Kinetics of the Liquid-phase Hydrogenation of Aromatic Nitro-compounds in the Presence of Tungsten Carbide Catalyst

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The kinetics of liquid-phase hydrogenation of aromatic nitro-compounds have been studied in the presence of tungsten carbide catalyst. The effects of temperature and hydrogen partial pressure on the hydrogenation rate have been investigated. It has been shown that the addition (deposition) of small amounts of noble metals (100—1000 p.p.m.) results in a significant increase in the catalytic activity of tungsten carbide. From a comparison of our results with those for electrochemical oxidation of hydrogen at tungsten carbide electrodes it may be assumed that the rate determining step of hydrogenation is the activation (dissociative adsorption) of hydrogen.

WE have previously [1] reported the selective catalytic behaviour of tungsten carbide in the liquid-phase hydrogenation of organic compounds. The preparative aspects of the problem were studied and no attempt was made to give a detailed kinetic analysis of the phenomena observed. This paper reports the kinetics of hydrogenation of aromatic nitro-compounds. As shown previously, these compounds react readily with hydrogen in the presence of tungsten carbide, forming the corresponding amines.

EXPERIMENTAL

The procedure described previously [1] was applied with different types of tungsten carbide (CWF-2; Ugine; Murex). The reactions were carried out with tungsten carbide (1—4 g) in aqueous M-H_2SO_4. The following compounds have been chosen as models: p-nitrophenol, p-nitrobenzamide, and nitrobenzene. The effects of hydrogen pressure and temperature on the reaction rate were studied systematically.

Some of the experiments were carried out with tungsten carbides activated by noble metals (Pt or Pd). Activation was accomplished by addition of a solution of the required amount of noble metal salt (H_2PtCl_6 or $PdCl_2$) to a suspension of tungsten carbide in M-H_2SO_4 solution previously saturated with hydrogen.

RESULTS

The rate of hydrogenation (defined as hydrogen uptake referred to unit mass of catalyst) is independent of the amount of substrate present.[1] The rate of hydrogen uptake does not change during hydrogenation except at the very end of the process. This observation has been confirmed for our model compounds.

The hydrogenation rate of the models is the same under given conditions (catalyst sample; temperature, etc.). A relationship has been found between the amount of catalyst and the hydrogen uptake rate.

The dependence of the hydrogenation rate on the partial pressure of hydrogen has been studied at various temperatures, and a relationship has been found (Figure 1). From the slopes of the curves in Figure 1 the temperature dependence of the hydrogenation rate can be evaluated. From a plot of log k at a given partial pressure of hydrogen (760 mmHg) against $1/T$, an apparent activation energy of 10 ± 1 kcal mol^{-1} can be calculated. It must be mentioned that an activation energy of 4—5 kcal mol^{-1} is expected for the case when the diffusion of hydrogen is rate determining.

[1] G. Vertes, G. Horányi, and S. Szakács, J.C.S. Perkin II, 1973, 1400.

Effect of Noble Metal Additives on Rate of Hydrogenation.— The catalytic activity of tungsten carbide may be elevated
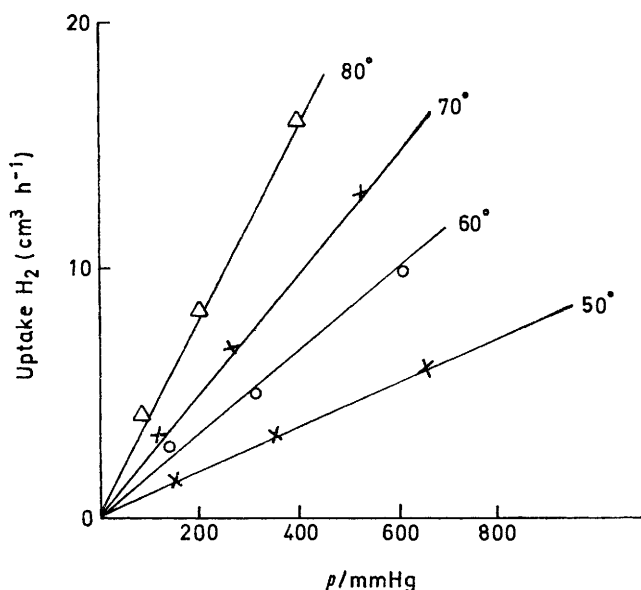

FIGURE 1 Hydrogenation rate per 1 g tungsten carbide of p-nitrobenzamide as a function of hydrogen pressure at different temperatures
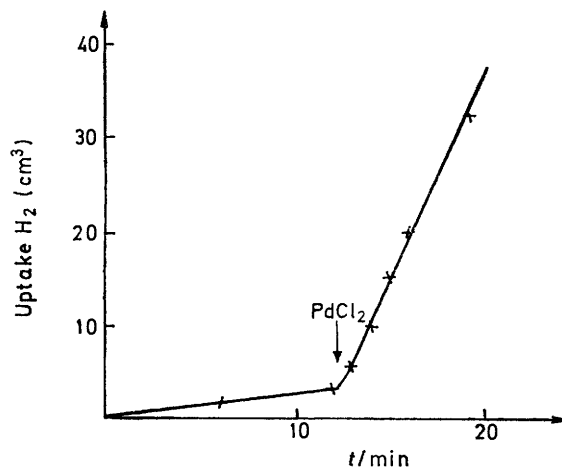

FIGURE 2 Effect of the addition of $PdCl_2$ on catalytic activity

by depositing on its surface a small amount of noble metal (Pd or Pt) (Figure 2). During hydrogenation of p-nitrophenol in the presence of catalyst (1 g), an amount of $PdCl_2$

(in 1 cm³ solution) corresponding to 1 mg Pd was added to the system as shown. Similar experiments were carried out (i) in the absence of tungsten carbide and (ii) using Al_2O_3 and WO_3 instead of tungsten carbide. The results are in the Table. From the data it can be assumed that

Rate of hydrogenation of p-nitrophenol in M-H_2SO_4 solution at 80°, on support (1 g) in the presence of palladium (1 mg)

Support	Uptake of hydrogen (cm³ l⁻¹)
Al_2O_3	60
WO_3	50
WC	320
None	20

the noble metal is deposited on tungsten carbide and that the latter is an active support. (Simple mixing of tungsten carbide and noble metal catalysts does not result in a significant increase in catalytic activity.)

There is no simple correlation between the amount of noble metal and the rate of hydrogenation (Figure 3 for the
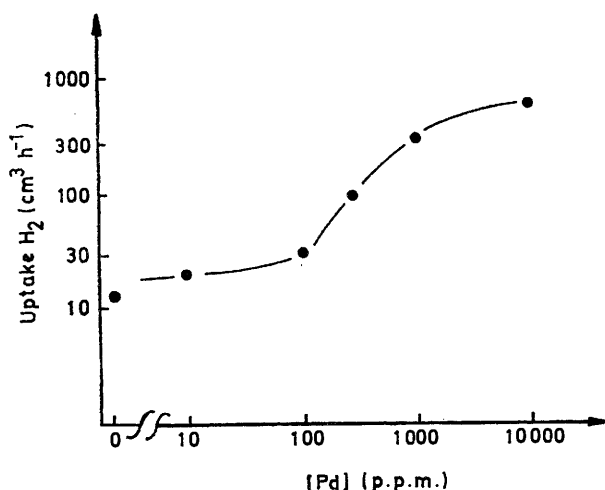

FIGURE 3 Hydrogenation rate per 1 g tungsten carbide as a function of the amount of Pd deposited on the catalyst

case of Pd). Above 1000 p.p.m. the increase in activity with the amount of Pd is very small. Below 100 p.p.m. there is no significant change in the catalytic activity compared with that of pure tungsten carbide.

In our previous communication [1] it was stated that the tungsten carbide is a selective catalyst, e.g. nitro-groups may be hydrogenated in the presence of C=C bonds and/or C=O groups and aromatic nuclei.
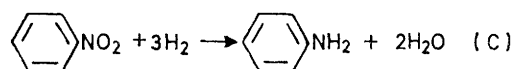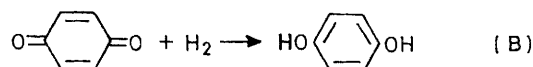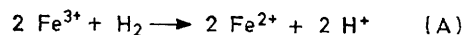
On palladized or platinized tungsten carbide, hydrogenation of double bonds is observed, but the selectivity with respect to C=O groups and aromatic nuclei remains unaltered. When 4-amino-3-nitrobenzophenone was hydrogenated at 60° in propan-2-ol-2N-HCl in the presence of tungsten carbide containing Pd, after consumption of sufficient hydrogen for hydrogenation of the nitro-group, the rate decreased sharply and 3,4-diaminobenzophenone monohydrochloride was obtained in 91% yield. This shows that neither the oxo-group nor the aromatic nucleus was attacked during hydrogenation. Secondly 2,5-dimethoxy-1,4-benzenequinone on hydrogenation in the

[2] ' Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 1955—1956, p. 1608.

presence of tungsten carbide and Pt (1000 p.pm.) gave 2,5-dimethoxyhydroquinone in 85% yield.

DISCUSSION

In order to explain the phenomena observed, some observations and conclusions reported previously [1] must be taken into consideration. (i) For different substrates similar hydrogenation rates are observed. The same rate was measured, for example, for reactions

$$2\ Fe^{3+} + H_2 \longrightarrow 2\ Fe^{2+} + 2\ H^+ \qquad (A)$$

$$O=\!\!\!\!\bigcirc\!\!\!\!=O + H_2 \longrightarrow HO\!\!-\!\!\bigcirc\!\!-\!\!OH \qquad (B)$$

$$\bigcirc\!\!-\!\!NO_2 + 3H_2 \longrightarrow \bigcirc\!\!-\!\!NH_2 + 2H_2O \qquad (C)$$

(A)—(C). (ii) Tungsten carbide is a selective catalyst. It does not promote the hydrogenation of double and triple bonds. It is well known that the catalytic hydrogenation of compounds containing double and triple bonds takes place by reaction of adsorbed hydrogen and adsorbed substrate. The hydrogenation of quinones, nitro-compounds, and Fe^{3+} ions occurs by the ionization of hydrogen and consecutive reduction of the compound by transfer of electrons originating from the ionization. Thus hydrogenation of nitro-compounds involves protons. There is no doubt that the rate for the reduction of Fe^{3+} by molecular hydrogen corresponds to the rate of the ionization of molecular hydrogen. Thus the rate-determining step of hydrogenation is either diffusion or activation (dissociative adsorption) of hydrogen. On the basis of the high value of the activation energy, rate-determining diffusion may be excluded. The increase in catalytic activity by addition of noble metals can be explained by the well known fact that both palladium and platinum bring about ready dissociation of hydrogen.

The rate of hydrogenation is described by equation (1)

$$w = kmp_{H_2} \qquad (1)$$

where m is the mass of the catalyst, p_{H_2} the partial pressure of hydrogen, and k the apparent rate constant referred to 1 g catalyst. According to Henry's law there exists a relationship (2) between the partial

$$c_{H_2} = Kp_{H_2} \qquad (2)$$

pressure and concentration of hydrogen in the solution phase. Thus, from (1) equation (3) is obtained.

$$w = kKc_{H_2}m \qquad (3)$$

The Henry constant does not depend significantly on the temperature in the interval studied (40—90°).[2] It follows that the temperature dependence of the rate of hydrogenation is not a function of K.

It is known from studies of the electrochemical hydrogenation of aromatic nitro-compounds in the liquid (aqueous) phase in the presence of a noble metal

catalyst that hydrogenation is composed of two coupled electrochemical reactions.

(i) The electrochemical reduction of nitro-compounds is characterised by the overall process (D). The rate

$$-NO_2 + 6H^+ + 6e^- \longrightarrow -NH_2 + 2H_2O \quad (D)$$
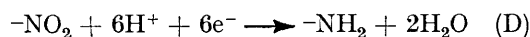
of reaction (D) is described by equation (4) where w_s

$$w_s = w_0 10^{-bE} \quad (4)$$

and b are constants depending on the nature of the catalyst and the substrate and E is the potential of the catalyst. This type of kinetic equation corresponds to a rate-determining step characterised by the reactions of the type $S + e \longrightarrow S^-$ followed by $S^- + H^+ \longrightarrow SH$
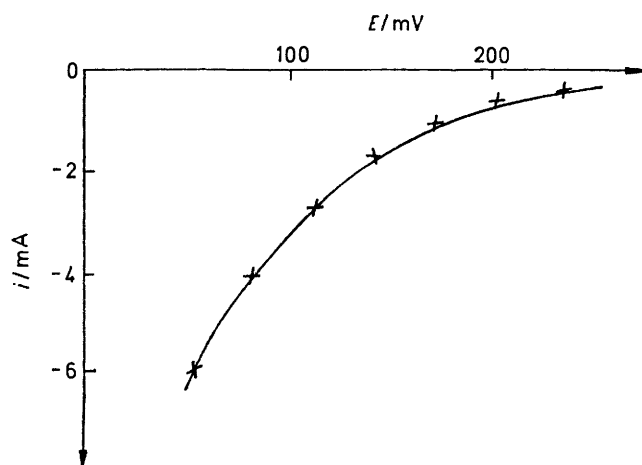

FIGURE 4 Polarization curve of p-nitrophenol on tungsten carbide powder at 70° (1 g catalyst; supporting electrolyte M-H$_2$SO$_4$; concentration of p-nitrophenol 5×10^{-2}M; potential measured against a hydrogen electrode immersed in the supporting electrolyte)

or $S + H^+ + e \longrightarrow SH$ where S and SH are intermediates formed in the course of electroreduction of the nitro-compound.

From our kinetic considerations the specific nature of the intermediates and the pathway to the amino-compound is unimportant (see ref. 3 for a detailed mechanistic treatment). It is important, however, that the electrochemical reduction occurs by participation of protons and electrons in the absence of hydrogen.

Similar results have been obtained for the electro-reduction of p-nitrophenol on a tungsten carbide powder deposited on a platinum sheet. The polarization curve is given in Figure 4 which shows that the electro-

3 M. J. Allen, ' Organic Electrode Processes,' Reinhold, New York, 1958.
4 F. A. Pohl and H. Böhm, Proceedings of the 3rd Journées Internationales d'Etude des Piles á Combustible, Bruxelles, 1969, p. 180; *Wiss. Ber. AEG-Telefunken*, 1968, **41**, 46; H. Böhm, *Electrochim. Acta*, 1970, **15**, 1273.

reduction of p-nitrophenol on tungsten carbide takes place at relatively high potentials (measured against a hydrogen electrode immersed in the supporting electrolyte).

(ii) The second reaction is the electrochemical oxidation of hydrogen [reaction (E) where subscript a

$$H_2 \rightleftharpoons 2H_a \quad (Ei)$$

$$H_a \rightleftharpoons H^+ + e \quad (Eii)$$
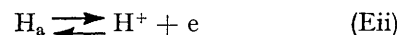
indicates the adsorbed state]. The oxidation of hydrogen on tungsten carbide has been the subject of several studies of fuel cells.[4-6] It has been found that the dissociative adsorption of hydrogen is rate determining and a limiting current (rate) is reached with increasing potential. The limiting current is proportional to the concentration of hydrogen in solution. Process (Ei) is described by equation (5) (assuming Langmuir conditions). The limiting rate (current) is reached at

$$w_H = k_a c_{H_2}(1 - \theta_H)^2 - k_d \theta_H^2 \quad (5)$$

$\theta \ll 1$ and in this case equation (6) is obtained. The

$$w^l_H = k_a c_{H_2} \quad (6)$$

relationship between θ_H and E is given by equation (7).

$$w_H = k_+ \theta_H \exp\left(\frac{\alpha F}{RT} E\right) -$$
$$k_-[H^+](1 - \theta_H) \exp\left[-\frac{(1 - \alpha)F}{RT} E\right] \quad (7)$$

Assuming a quasi-equilibrium for reaction (Eii), relationship (8) is obtained, where $K_e = k_-[H^+]/k_+$. From

$$\theta_H = \frac{K_e \exp - \dfrac{F}{RT} E}{1 + K_e \exp - \dfrac{F}{RT} E} \quad (8)$$

equation (8) it follows that an increase of E results in a decrease of θ_H and the limiting current is reached according to equation (5).

Conclusions.—The kinetic laws of hydrogenation correspond to those of electrochemical oxidation of hydrogen when the process takes place at potentials which correspond to those of the limiting current. The reaction is of zero order with respect to the substrate. It is first order with respect to hydrogen. The same rate may be observed for substrates of different chemical nature.

5 H. Binder, A. Köhling, W. Kuhn, W. Lindner, and G. Sandstede, *Energy Conversion*, 1970, **10**, 29; *Nature*, 1969, **224**, 1299.
6 D. Baresel, W. Gellert, J. Heidemeyer, and P. Scharner, *Angew. Chem.*, 1971, **83**, 213.