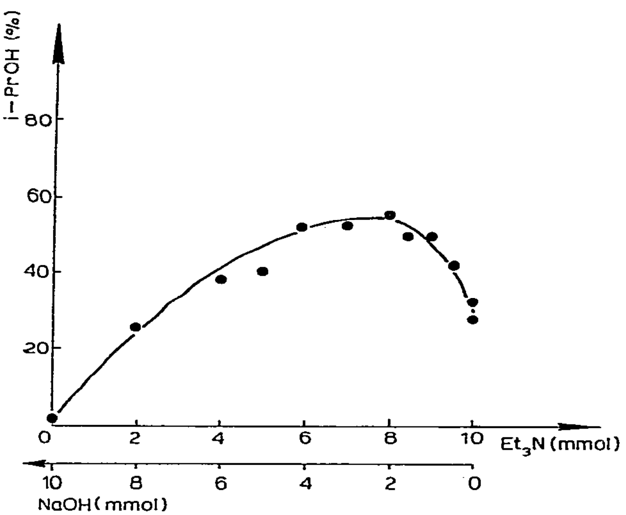


Fig. 6. Effect of base composition on the catalytic hydrogenation of acetone. Reaction conditions: 10 mmol acetone, 10 mmol base (Et_3N + NaOH), 0.33 mmol $Fe_3(CO)_{12}$, 5.4 ml water, 100 bar CO, 100°C, 2 h.

The inhibiting effect of alcohols is in sharp contrast to the favourable effect of methanol in the water gas shift reaction, which is catalyzed by the $Fe(CO)_5$ + NaOH catalyst system at higher temperatures [13]. The formation of hydrogen was negligible under our mild conditions, only about 1% of H_2 being present in the product gases.

Another important difference between the acetone hydrogenation and the water gas shift reaction is the apparently different role of the base in the two reactions. King has shown [13] that in the case of the water gas shift reaction the role of the base is only to form the OH^- ion, and since both NaOH and Na_2CO_3 are rapidly transformed to sodium formate the three bases are equally effective. In our case, however, Et_3N was far more effective than NaOH or Na_2CO_3, and NaOOCH was almost inactive (Table 1).

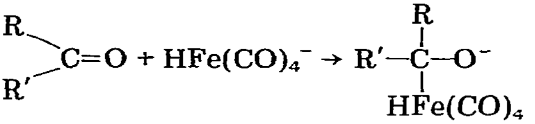
The more complex role of the base is shown even more clearly by experiments using NaOH and Et_3N together in different ratios (Fig. 6). There is a synergistic effect between the two bases, and the highest reaction rates were obtained with a Et_3N/NaOH ratio of 4/1. This result prompted us to investigate the stoichiometric reaction between the hydridotetracarbonyl ferrate anion and simple organic carbonyl compounds. Ethanolic solutions of $Et_3NH \cdot HFe(CO)_4$ and $NaHFe(CO)_4$ were prepared from $H_2Fe(CO)_4$ [14] and treated with aldehydes and ketones at room temperature. Ketones did not react under these conditions, but the reaction between aldehydes and $Et_3NH \cdot HFe(CO)_4$ was found to be fast, and $HFe(CO)_4^-$ was converted into $Fe(CO)_5$ and $HFe_3(CO)_{11}^-$ within a few minutes.

This reaction was investigated in detail with n-butyraldehyde as a model substance. The formation of $HFe_3(CO)_{11}^-$ was indicated by the infrared spectrum, and the $Fe(CO)_5$ could be extracted with hexane. It was estimated by IR spectroscopy to represent 20—25% of the iron content of the mixture. At the same time 0.65—0.75 mol alcohol per mol of iron was formed. These results suggest the following stoichiometry for the reaction:

$$3\ \text{n-PrCHO} + 4\ Et_3NH \cdot HFe(CO)_4 \rightarrow 3\ \text{n-PrCH}_2OH + Et_3NH \cdot HFe_3(CO)_{11}^- + Fe(CO)_5 + 3\ Et_3N$$

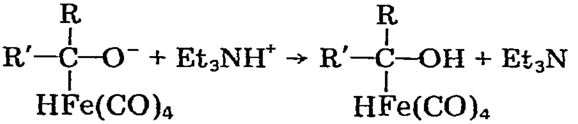
No reaction was observed when $NaHFe(CO)_4$ was used instead of $Et_3NH \cdot HFe(CO)_4$ in the above experiment. Alcohol formation started immediately, however, when an equivalent amount of $Et_3N \cdot HCl$ was added to the reaction mixture (Fig. 7). Clearly the Et_3NH^+ cation was needed for the stoichiometric hydrogenation of aldehyde to alcohol, and this accounts for the pronounced difference between NaOH and Et_3N in the catalytic experiments.

We therefore propose the following mechanism (eq. 2—6) for the catalytic hydrogenation of aldehydes and ketones in the presence of $HFe(CO)_4^-$:



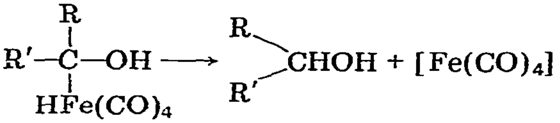
$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}O + HFe(CO)_4^- \rightarrow R'{-}\underset{HFe(CO)_4}{\overset{R}{\underset{|}{\overset{|}{C}}}}{-}O^- \qquad (2)$$

(I)



$$R'{-}\underset{HFe(CO)_4}{\overset{R}{\underset{|}{\overset{|}{C}}}}{-}O^- + Et_3NH^+ \rightarrow R'{-}\underset{HFe(CO)_4}{\overset{R}{\underset{|}{\overset{|}{C}}}}{-}OH + Et_3N \qquad (3)$$

(II)



$$R'{-}\underset{HFe(CO)_4}{\overset{R}{\underset{|}{\overset{|}{C}}}}{-}OH \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!CHOH + [Fe(CO)_4] \qquad (4)$$

$$[Fe(CO)_4] + CO \rightarrow Fe(CO)_5 \qquad (5)$$

$$Fe(CO)_5 + HO^- \rightarrow HFe(CO)_4^- + CO_2 \qquad (6)$$

In the first step (eq. 2) the $HFe(CO)_4^-$ anion carries out a nucleophilic attack in in the carbonyl groups. Aldehydes are much more reactive in this type of reaction, and this accounts for the reactivity difference observed in the stoichiometric experiments. In the second step (eq. 3) adduct I is protonated by the relatively strong acid Et_3NH^+. In the absence of Et_3NH^+ only water or alcohol, which are both very weak acids, can function as proton donors. Apparently, I is a too weak base to abstract the proton from water or alcohols, and this explains the low rates of hydrogenation in the absence of Et_3N.

The third step (eq. 4) is the reductive elimination of the alcohol from II. The $[Fe(CO)_4]$ fragment is either captured by $HFe(CO)_4^-$ (ultimately yielding the $HFe_3(CO)_{11}^-$ cluster anion) or transformed by CO into $Fe(CO)_5$ (eq. 5). Under catalytic conditions (high P_{CO}) the second route may be the main one, and the $Fe(CO)_5$ so formed then reacts with the OH^- anion (generated by the base present) to re-form $HFe(CO)_4^-$ (eq. 6) [13].

Reaction 5 is obviously favoured by increasing the concentration of OH^-,

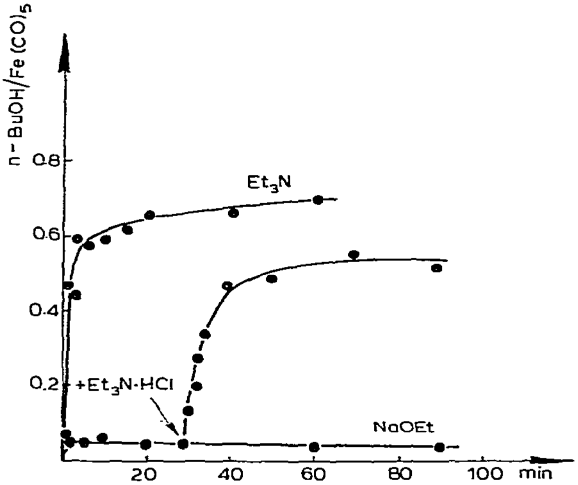


Fig. 7. Stoichiometric hydrogenation of n-butyraldehyde with $H_2Fe(CO)_4$ in ethanol solution in the presence of Et_3N or NaOEt. Effect of added $Et_3NH \cdot HCl$.

and this explains the rate increase when small amounts of NaOH (a strong base) partly replace Et_3N (a weak base). If the concentration of the latter is greatly diminished, the rate of the reaction decreases, however, because of the deficiency of the strongly acidic proton donor Et_3NH^+.

The homogeneous hydrogenation of carbonyl compounds catalyzed by $HFe(CO)_4^-$ thus follows an A_N mechanism typical of organic carbonyl groups, and is catalyzed at the same time by acid and base. The two hydrogen atoms are transferred in two different forms to the carbonyl group; one of them as a proton and the other one as a hydride ion.

Experimental

Catalytic experiments

10 mmol of acetone (0.74 ml), 10 mmol of Et_3N (1.39 ml), 0.33 mmol of $Fe_3(CO)_{12}$ (168 mg) and 300 mmol of water (5.4 ml) were placed in a 20 ml stainless steel autoclave which was then flushed with Ar and pressured with CO to 100 bar. The autoclave was rocked for 6 hours at 100° C. A colourless aqueous solution containing a few drops of a red oily substance was formed. The aqueous solution was analyzed by GLC, and the only product observed was isopropyl alcohol.

Stoichiometric experiments

20 mmol of $Fe(CO)_5$ (2.8 ml) were treated under Ar with 8 ml of 50% aqueous NaOH in 40 ml of ethanol at room temperature with stirring for 1 hour, and the colourless suspension then acidified with dilute HCl in the presence of 50 ml hexane at 0° C (to minimize the decomposition of $H_2Fe(CO)_4$). The hexane layer was separated and to 40 ml of it was added 4.0 ml of Et_3N (29 mmol), which produced a red oil. The hexane was decanted off and 42 mmol of n-butyraldehyde (3.8 ml) in 25 ml ethanol were added to the red oil. 2 ml sam-

ples were withdrawn by syringe from the reaction mixture at appropriate intervals and injected into an ethanolic iodine solution to stop the hydrogenation. (The iodine immediately oxidised the $HFe(CO)_4^-$ anion to $HFe_3(CO)_{11}^-$, as indicated by the IR spectrum and evolution of CO). The products were quantitatively analysed for butyl alcohol by GLC using an internal standard.

The infrared spectrum of an ethanolic solution of the red oil produced by the addition of Et_3N showed bands at 2000w, 1920(sh) and 1890vs cm^{-1}, indicating it to contain mainly $HFe(CO)_4^-$ [15] and some $HFe_3(CO)_{11}^-$ (the strongest band of $HFe_3(CO)_{11}^-$ appears at 2000 cm^{-1} [16]. This was consistent with the colour. When NaOEt in ethanol was used instead of Et_3N, a similar red oil with identical infrared spectrum was obtained, and the rest of the experiment was performed as above.

The yield of $HFe(CO)_4^-$ was 93—97%. The water layers obtained after acidification contained about 2% of the total iron, and the hexane solution left after separation of the red oil was shown by IR spectroscopy to contain 1—5% of the initial $Fe(CO)_5$.

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