

ketones and suggests some polarization of the C=O bond which would facilitate its reactivity. The least that can be said is that there is no serious modification of electron density around C(4) due to the presence of the metal ion which would modify the kinetics or thermodynamics of Schiff-base formation with amines. Thus neither the carbonyl bond angles or distances nor the i.r. spectrum suggest that there should be difficulty in forming Schiff-base adducts with this complex. A possible complicating factor in forming amine-adducts to the ketone may be the replacement of Cl^- by either OH^- in water or by the reacting amine. It is well known⁽⁹⁾ that square-planar complexes (especially Pt^{II} and Pd^{II}) are relatively unreactive to substitution by OH^- . The rate law for substitution generally is: $\text{rate}/[\text{complex}] = k_0 + k[\text{amine}]$. Thus it is very likely that competition between Schiff-base formation and Cl^- substitution by amine will be a serious complication in preparing imine dichloropalladium complexes from the keto-complex. Work is progressing along these lines.

Acknowledgements

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Hydrogenation of Aldehydes and Ketones with Molecular Hydrogen Using Iron Pentacarbonyl as Catalyst Precursor

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Summary

The hydrogenation of aldehydes and ketones with molecular hydrogen is catalyzed by $\text{Fe}(\text{CO})_5$ as catalyst precursor if a tertiary amine is used as solvent. The actual catalyst system is probably $\text{HFe}(\text{CO})_4^-$ and the protonated amine. The amine also functions as a base and therefore more strongly basic amines like Et_3N yield more active catalysts. Oxygen bases (even strong ones) furnish rather inefficient catalyst systems.

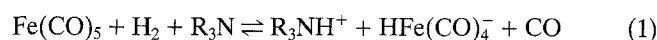
Introduction

Iron pentacarbonyl is generally regarded as a rather poor catalyst for the hydrogenation of unsaturated organic compounds with molecular hydrogen⁽¹⁾. Detailed investigations have only been carried out with polyunsaturated esters^(2–4) where (diene) $\text{Fe}(\text{CO})_3$ type complexes are the intermediates. Scattered reports have appeared on the hydrogenation of methyl acrylate⁽⁵⁾ and nitriles⁽⁶⁾.

Reductions with $\text{Fe}(\text{CO})_5$ as catalyst have been more commonly carried out by using $\text{CO} + \text{H}_2\text{O}$ in the presence of a

base as the hydrogen source⁽¹⁾ and recently we have reported the reduction of ketones and aldehydes with such a catalyst system⁽⁶⁾. These investigations have shown that in this case the two hydrogen atoms necessary for the reduction of the organic carbonyl compound to the corresponding alcohol are furnished by the $\text{HFe}(\text{CO})_4^-$ anion and the Et_3NH^+ cation. Thus it became apparent that to develop a more useful catalytic system based on H_2 and $\text{Fe}(\text{CO})_5$ as catalyst precursor, conditions have to be found which favour the heterolytic splitting of the hydrogen molecule.

It occurred to us that a simple way to achieve this would be to use a tertiary amine as the solvent for hydrogenation since this could make the following reaction possible



In fact, preliminary experiments showed that under 100 bar H_2 pressure $\text{Fe}(\text{CO})_5$ became an active catalyst for the hydrogenation of acetophenone above 100 °C if Et_3N was used as solvent.

Later we recognized that the above reaction between $\text{Fe}(\text{CO})_5$, H_2 and a tertiary amine has already been described⁽⁸⁾ but apparently not used till now for the activation of molecular hydrogen. Furthermore, it was observed by Fell⁽⁹⁾ that the addition of $\text{Fe}(\text{CO})_5$ to the conventional hydroformylation

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catalyst $\text{Co}_2(\text{CO})_8$ and the use of *N*-methylpyrrolidine as a solvent leads to the complete hydrogenation of the aldehydes formed as primary products and thus to an efficient one-step synthesis of alcohols. This effect can probably be explained by the formation of the $\text{R}_3\text{NH}^+ + \text{HFe}(\text{CO})_4^-$ catalyst system under their conditions (180 °C, 180 bar starting pressure, $\text{H}_2 : \text{CO} = 2:1$) but the authors gave no explanation for their results.

Results and Discussion

Acetophenone was used as a model substance and the usual reaction conditions were 150 °C, 100 bar starting pressure (about 120 bar working pressure at the reaction temperature) and Et_3N solvent. Dihydrogen containing 1.5% CO was used for the hydrogenation in most cases, for two reasons. First, if pure hydrogen was used, a small amount of CO was always found in the gas at the end of the experiments. This was attributed in part to reaction (1) and in part to some decomposition of the catalyst, as indicated by a fine black precipitate in the otherwise clear yellow products (especially at higher temperatures). By use of 1.5% CO at the start of the experiments this decomposition was avoided at temperatures below 180 °C. Second, carbon monoxide strongly inhibits the hydrogenation (Figure 1) and therefore to achieve reproducible results constant CO pressure is necessary. Since the amount of CO liberated from $\text{Fe}(\text{CO})_5$ (as discussed above) depends on the amount of catalyst, the volume of the autoclave, the temperature, etc., reproducible results can only be achieved if a constant p_{CO} is provided.

Under such conditions the rate of hydrogenation increases with increasing hydrogen pressure (Figure 1), $\text{Fe}(\text{CO})_5$ and Et_3N concentration (Figure 2). The reaction is first order in acetophenone ($k_{\text{obs}} = 0.46 \text{ h}^{-1}$ if $\text{Fe}(\text{CO})_5 = 0.25 \text{ M}$, $p_{\text{H}_2} = 118 \text{ bar}$ and $p_{\text{CO}} = 1.8 \text{ bar}$) and thus the following mechanism is proposed for the catalytic cycle based on these results (*cf.* ref. 7):

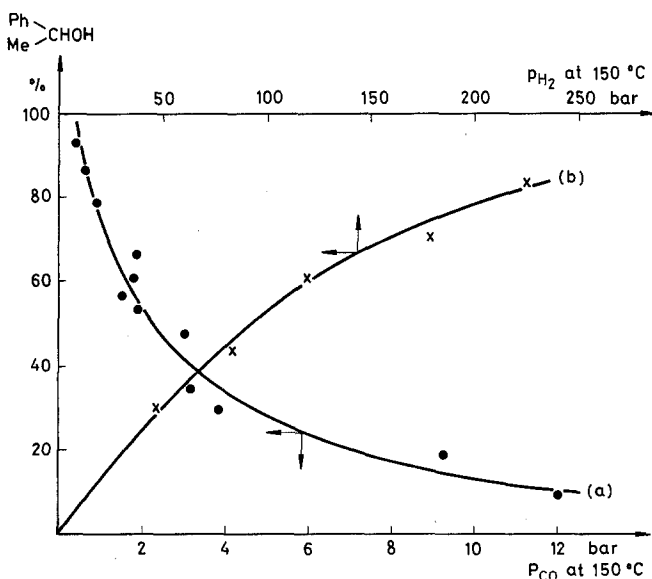
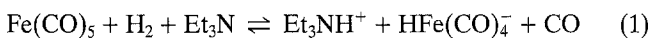


Figure 1. Effect of p_{CO} and p_{H_2} on hydrogenation of acetophenone. Reaction conditions: 10 mmol acetophenone, 1 mmol $\text{Fe}(\text{CO})_5$, 4 cm³ Et_3N , 150 °C, 3 h. (a): 120 bar total pressure ($\text{H}_2 + \text{CO}$). (b): p_{CO} 2 bar.

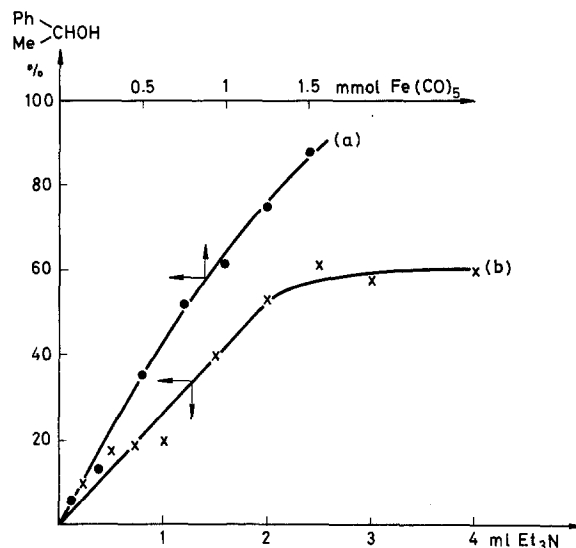
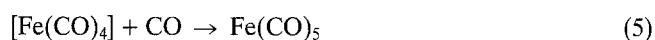
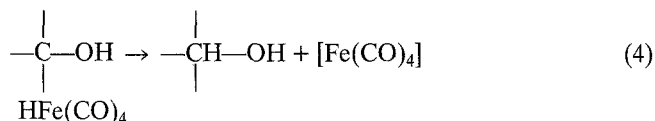
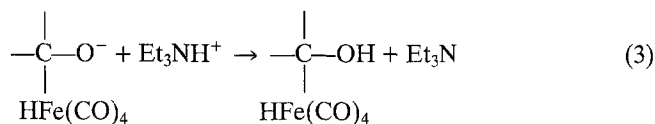
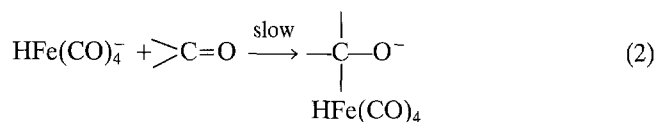


Figure 2. Effect of $\text{Fe}(\text{CO})_5$ and Et_3N concentration on hydrogenation of acetophenone. Reaction conditions: 10 mmol acetophenone, 4 cm³ solvent, 120 bar total pressure (98.5% $\text{H}_2 + 1.5\% \text{CO}$), 150 °C, 3 h. (a): solvent Et_3N . (b): solvent $\text{Et}_3\text{N} + \text{THF}$; 1 mmol $\text{Fe}(\text{CO})_5$.



The new catalyst system can be used for the hydrogenation of aliphatic and aromatic aldehydes and ketones (Table 1). Aldehydes are hydrogenated more rapidly than ketones and therefore lower temperatures may be sufficient (Figure 3).

Table 1. Hydrogenation of different carbonyl compounds^{a)}

Substrate	Conversion to alcohol, %
acetophenone	61.6
benzophenone	0
acetone	100
methylisobutylketone	30.2
cyclohexanone	99.6
4- <i>t</i> -Bu-cyclohexanone	99.2 ^{b)}
benzaldehyde	95.2
<i>n</i> -butyraldehyde	98.0
4-methylpenten-3-one-2	38.0 ^{c)}
	11.6 ^{d)}
	23.0 ^{e)}

^{a)} Reaction conditions: 10 mmol substrate, 1 mmol $\text{Fe}(\text{CO})_5$, 4 cm³ Et_3N , 100 bar total pressure (98.5% $\text{H}_2 + 1.5\% \text{CO}$) at 20 °C, 150 °C, 3 h. ^{b)} *cis:trans* = 1.69:1. ^{c)} methylisobutylketone. ^{d)} 4-methylpenten-3-ol-2. ^{e)} 4-methylpentanol-2.

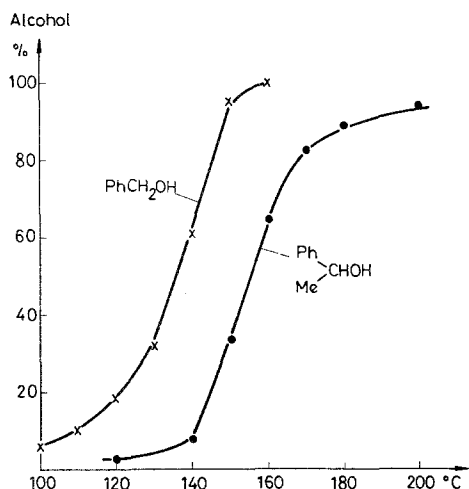


Figure 3. Effect of temperature on hydrogenation of benzaldehyde and acetophenone. Reaction conditions: 10 mmol substrate, 1 mmol $\text{Fe}(\text{CO})_5$, 4 cm^3 Et_3N , 100 bar total pressure at 20 °C (98.5% H_2 + 1.5% CO for benzaldehyde; 97.7% H_2 + 2.3% CO for acetophenone), 3 h.

Table 2. Hydrogenation of acetophenone in different solvents and in presence of different bases^{a)}

Solvent	Base, mmol	Conversion to alcohol, %
Et_3N	—	61.6
Et_3N	PPh_3 , 1	0.5
Pyridine	—	18.2 ^{b)}
PhNEt_2	—	0 ^{c)}
EtOH	—	1.2 ^{c)}
THF	—	0.9 ^{c)}
MeOH	MeONa , 1	1.0 ^{b)}
MeOH	PhONa , 1	4.3 ^{b)}
MeOH	PhONa , 5	7.8 ^{b)}
Hexane	—	1.4 ^{c)}

^{a)} Reaction conditions: 10 mmol acetophenone, 1 mmol $\text{Fe}(\text{CO})_5$, 4 cm^3 solvent, 100 bar total pressure at 20 °C (98.5% H_2 + 1.5% CO), 150 °C, 3 h. ^{b)} Product deep red. ^{c)} Precipitate in product.

The catalyst was not active for the hydrogenation of methyl benzoate up to 200 °C.

The structure of the amine (or more generally speaking that of the base) has a significant influence on the activity of the catalyst (see Table 2). Among the amines tested Et_3N was found to give the best results, pyridine furnished a somewhat less active system and *N,N*-diethylaniline was unsuitable. This order of reactivity corresponds to that of basicity, and proves that a sufficiently strong base is needed to make reaction (1) possible. The same reasoning may be used to explain the negative results obtained with methanol or tetrahydrofuran (THF). The rather low activity of the catalysts obtained from MeONa

or PhONa cannot be explained in this way since both MeO^- and PhO^- are strong bases. In these cases it may be the absence of a species capable of transferring protons [see step (3)] which causes the low rate, as has been demonstrated already earlier⁽⁷⁾. Tertiary phosphines strongly inhibit the reaction.

That the formation of the $\text{HFe}(\text{CO})_4^-$ anion is not the only requirement for an active hydrogenation catalyst was clearly demonstrated by the infrared spectra of samples taken during catalytic runs. When Et_3N was used as solvent and base, the only iron carbonyl species which was detected was $\text{Fe}(\text{CO})_5$, indicating that only very small amounts of the $\text{HFe}(\text{CO})_4^-$ anion may have been formed according to equation (1). Hydrogenation nevertheless proceeded rapidly. On the other hand, if NaOMe was used as a base in ethanol as solvent (this solvent was used because it provides much better infrared spectra than methanol) significant amounts of the $\text{HFe}(\text{CO})_4^-$ anion were detected in the samples. About one fourth of the iron was present in the form of $\text{HFe}(\text{CO})_4^-$, as estimated from the intensity of its absorption band at 1890 cm^{-1} [the rest was $\text{Fe}(\text{CO})_5$]. Despite this, almost no hydrogenation took place, the rate of reaction was about two orders of magnitude smaller than that observed in the experiment with Et_3N . These observations are in agreement with our earlier results and demonstrate the importance of the proton-transfer step (3).

Some additional support for the nucleophilic attack of the $\text{HFe}(\text{CO})_4^-$ anion at the organic carbonyl group as part of the mechanism was furnished by the product composition obtained when 4-*t*-butylcyclohexanone was hydrogenated. The predominance of the *cis*-isomer over the *trans*-isomer is in accordance with the attack of the bulky $\text{HFe}(\text{CO})_4^-$ group at the carbonyl carbon atom from the sterically less hindered equatorial direction.

Experimental

Experiments were usually performed in 20 cm^3 stainless steel rocking autoclaves. The substrate, solvent and catalyst were loaded under argon, the autoclave closed, flushed several times with hydrogen, and pressurized. Products were analyzed by g.l.c. If samples were taken during the reaction, 100 cm^3 autoclaves were used.

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