HOMOGENEOUS HYDROGENATION OF KETONES USING CHROMIUM HEXACARBONYL AS CATALYST PRECURSOR IN THE PRESENCE OF BASES

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Summary

The hydrogenation of ketones at 100–120°C and 100 bar H_2 is catalyzed by $Cr(CO)_6$ in methanol solution in the presence of NaOMe. The reaction is inhibited by CO and the rate increases with increasing H_2 pressure and base:chromium ratio. In a stoichiometric reaction at 75°C, $HCr(CO)_5^-$ hydrogenates ketones to alcohols, while forming $Cr_2(CO)_{10}^{2-}$. A catalytic cycle involving alkoxychromium complexes, $R_2CHOCr(CO)_5^-$, as intermediates is proposed. Similar hydrogenation catalysts are obtained from $W(CO)_6$ and $Mo(CO)_6$; the latter is the most active and may be used even at 70–80°C.

Introduction

The activity of systems composed of metal carbonyls and bases as homogeneous catalysts for the water gas shift reaction is now well recognized and several metal carbonyls have been tested for this reactivity [1]. Ruthenium [2,3], the Group VI metals (Cr, Mo, W) [4], and iron [5] have been investigated in the most detail and in all cases anionic metal carbonyl hydrides were found, or thought to be present, in the reaction mixtures and to play an important role in the catalytic cycles.

We have shown that $HFe(CO)_4^-$ and Et_3NH^+, formed from $Fe(CO)_5$ under the conditions of the water gas shift reaction, is an active catalysts for the hydrogenation of ketones [6] and that the same catalyst system is produced from $Fe(CO)_5$ and H_2 if Et_3N is used as the solvent [7]. With these observations in mind it seemed reasonable to test other metal carbonyls which form anionic metal hydrides under water gas shift conditions as catalysts for the hydrogenation of ketones in the presence of bases. In this paper we report the results obtained with $Cr(CO)_6$ and, to some extent, with $Mo(CO)_6$ and $W(CO)_6$.

Results and discussion

Catalytic experiments

The results of our preliminary experiments on the hydrogenation of acetophenone using the three Group VI metal carbonyls as catalyst precursors are compiled in Table 1. The following conclusions can be drawn from these results.

Active catalysts are formed only in the presence of a relatively strong base, which may be either Et_3N (which also serves as the solvent) or NaOMe (in which case methanol is the solvent). All three hexacarbonyls provided more active catalysts with
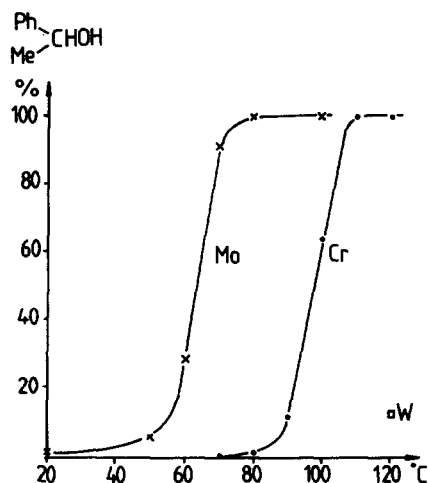

Fig. 1. Effect of temperature on the hydrogenation of acetophenone with $Mo(CO)_6$ (Mo), $Cr(CO)_6$ (Cr) or $W(CO)_6$ (W) as catalyst precursor. Reaction conditions: 10 mmol acetophenone, 0.5 mmol $M(CO)_6$, 1 mmol NaOMe, 4 ml MeOH, 100 bar H_2 at 20°C, 3 h.

TABLE 1

HYDROGENATION OF ACETOPHENONE WITH $M(CO)_6$ CATALYSTS

(M = Cr, Mo, W) [a]

Metal carbonyl	Solvent	Base (mmol)	Temperature (°C)	Conversion to alcohol (%)
$Cr(CO)_6$	Et_3N	–	160	62.4
	Pyridine	–	160	3.0
	Hexane	–	160	0.3 [b]
	MeOH	–	160	3.1 [b]
	MeOH	NaOMe (1)	100	63.5
$Mo(CO)_6$	Et_3N	–	220	47.0
	MeOH	NaOMe (1)	70	91.2
$W(CO)_6$	Et_3N	–	160	55.3
	MeOH	NaOMe (1)	120	12.0
$Fe(CO)_5$	Et_3N	–	150	34.8 [c]
	MeOH	NaOMe (1)	150	1.0 [c,d]

[a] Reaction conditions: 10 mmol acetophenone, 0.5 mmol $M(CO)_6$, 4 ml solvent, 100 bar H_2 at 20°C, 3 h.
[b] Precipitate in product. [c] Ref. 7. [d] 1 mmol $Fe(CO)_5$.

NaOMe but their order of reactivity varied; it was Cr > W > Mo with Et_3N and Mo > Cr > W with NaOMe (Fig. 1). The activity of the $M(CO)_6$ + NaOMe catalyst system is in sharp contrast to the inactivity of the $Fe(CO)_5$ + NaOMe system investigated earlier [7] and points to different mechanisms of hydrogenation in the two cases.

To get more insight into the chemistry of these new hydrogenation catalysts, the $Cr(CO)_6$ + NaOMe system was investigated in detail. The effect of temperature, $Cr(CO)_6$ concentration, NaOMe concentration, and of the H_2 and CO partial pressures are shown in Figs. 2–4. The rate of hydrogenation increases with increas-
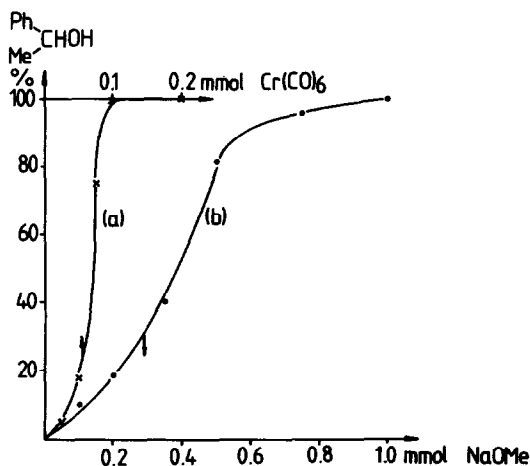

Fig. 2. Effect of the concentration of $Cr(CO)_6$ (a) and NaOMe (b) on the hydrogenation of acetophenone. Reaction conditions: 10 mmol acetophenone, 4 ml MeOH, 100 bar H_2 at 20°C, 120°C, 3 h, 1 mmol NaOMe (a), or 0.5 mmol $Cr(CO)_6$ (b).
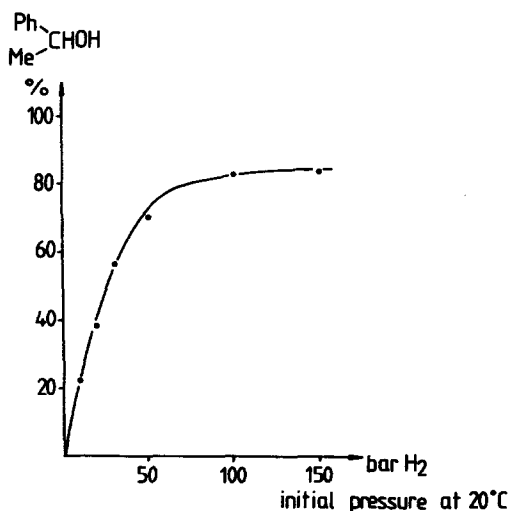

Fig. 3. Effect of H_2 starting pressure on the hydrogenation of acetophenone. Reaction conditions: 2 mmol acetophenone, 0.2 mmol $Cr(CO)_6$, 0.6 mmol NaOMe, 10 ml MeOH, 100°C, 1 h.

ing concentration of $Cr(CO)_6$ and of NaOMe (Fig. 2) and with increasing H_2 pressure (Fig. 3). Carbon monoxide inhibits the reaction (Fig. 4). If significant amounts of CO are present methyl formate is formed according to eq. 1 and can be detected in the product by GLC. This reaction is catalyzed by NaOMe [8].

$$CH_3OH + CO \rightarrow HCOOCH_3 \qquad (1)$$

The formation of methyl formate reduces the CO content of the $H_2 + CO$ mixture (see Fig. 3).

Both aliphatic and aromatic ketones can be hydrogenated in good yield (Table 2), but methyl benzoate is not affected even at higher temperatures. Aldehydes are usually unfavorable substrates for the more active $Cr(CO)_6 + $ NaOMe-containing
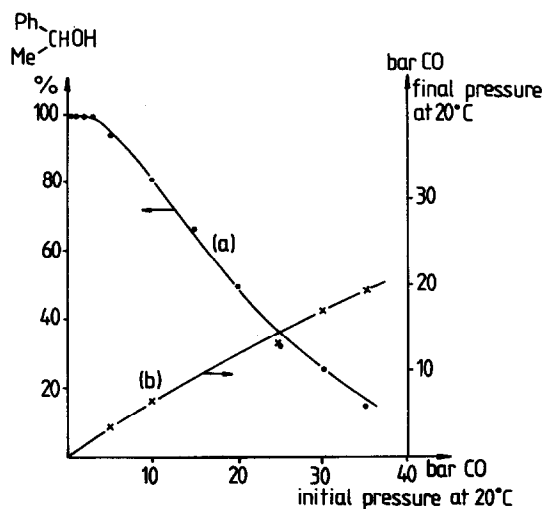

Fig. 4. Effect of CO starting pressure on the hydrogenation of acetophenone (a) and the decrease of CO content (b) due to the formation of methyl formate. Reaction conditions 10 mmol acetophenone, 0.5 mmol $Cr(CO)_6$, 1 mmol NaOMe, 4 ml MeOH, 100 bar total pressure ($H_2 + CO$) at 20°C, 120°C, 3 h.

TABLE 2

HYDROGENATION OF CARBONYL COMPOUNDS

Substrate	Conversion to alcohol (%)	
	With Et$_3$N [a]	With NaOMe [b]
Acetophenone	62.4	99.8
Cyclohexanone	78.4	100
Acetone	24.0	100
Isobutyl methyl ketone	17.3	98.8
Benzaldehyde	98.8	99.6
n-Butyraldehyde	100	–
Methyl benzoate	0	0 [c]
4-t-Bu-cyclohexanone	86.8 [d]	99.4 [e]

[a] Reaction conditions: 10 mmol substrate, 0.5 mmol $Cr(CO)_6$, 4 ml Et$_3$N, 100 bar H_2 at 20°C, 160°C, 3 h. [b] Reaction conditions: 10 mmol substrate, 0.5 mmol $Cr(CO)_6$, 1.0 mmol NaOMe, 4 ml MeOH, 100 bar H_2 at 20°C, 120°C, 3 h. [c] 160°C. [d] cis/trans = 0.63/1. [e] cis/trans = 0.34/1.

catalyst system since the strongly basic conditions may induce secondary reactions.

The reaction shows a pronounced induction period, the length of which depends only on temperature and is not influenced either by $Cr(CO)_6$ or NaOMe concentration or by H_2 or CO pressure. Typical time vs. conversion plots are given in Fig. 5. The start of the reaction is accompanied by a significant change in the IR spectrum of the reaction mixture. In the spectra of samples taken from the autoclave only that of $Cr(CO)_6$ can be seen as long as no hydrogenation has occurred; at the end of the induction period, however, the characteristic $\nu(CO)$ bands of $HCr_2(CO)_{10}^-$ appear [9]. The amount of $HCr_2(CO)_{10}^-$ may be estimated from these spectra, and under favorable conditions approximately half of the total chromium will be present as $HCr_2(CO)_{10}^-$, the other half being in the $Cr(CO)_6$.

From an examination of the samples taken from the reaction mixture under different conditions it is apparent that there is a close correlation between the rate of hydrogenation and the concentration of $HCr_2(CO)_{10}^-$ in the reaction mixture. After the induction period the concentration of $HCr_2(CO)_{10}^-$ increases to a limiting value, which depends on the reaction parameters. This final concentration of $HCr_2(CO)_{10}^-$ increases with H_2 pressure (Fig. 6) and is strongly diminished by the addition of a small amount of CO (Fig. 7, experiments 1 and 2), suggesting the presence of the overall equilibrium 2:

$$2\ Cr(CO)_6 + H_2 + MeO^- \rightleftharpoons HCr_2(CO)_{10}^- + 2CO + MeOH \tag{2}$$
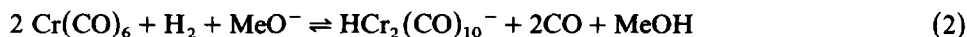
The rate of $HCr_2(CO)_{10}^-$ formation apparently does not depend on the H_2 pressure (Fig. 6).

As the length of the induction period of the hydrogenation (which is equal to the time necessary to start the formation of $HCr_2(CO)_{10}^-$) depends only on the temperature, the conclusion seems to be justified that the formation of the catalyst is started by the thermal dissociation of $Cr(CO)_6$ (eq. 3):
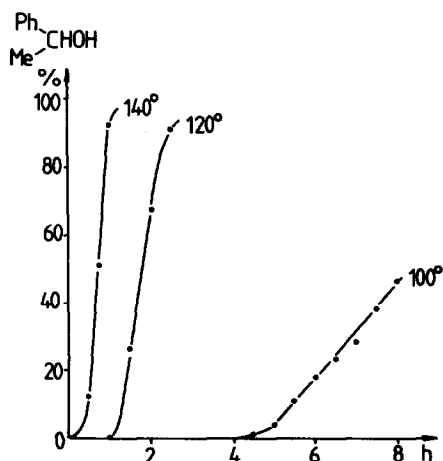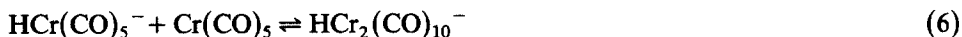
$$Cr(CO)_6 \rightarrow Cr(CO)_5 + CO \tag{3}$$

Fig. 5. Induction period in the acetophenone hydrogenation at different temperatures. Reaction conditions: 50 mmol acetophenone, 1 mmol $Cr(CO)_6$, 3 mmol NaOMe, 20 ml MeOH, 100 bar H_2 pressure at 20°C.

Most probably this step is followed by the oxidative addition of H_2 (eq. 4), the deprotonation of the very unstable [10] $H_2Cr(CO)_5$ (eq. 5), and the trapping of the reactive $HCr(CO)_5^-$ anion [11] in the form of $HCr_2(CO)_{10}^-$ by a $Cr(CO)_5$ fragment (eq. 6):

$$Cr(CO)_5 + H_2 \rightleftharpoons H_2Cr(CO)_5 \tag{4}$$

$$H_2Cr(CO)_5 + MeO^- \rightleftharpoons HCr(CO)_5^- + MeOH \tag{5}$$

$$HCr(CO)_5^- + Cr(CO)_5 \rightleftharpoons HCr_2(CO)_{10}^- \tag{6}$$

Reactions 4–6 are thought to be equilibrium reactions under the conditions used; 4 is strongly shifted to the left while 5 and 6 are strongly shifted to the right. After some $HCr(CO)_5^-$ has been formed by reactions 3–5 it is probable that the direct attack of this anion on $Cr(CO)_6$ becomes the main pathway to $HCr_2(CO)_{10}^-$ (eq. 7):

$$HCr(CO)_5^- + Cr(CO)_6 \rightarrow HCr_2(CO)_{10}^- + CO \tag{7}$$
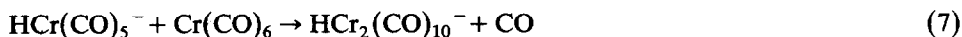
This reaction has been found to be more rapid than the loss of CO from $Cr(CO)_6$ [11]. Such an autocatalytic mechanism would explain the relatively rapid formation of $HCr_2(CO)_{10}^-$ after the induction period.

If the equilibrium composition of chromium complexes is prepared separately at the reaction temperature by treating $Cr(CO)_6$ and NaOMe in MeOH with H_2 and acetophenone is only added afterwards, no induction period can be observed (Fig. 7, experiment 3).

After the induction period the rate is first order in acetophenone ($k_{obs} = 3.5 \times 10^{-4}$ s^{-1} at 100°C if the $Cr(CO)_6$ is 0.05 M, the NaOMe is 0.15 M, and $P(H_2) = 120$ bar).

Stoichiometric experiments

The experimental results given in the previous section suggest that an anionic
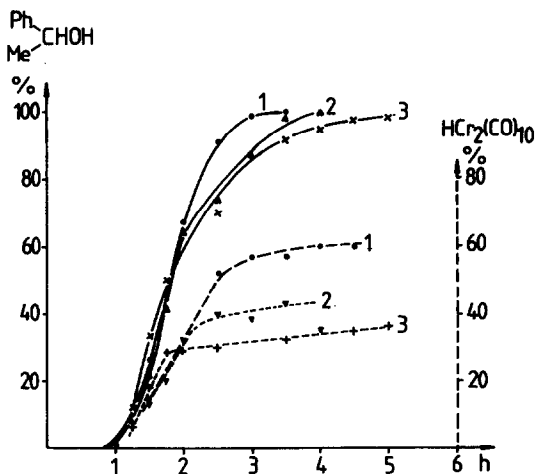

Fig. 6. Effect of hydrogen pressure on the rate of acetophenone hydrogenation and the concentration of $HCr_2(CO)_{10}^-$ in the reaction mixture, showing acetophenone conversion (———) and fraction of Cr present in the form of $HCr_2(CO)_{10}^-$ (— — —). Reaction conditions: 50 mmol acetophenone, 1 mmol $Cr(CO)_6$, 3 mmol NaOMe, 20 cm³ MeOH, 120°C, starting H_2 pressure at 20°C: 100 bar (1); 50 bar (2); 30 bar (3).

chromium carbonyl hydride is involved in the catalytic cycle of acetophenone hydrogenation. The obvious candidates for this hydride are $HCr(CO)_5^-$ and $HCr_2(CO)_{10}^-$ and therefore experiments were performed to investigate the reactions of these hydrides with ketones.

As could be expected, the mononuclear $HCr(CO)_5^-$ proved to be significantly more reactive than the dinuclear $HCr_2(CO)_{10}^-$ which has a bridging hydride ligand [12]. When both hydrides, in the form of their Et_4N salts, were mixed with neat acetophenone at 75°C under Ar the mononuclear complex was completely converted into $Cr_2(CO)_{10}^{2-}$ and $HCr_2(CO)_{10}^-$ within a few hours and α-phenylethanol was detected in the reaction mixture by GLC, whereas the dimeric hydride remained unchanged. When the temperature was raised to 120°C the $HCr_2(CO)_{10}^-$ also reacted with the acetophenone to give $Cr_2(CO)_{10}^{2-}$ and α-phenylethanol, but because of the much higher reactivity of $HCr(CO)_5^-$ this reaction is only of minor interest. The higher temperature necessary to effect the stoichiometric hydrogenation of acetophenone with this complex suggests that the monomeric hydride has first to be formed by thermal disssociation (eq. 6) and that actually this monomeric species is the active reducing agent.

The reaction between $HCr(CO)_5^-$ and acetophenone was followed by taking samples from the reaction mixture and analyzing these by IR spectroscopy (for the individual chromium carbonyl species) and by GLC (for α-phenylethanol). The results of such an experiment are shown in Fig. 8. As can be seen, the conversion of $HCr(CO)_5^-$ into mainly $Cr_2(CO)_{10}^{2-}$ and some $HCr_2(CO)_{10}^-$ is complete within about 3 h, and at the same time the ketone is reduced to the alcohol. After longer reaction times slow decomposition reactions set in. The shape of the curves suggests
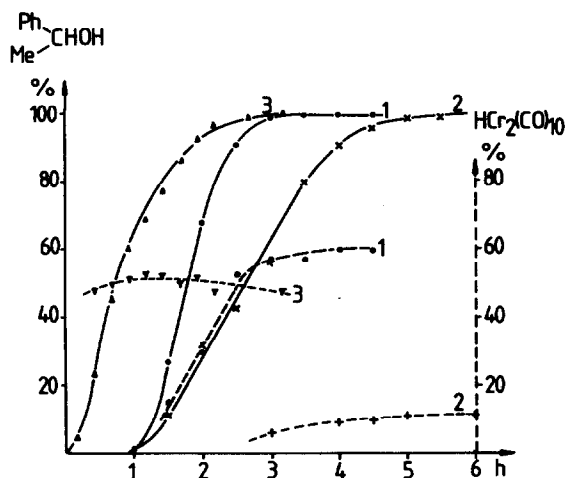

Fig. 7. Effect of different reaction parameters on the rate of acetophenone hydrogenation and the concentration of $HCr_2(CO)_{10}^-$ in the reaction mixture, showing acetophenone conversion (————), and the fraction of Cr present in the form of $HCr_2(CO)_{10}^-$ (— — —). Reaction conditions: 50 mmol acetophenone, 1 mmol $Cr(CO)_6$, 3 mmol NaOMe, 20 cm^3 MeOH, 100 bar total pressure (H_2 + CO) at 20°C, 120°C, with pure H_2 (1); with starting CO partial pressure 1.1 bar and final CO partial pressure 0.5 bar (2); as 1, but acetophenone not added until after the catalyst had been 3 h at the reaction conditions (3).

a clear stoichiometry between the formation of the dimeric chromium species and the alcohol.

To elucidate the stoichiometry of this hydrogenation, the following additional experiments were carried out:

(a) On heating $(Et_4N)[HCr(CO)_5]$ in acetonitrile solution at 75°C for 5 h under Ar, gradual decomposition of the hydride was observed but $Cr_2(CO)_{10}^{2-}$ was formed only in traces. This means that the thermal decomposition of $HCr(CO)_5^-$ into H_2 and $Cr_2(CO)_{10}^{2-}$ need not be considered under the conditions of stoichiometric hydrogenation.

(b) The salt $(Et_4N)[HCr(CO)_5]$ reacts vigorously with methanol at room temperature, with H_2 evolution and the formation of $HCr_2(CO)_{10}^-$. The same reaction with α-phenylethanol requires 75°C and is complete within about 2 h.

(c) The dinuclear salt $(Et_4N)_2[Cr_2(CO)_{10}]$, dissolved in acetonitrile, reacts with methanol at 55°C and the dianion is completely converted into $HCr_2(CO)_{10}^-$ within 30 min (eq. 8):

$$Cr_2(CO)_{10}^{2-} + MeOH \rightarrow HCr_2(CO)_{10}^- + MeO^- \tag{8}$$
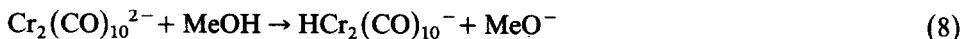
The same protonation could not be achieved with α-phenylethanol and the dianion remained unchanged at 75°C over 7 h. Accordingly, this reaction also need not be considered under the conditions of stoichiometric hydrogenation, but should be significant under the conditions of the catalytic experiments.

From these results we conclude that the consecutive reactions shown in eqs. 9 and 10 take place during the stoichiometric hydrogenation of acetophenone. It follows from these equations that the amount of free α-phenylethanol in the reaction mixture should be equal to the amount of $Cr_2(CO)_{10}^{2-}$ minus the amount of $HCr_2(CO)_{10}^-$. The results shown in Fig. 8 prove, within experimental error, that this assumption is correct.

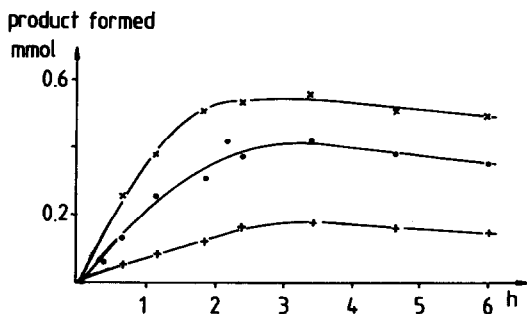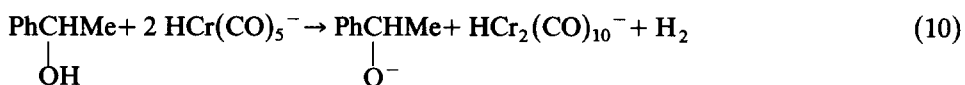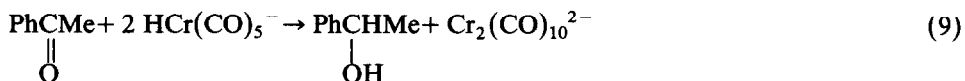$$PhCMe + 2\,HCr(CO)_5^- \rightarrow PhCHMe + Cr_2(CO)_{10}^{2-} \tag{9}$$
$$\underset{O}{\Vert} \qquad\qquad\qquad \underset{OH}{|}$$

$$PhCHMe + 2\,HCr(CO)_5^- \rightarrow PhCHMe + HCr_2(CO)_{10}^- + H_2 \tag{10}$$
$$\underset{OH}{|} \qquad\qquad\qquad\qquad \underset{O^-}{|}$$

Fig. 8. Stoichiometric hydrogenation of acetophenone with $(Et_4N)[HCr(CO)_5]$ at 75°C, showing formation of α-phenylethanol (●), $Cr_2(CO)_{10}^{2-}$ (×) and $HCr_2(CO)_{10}^-$ (+).

The mechanism of catalytic hydrogenation

By combining equations 4–6, 8 and 9 a catalytic cycle for ketone hydrogenation catalyzed by $Cr(CO)_6$ + NaOMe can be constructed, but reaction 9 is still complex and needs further investigation. Some additional information regarding this part of the catalytic cycle can be obtained by hydrogenating 4-t-butylcyclohexanone and determining the relative amount of the stereoisomeric 4-t-butylcyclohexanols formed.

It has been found that with all the catalyst combinations investigated the *trans* isomer is formed as the main product: 62% with the $Cr(CO)_6$ + Et_3N system at 160°C, 75% with the $Cr(CO)_6$ + NaOMe catalyst at 120°C and 78% when $Mo(CO)_6$ and NaOMe were used as the catalyst at 80°C. This is in remarkable contrast to the result obtained with the analogous $Fe(CO)_5$ + Et_3N catalyst [7] which furnishes only 38% *trans* alcohol at 150°C. We therefore suggest that the first intermediate formed in the reaction between $HCr(CO)_5^-$ and the ketone is an alkoxy complex with the structure $RR'CHOCr(CO)_5^-$. The large $OCr(CO)_5$ group in such an intermediate would tend to occupy the less crowded equatorial position of the cyclohexane ring and thus lead to the predominant formation of the *trans* alcohol. Alkoxypenta-carbonylchromates have not yet been described but a large number of the $XCr(CO)_5^-$ type complexes are known, among them representatives with X = HO [13] and CH_3COO [14].

The reaction between $HCr(CO)_5^-$ and the ketone may be regarded as a nucleophilic attack of the hydride at the carbon atom of the organic carbonyl group. A mechanism for ketone hydrogenation based on a similar nucleophilic attack at the carbonyl group has already been proposed for $HFe(CO)_4^-$ as the catalyst [6,7]. The significant difference between the two anionic metal carbonyl hydride species is that whereas $HCr(CO)_5^-$ is a hexacoordinate complex with no free coordination site available, $HFe(CO)_4^-$ is only pentacoordinate. This may be the reason why in the latter case an alkyliron hydride $HFe(CO)_4(RR'CO)^-$, with an Fe–C bond, is formed as an intermediate and with chromium the alkoxy complex $RR'CHOCr(CO)_5^-$, containing a Cr–O bond, is the product of this interaction. The difference in the structures of these catalytic intermediates explains the stereochemical differences observed in the hydrogenation of 4-t-butylcyclohexanone.

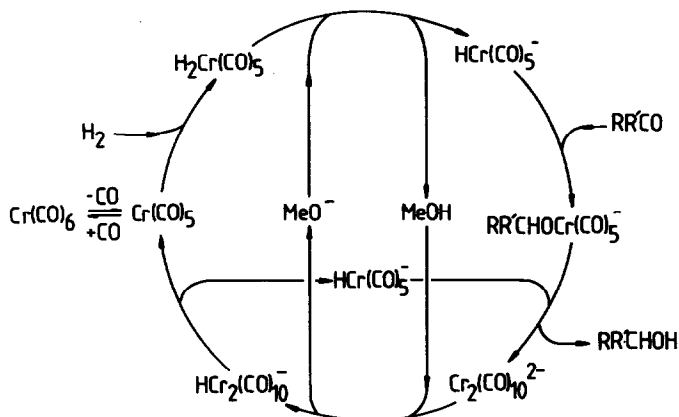Experiments have been performed to obtain more evidence in favor of the

Fig. 9. Mechanism of catalytic hydrogenation.

supposed alkoxychromium intermediates. When $HCr(CO)_5^-$ reacts with different organic carbonyl compounds the reaction products in some cases have IR absorptions which can be attributed to complexes of the type $XCr(CO)_5^-$, and thus may be the alkoxy complexes. Experiments to isolate and characterize these substances are under way.

Taking into account all the information currently available the mechanism illustrated in Fig. 9 is proposed for the hydrogenation of ketones with $Cr(CO)_6$ as catalyst precursor in the presence of NaOMe in methanol as solvent.

Experimental

The complexes $(Et_4N)[HCr(CO)_5]$, $(Et_4N)[HCr_2(CO)_{10}]$ and $(Et_4N)_2[Cr_2(CO)_{10}]$ were prepared as described in the literature [15]. The IR spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer. Analysis of the organic products was performed on a Carlo Erba ATC/f gas chromatograph using a 2 m column.

Stoichiometric hydrogenation of acetophenone with $(Et_4N)[HCr(CO)_5]$

All manipulations were carried out under Ar. The salt $(Et_4N)[HCr(CO)_5]$ (460 mg, 1.42 mmol) and acetophenone (1.5 ml, 12.9 mmol) were heated to 75°C in a Schlenk tube immersed in an oil bath and equipped with magnetic stirring. The light yellow hydride complex dissolved in the ketone at this temperature to give a clear dark yellow solution. Samples were withdrawn for analysis at different time intervals using a syringe. The samples for IR (30 μl) were diluted with MeCN (1 ml). The samples for GLC (15 μl) were injected into hexane (0.5 ml), which did not dissolve the anionic chromium carbonyls, and the clear hexane solution was used for chromatography (3% 20M PEG on Chromosorb P, 180°C, TCD). The IR spectra were evaluated quantitatively using the following characteristic absorption bands of $HCr_2(CO)_{10}^-$ [9] and $Cr_2(CO)_{10}^{2-}$ [15]:

$HCr_2(CO)_{10}^-$, 1940 cm^{-1}, ε 13600

$Cr_2(CO)_{10}^{2-}$, 1788 cm^{-1}, ε 2950

The values of the molar extinction coefficient ε (in dm^3 cm^{-1} mol^{-1}) were determined experimentally by using model solutions of $(Et_4N)[HCr_2(CO)_{10}]$ and $(Et_4N)_2[Cr_2(CO)_{10}]$ in MeCN.

Catalytic experiments

The hydrogenation experiments were usually performed in 20 cm^3 stainless steel rocking autoclaves. The substrate, solvent and catalyst were loaded under argon and the autoclave was closed. It was filled several times with hydrogen to about 30 bar, and the pressure released after shaking, and finally filled to the desired working pressure (in most cases 100 bar). Small amounts of oxygen which possibly remain in the system had a profound negative effect on the rate of reaction but did not influence the length of the induction period. The products were analyzed by GLC. When samples were to be taken during the reaction, 100 cm^3 autoclaves were used. The amounts of chromium carbonyls in the samples were estimated by IR spec-

troscopy using the following characteristic absorption bands:

$Cr(CO)_6$, 1981 cm^{-1}, ε 14700

$HCr_2(CO)_{10}^-$, 1942 cm^{-1}, ε 19600

The values of ε (in dm^3 cm^{-1} mol^{-1}) were determined experimentally by using model solutions of $Cr(CO)_6$ and $(Et_4N)[HCr_2(CO)_{10}]$ in MeOH.

Acknowledgement

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