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HYDROGENATION OF *N*-BENZYLIDENEANILINE WITH MOLECULAR HYDROGEN USING IRON PENTACARBONYL AS CATALYST PRECURSOR

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Summary

N-benzylideneaniline is hydrogenated to *N*-benzylaniline by H_2 in the presence of $Fe(CO)_5$, as catalyst precursor, in alcohol solution at 150°C and about 100 bar H_2 pressure. The reaction is inhibited by CO. In a stoichiometric reaction, $H_2Fe(CO)_4$ hydrogenates the Schiff base rapidly at room temperature.

Introduction

Iron pentacarbonyl is regarded as a poor catalyst for homogeneous hydrogenations with molecular hydrogen [1] and only a few papers deal with its application for this purpose [2–6]. Recently we have shown, however, that in Et_3N as solvent, $Fe(CO)_5$ is an active catalyst for the hydrogenation of aldehydes and ketones at 120–160°C and 100 bar [7]. We now report the successful application of $Fe(CO)_5$ as a catalyst for the hydrogenation of *N*-benzylideneaniline, a compound with a C=N double bond.

Results and discussion

Hydrogenation of aldehydes or ketones with $Fe(CO)_5$ as catalyst proceeds well only in a tertiary amine as solvent, because the amine (as a relatively strong base) is necessary for the heterolytic activation of the H_2 molecule [7]:

$$Fe(CO)_5 + H_2 + Et_3N \rightleftharpoons HFe(CO)_4^- + Et_3NH^+ + CO \qquad (1)$$

Althought direct experimental evidence is not available at present, the role of Et_3N is most probably that it stabilizes the very small amounts of $H_2Fe(CO)_4$ which may be formed from $Fe(CO)_5$ and H_2 (eq. 2):

$$Fe(CO)_5 \overset{-CO}{\rightleftharpoons} Fe(CO)_4 \overset{H_2}{\rightleftharpoons} H_2Fe(CO)_4 \overset{Et_3N}{\rightleftharpoons} HFe(CO)_4^- + Et_3NH^+ \qquad (2)$$

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TABLE 1

HYDROGENATION OF *N*-BENZYLIDENEANILINE IN DIFFERENT SOLVENTS[a]

Solvent	Conversion to *N*-benzylaniline (%)
MeOH	98.0
EtOH	95.7
n-Pentanol	18.6
Acetone	56.3
THF	8.5[b]
Et_3N	63.9
$n\text{-}Bu_3N$	24.2
$PhNEt_2$	31.1
Pyridine	41.2
Toluene	34.6
n-Hexane	21.6

[a] Reaction conditions: 10 mmol *N*-benzylideneaniline, 0.5 mmol $Fe(CO)_5$, 5 ml solvent, 100 bar total pressure at 20°C (98.5% H_2 + 1.5% CO), 150°C, 3 h. [b] Five additional compounds formed in about 30% yield.

When using $Fe(CO)_5$ for the homogeneous hydrogenation of *N*-benzylideneaniline it was found that, in this case, the activity of the catalyst is far less dependent on the structure of the solvent. Alcohols, ketones, ethers, amines, pyridine and even hydrocarbons could be used with more or less success. The best results were achieved with methanol and ethanol (see Table 1).

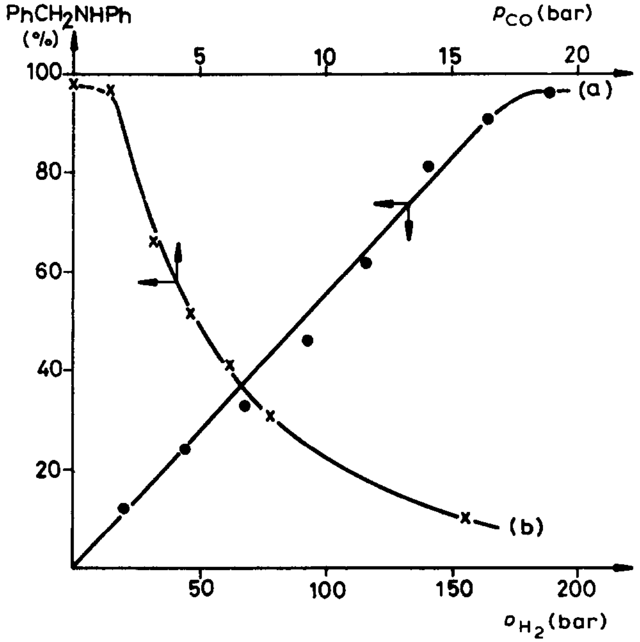


Fig. 1. Effect of p_{H_2} (a) and p_{CO}(b). Reaction conditions: 10 mmol *N*-benzylideneaniline, 0.38 mmol $Fe(CO)_5$, 5 ml MeOH, 150°C, 3 h; (a): total pressure, $p_{H_2} + p_{CO}$; p_{CO} in all experiments 3.1 bar; (b): Total pressure, $p_{H_2} + p_{CO}$, 120 bar.

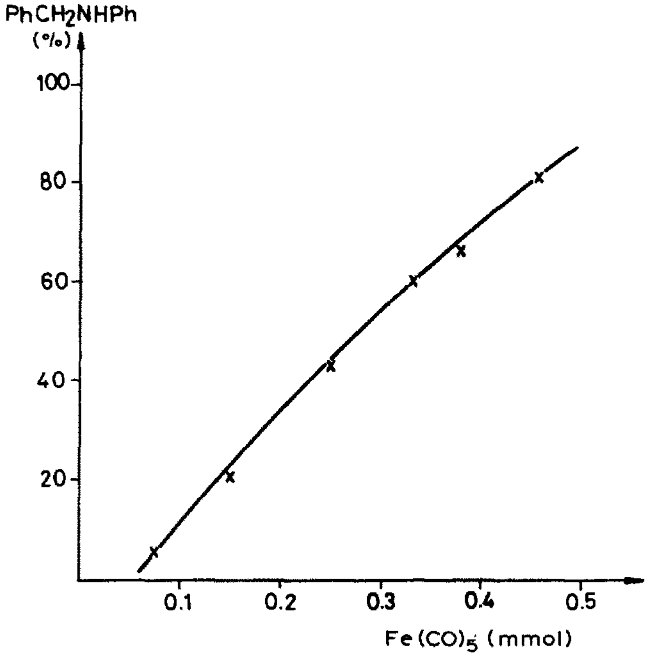


Fig. 2. Effect of Fe(CO)$_5$ concentration. Reaction conditions: 10 mmol *N*-benzylideneaniline, 5 ml MeOH, 150°C, 120 bar total pressure (98.5% H_2 + 1.5% CO), 3 h.

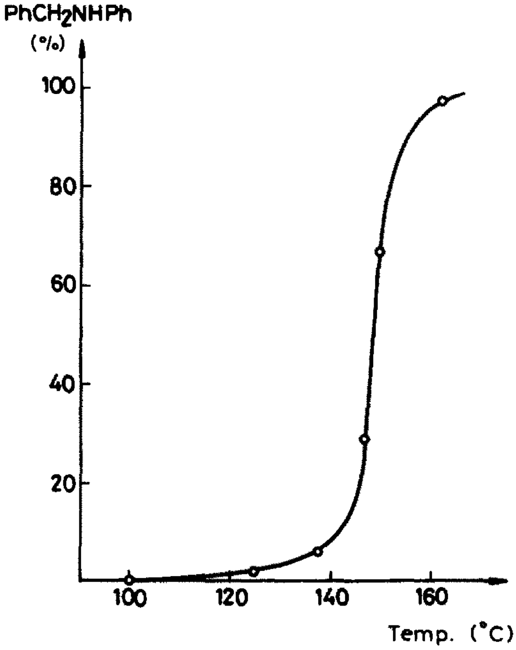


Fig. 3. Effect of temperature. Reaction conditions: 10 mmol *N*-benzylideneaniline, 0.38 mmol Fe(CO)$_5$, 5 ml MeOH, 100 bar total pressure at 20°C (98.5% H_2 + 1.5% CO), 3 h.

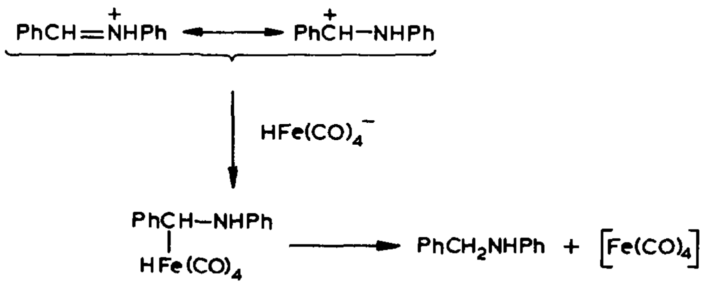
Nevertheless, the reaction shows several of the features which were observed when aldehydes or ketones were hydrogenated. Thus the rate increases with H_2 pressure, and CO inhibits the reaction (Fig. 1). To improve the reproducibility of the results, hydrogen containing about 2% CO was used in most experiments. The yield of hydrogenated product increases with $Fe(CO)_5$ concentration (Fig. 2) and is strongly dependent on temperature (Fig. 3). Useful rates were obtained at about 150°C.

The observation that the hydrogenation of benzylideneaniline with $Fe(CO)_5$ can be performed without any added base suggests that apparently the substrate itself (although being an aromatic amine and therefore a weak base) ensures, according to eq. 2, a sufficient concentration of $HFe(CO)_4^-$. This is at first sight an unexpected result, since the hydrogenation of aldehydes and ketones does not proceed in an aromatic amine as solvent [7].

If instead of Et_3N a much weaker base is sufficient to form an active catalyst system, then even the very small concentration of $HFe(CO)_4^-$ present in such a case * has to be large enough to run the catalytic reaction at a reasonable rate. With other words, this means that a C=N double bond must be much more susceptible towards the attack of the $HFe(CO)_4^-$ anion than a C=O double bond. This does not seem obvious at first but can be explained by looking at the form of the catalyst-forming reaction, 1, with benzylideneaniline as the base (eq. 3):

$$PhCH{=}NPh + Fe(CO)_5 + H_2 \rightleftharpoons HFe(CO)_4^- + PhCH{=}\overset{+}{N}HPh + CO \quad (3)$$

It can be seen that the formation of the $HFe(CO)_4^-$ anion is accompanied by protonation of the substrate. The cation formed in this way should be very susceptible towards attack by the nucleophile, and this reaction may lead almost immediately to the product (see Scheme 1). We suggest that this simultaneous activation of both the iron carbonyl and the substrate, according to eq. 3, is responsible for the unexpectedly easy hydrogenation of *N*-benzylideneaniline with $Fe(CO)_5$ as catalyst.



SCHEME 1

If the above reasoning is correct, the essential step of the catalytic cycle is the reaction of $H_2Fe(CO)_4$ with benzylideneaniline and this reaction should be fast. This conclusion was therefore tested experimentally and $H_2Fe(CO)_4$ was reacted with benzylideneaniline in a hexane-ethanol solution at room temperature. A practically instantaneous reaction, yielding benzylaniline, was observed (eq. 4);

$$PhCH{=}NPh + H_2Fe(CO)_4 \rightarrow PhCH_2NHPh + [Fe(CO)_4] \quad (4)$$

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* IR spectra of the reaction mixtures show only bands characteristic of $Fe(CO)_5$, cf. ref. 7.

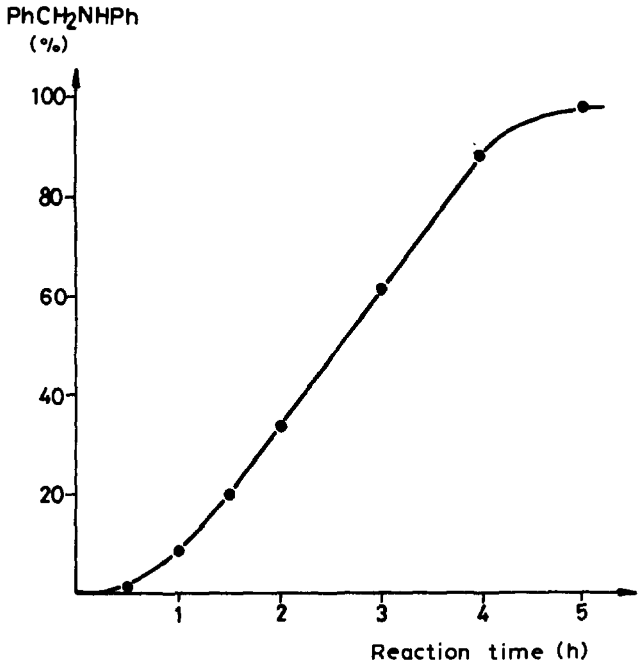

Fig. 4. Hydrogenation of benzylideneaniline as a function of reaction time; 50 mmol benzylideneaniline, 1.9 mmol $Fe(CO)_5$, 25 ml MeOH, 190–210 bar total pressure (98.3% H_2 + 1.7% CO), 150°C.

One mol $H_2Fe(CO)_4$ hydrogenated 0.90–0.95 mol benzylideneaniline and, as shown by IR spectroscopy, the $Fe(CO)_4$ fragment was stabilized as $Fe(CO)_5$ and $HFe_3(CO)_{11}^-$. A comparison of this easy stoichiometric hydrogenation of the C=N bond with the earlier observation that the stoichiometric hydrogenation of the C=O bond with $H_2Fe(CO)_4$ takes place only in the presence of Et_3N [8] demonstrates the unusually efficient activation of the two hydride ligands in $H_2Fe(CO)_4$ by an unsaturated, *N*-containing organic molecule.

Additional information about the mechanism of the catalytic reaction was obtained from experiments in which the course of the reaction was followed by taking samples from the reaction mixture. As shown on Fig. 4, apart from an induction period the rate of hydrogenation is zero order with respect to substrate. This means, that it is the formation of $H_2Fe(CO)_4$ which is rate determining and compared to this its reaction with the Schiff base (eq. 4) is very fast. The cause of the induction period is not quite clear. It is not influenced by adding some of the hydrogenated product and is therefore not caused by the change of the organic base during the reaction.

Experimental

Catalytic experiments

Experiments were performed in 20 or 100 ml stainless steel autoclaves as described earlier [7].

Stoichiometric hydrogenation with $H_2Fe(CO)_4$

$Fe(CO)_5$ (0.35 ml, 2.5 mmol) was treated under Ar with 1 ml 40% NaOH in 5 ml MeOH at room temperature, with stirring, for 1 h, and the colorless suspension was then acidified with 4 ml 1/1 HCl in the presence of 20 ml hexane at 0°C. The hexane layer, containing approximately 2.0 mmol $H_2Fe(CO)_4$ (as determined by Fe analysis and IR), was separated and to this hydride solution increasing amounts of a 0.1 *M* solution of benzylideneaniline in EtOH (containing n-dodecane as a GLC reference substance) were added. After each addition, the reaction mixture was stirred for 5 min, and a small sample was withdrawn by syringe and injected into an ethanolic iodine solution to oxidize unreacted hydride. The samples were then analyzed by GLC. The following numbers give, in mmol, the amount of benzylideneaniline added, the amount of unreacted Schiff base found, and the amount of benzylaniline formed: 1.00–0–1.02, 1.50–0.02–1.55, 1.70–0.06–1.71, 2.10–0.24–1.81, 2.46–0.96–1.88.

References

1 B.R. James, Homogeneous Hydrogenation, Wiley, New York, 1973.
2 E.N. Frankel, T.L. Mounts, R.O. Butterfield and H.J. Dutton, Adv. Chem. Ser., 70 (1968) 177.
3 N. Maoz and M. Cais, Isr. J. Chem., 6 (1968) 32P.
4 G. Cecchi and E. Ucciani, Rev. Fr. Corps Gras, 21 (1974) 423.
5 H. Uchida and K. Bando, Bull. Chem. Soc. Jpn., 29 (1956) 953.
6 D.R. Levering, U.S. Pat., 3,152,184 (1964); Chem. Abstr., 62 (1965) 427.
7 L. Markó and J. Palágyi, Transition Met. Chem., 8 (1983) 207.
8 L. Markó, M.A. Radhi and I. Ötvös, J. Organomet. Chem., 218 (1981) 369.