creasing time of reaction. This phenomenon is most likely due to the poisoning effect of the reaction product on the catalyst surface. Such a poison effect of aliphatic amines was also found by de Ruiter and Jungers[3] in their study of hydrogenation of aniline to cyclohexylamine over a nickel catalyst.

The hydrogenation of aromatic and aliphatic nitrocompounds over platinum also differ in their

(3) E. de Ruiter and J. L. Jungers, Bull. soc. chim. Belges, 58, 210 (1948).

response to the change of acidity of the solution. For aromatic nitrocompounds, the rate of hydrogenation increases with the addition of acid and base, the accelerating effect of the acid being much greater than that of base; whereas, for aliphatic nitrocompounds, the rate of hydrogenation decreases with the addition of acid or base. The reason for this effect is not yet known.

Kinetics of Liquid Phase Hydrogenation. III. The Nature of Platinum Oxide Catalysts

BY HSIEN CHENG YAO AND P. H. EMMETT

The rate of reduction by hydrogen at 25° of Adams platinum oxide catalyst suspended in liquids increases in the order neutral solution < alkaline solution < acid solution < glacial acetic acid. The hydrogenating activity of the platinum oxide for aromatic and aliphatic nitrocompounds is very low until partial reduction of the oxide occurs. The reduction of nitrophenol and nitromethane over the platinum formed by reduction of the oxide is first order with respect to hydrogen and, with small amounts of catalyst, first order with respect to the nitro compound.

Introduction

Adams, Cohen and Rees[1] in the study of solvent effects on the catalytic hydrogenation of nitrocompound over platinum oxide found that sodium hydroxide has a distinct poisoning effect. They assumed that the sodium hydroxide probably reacted with the nitrobenzene to form a compound or compounds poisonous to the catalyst. Keenan, Giesemann and Smith[2] studied the hydrogenation of benzene over platinum oxide and reported that the hydrogenation did not take place in the presence of platinum oxide alone. The use of methanol as solvent was ineffective. However, when acid such as acetic acid was employed as solvent, benzene accepted hydrogen readily. They also pointed out that when the platinum oxide was prereduced, it would hydrogenate benzene. They conclude that the platinum oxide catalyst prepared by the standard method contained sodium in some form which would inhibit the hydrogenation and would react with acetic acid to eliminate the inhibiting effect. Furthermore, Smith and Bedoit[3] reported that over platinum oxide catalyst, the kinetics of hydrogenation of aromatic nitrocompounds are different from that of aliphatic nitrocompounds; the former gives a zero order reaction whereas the latter is first order with respect to the substrate.

In the results presented previously on the kinetic study of hydrogenation of nitrocompounds over colloidal palladium, rhodium[4] and platinum catalysts,[5] there is no evidence of poisoning by sodium

(1) R. Adams, F. L. Cohen and O. W. Rees, THIS JOURNAL, 49, 1093 (1927).

(2) C. W. Keenan, B. W. Giesemann and H. A. Smith, ibid., 76, 229 (1954).

(3) H. A. Smith and W. C. Bedoit, Jr., J. Phys. and Colloid Chem., 55, 1085 (1951).

(4) Hsien-Cheng Yao and P. H. Emmett, J. Am. Chem. Soc., 81, 4125 (1959).

(5) Hsien-Cheng Yao and P. H. Emmett, ibid., 83, 796 (1961).

hydroxide or that the acid solution has any decisive advantage over the basic or neutral solutions for the hydrogenation reaction. The present investigation was undertaken in the hope of learning more as to the nature of platinum oxide catalysts and the reaction kinetics of the hydrogenation of nitrocompound over this catalyst.

II. Experimental and Results

Apparatus and Rate Measurements.—The apparatus and the rate measurements have been described previously.[34] Conventional BET apparatus was used to measure the surface area.

Catalyst.—The platinum oxide catalyst was purchased from the American Platinum Works, Newark, New Jersey.

The Reduction of Platinum Oxide with Hydrogen.—The platinum oxide was suspended in 100 ml. of 1% PVA aqueous solution (except the one with glacial acetic acid) and then reduced with hydrogen at 25° and 1 atm. The rate of reduction was followed by measuring the volume of hydrogen consumed at constant pressure. The total volume of solution used was 100 ml. and the shaking frequency was 280 min.$^{-1}$. The theoretical consumption of hydrogen is 32 cc. S.T.P. for 0.16 g. of PtO_2. The observed hydrogen consumptions shown in Fig. 1 ranged from about 36 cc. to 46 cc. at room temperature and 760 mm. pressure. These observed values include solubility of hydrogen in the solutions and probably some adsorption on the Pt product. The results of reduction in various solvents are shown in Figs. 1 and 2.

Rate Measurements of Hydrogenation of Nitrocompounds over a Reduced Catalyst.—In this study the platinum oxide solution was prepared by suspending platinum oxide in 100 ml. of 1% PVA aqueous solution and reduced with hydrogen at 25° prior to each rate measurement. The following results have been obtained by using the reduced catalyst.

1. The catalytic activity of the reduced platinum catalyst. The rates of hydrogenation of nitrobenzene and nitromethane in this case were measured by adding after reduction of the PtO_2 an excess of reactant (3 cc. of nitrobenzene or 2 cc. of nitromethane) in 100 cc. of aqueous solution that was neutral, acid (1 ml. of 70% $HClO_4$) or basic (3 cc. of 10% NaOH). One experiment with nitromethane was carried out in glacial acetic acid. About 0.16 g. of PtO_2 was in each 100 cc. of solution prior to reduction. The rates of hydrogenation of nitrobenzene were in the ratios 100:75:65 for acid, basic and neutral solutions; for nitromethane the
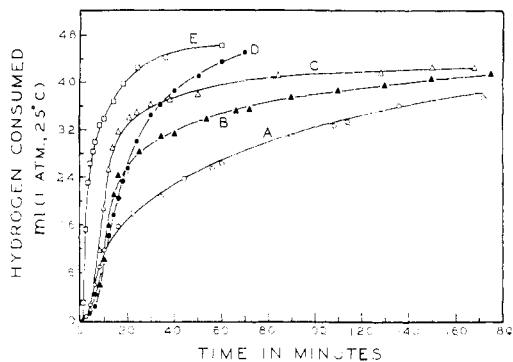
Fig. 1.—Rate curves of reduction of PtO_2 with hydrogen: A, 0.1591 g. of PtO_2 in 100 ml. of aqueous solution; B, 0.1586 g. of PtO_2 in 100 ml. of aqueous solution containing 3 ml. of 10% NaOH; C, 0.1620 g. of PtO_2 in 100 ml. of aqueous solution containing 1 ml. of 70% $HClO_4$; D, 0.1589 g. of PtO_2 in 100 ml. of a water–alcohol solution containing 10% by vol. of ethanol; E, 0.1595 g. of PtO_2 in 100 ml. of glacial acetic acid.
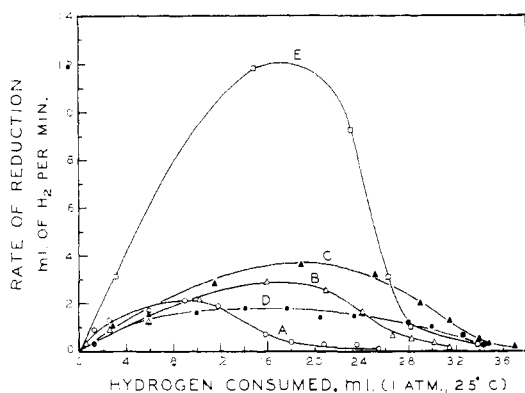

Fig. 2.—Replot of Fig. 1 as rate of reduction against the amount of hydrogen consumed. A, B, C, D and E are the same as those in Fig. 1.

ratios were 100:40:30:15 for glacial acetic acid, neutral, basic and acidic solutions, respectively. The catalytic activity of the reduced catalyst remained constant throughout each experiment.

2. The reaction order with respect to the nitrocompound. The rates of hydrogenation of p-nitrophenol and nitromethane over various amounts of the reduced catalyst and in different solvents have been measured. The results are shown in Figs. 3 and 4.

3. The reaction order with respect to the pressure of hydrogen. The rates were measured at constant volume of hydrogen and in the presence of excess of nitrocompound. The reactions for both nitromethane and nitrobenzene were found to be first order with respect to the hydrogen pressure within the pressure range of 300 mm. to 850 mm.

Rate Measurements of the Hydrogenation of Nitrocompounds over Unreduced Catalyst.—The platinum oxide catalyst solution was prepared by adding a known amount of platinum oxide (about 0.16 g.) into 100 ml. of 1% polyvinyl alcohol aqueous solution; then 2 ml. of nitromethane or 3 ml. of nitrobenzene was added. The rates of hydrogenation were measured at constant pressure of 1 atm. and 25°. This study was carried out in acidic, alkaline and neutral solutions; the results are shown in Figs. 5 and 6 for nitromethane and nitrobenzene, respectively.

Determination of Surface Area of Platinum Oxide.—The surface area of the platinum oxide was measured by nitrogen adsorption at −195°. V_m calculated from the adsorption isotherm using the BET equation was converted to surface area assuming the cross-sectional area of the adsorbed nitrogen molecules to be 16 Å.². The surface area thus calculated is 104 m.²/g.
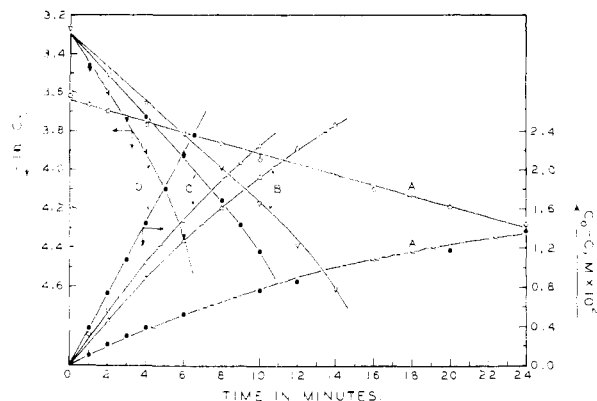

Fig. 3.—Rate curves of hydrogenation of p-nitrophenol in aqueous solution containing 15% by vol. of ethanol over reduced catalyst at 25°.

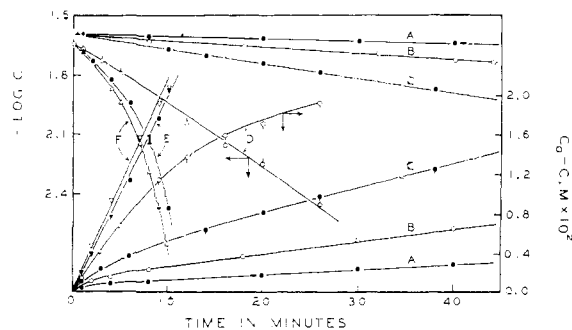|	PtO_2, mg.	C_0, M	Solvent
A	24.4	0.0268	Neutral
B	48.8	.0346	Neutral
C	73.2	.0346	Neutral
D	73.2	.0346	Acidic

Fig. 4.—Rate curves for the hydrogenation of nitromethane over reduced catalyst at 25°: A, B, C, D in 100 ml. of aqueous solution. E, F in 100 ml. of aqueous solution containing 5% by vol. of acetic acid.

	PtO_2.g.	C_0, M		PtO_2.g.	C_0,M
A	0.1092	0.0260	D	0.7870	0.0227
B	.2318	.0260	E	.7870	.0227
C	.4514	.0260	F	1.4364	.0227

III. Discussion

The initial rate of hydrogenation of both aliphatic and aromatic nitrocompounds over unreduced platinum oxide catalyst was found to be very low. Comparison of Figs. 5 and 6 with Fig. 1 shows that the initial rates of hydrogenation over unreduced catalyst are much less than would be expected for reduction of the catalyst alone, especially with the aromatic nitrocompound. A sharp rise in rate was observed after about 20 ml. of hydrogen was consumed except in the case of the aromatic nitrocompound in neutral solution. The rates in this rising part are of the same order of magnitude as that over the pre-reduced catalyst. Such results are consistent with these reaction characteristics:

(1) Platinum oxide is not catalytically active for the hydrogenation of nitrocompounds. Hydrogenation takes place only over the surface of reduced catalyst.
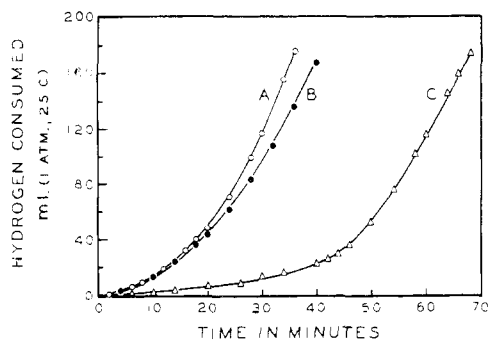
Fig. 5.—Rate curves of hydrogenation of excess amount of nitromethane in aqueous solution over PtO₂ at 25°: A, 0.1603 g. of PtO₂ in 102 ml. of neutral solution containing 2 ml. of nitromethane; B, 0.1571 g. of PtO₂ in 102 ml. of acidic solution (1 ml. of 70% HClO₄) containing 2 ml. of nitromethane; C, 0.1590 g. of PtO₂ in 102 ml. of alkaline solution (3 ml. of 10% NaOH) containing 2 ml. of nitromethane.
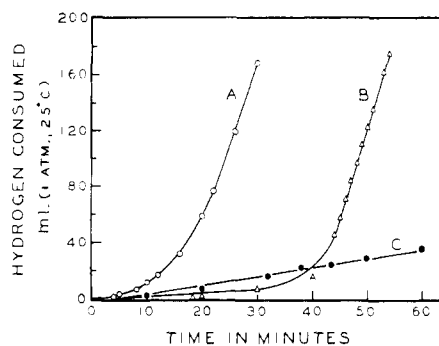
Fig. 6.—Rate curves of hydrogenation of excess amount of nitrobenzene in aqueous solution over PtO₂ at 25°: A, 0.1608 g. of PtO₂ in 103 ml. of acidic solution (1 ml. of 70% HClO₄) containing 3 ml. of nitrobenzene; B, 0.1590 g. of PtO₂ in 103 ml. of alkaline solution (3 ml. of 10% NaOH), containing 3 ml. of nitrobenzene; C, 0.1591 g. of PtO₂ in 103 ml. of neutral solution, containing 3 ml. of nitrobenzene.

(2) Nitrocompounds inhibit the reduction of platinum oxide to platinum. This inhibiting effect varies with the nature of the nitrocompound and the reaction medium, and it is greatest in the case of aromatic nitrocompounds in neutral or alkaline solution. This may be due to the fact that aromatic nitrocompounds are adsorbed on the unreduced platinum oxide more strongly than the aliphatic nitrocompounds. Smith and his co-workers[6] reported that nitrobenzene inhibits the deuterium–hydrogen exchange over platinum oxide while nitroethane does not; this agrees with the present observation. That Adams, Cohen and Rees[1] found that sodium hydroxide in solution poisons the hydrogenation of nitrobenzene over platinum oxide is also in agreement with our results.

The plot of reduction rate of platinum oxide against the amount of hydrogen uptake as shown in Fig. 2 indicates that the reduction is self-catalyzed initially. A maximum in rate is reached as 16–18 ml. (1 atm., 25°) of hydrogen is consumed (except the one in neutral solution which gave a maximum rate when 8 ml. of hydrogen was taken up). On the assumption that each surface PtO₂ molecule reacts with two hydrogen molecules, this maximum point (16–18 ml.) corresponds roughly to complete reduction of one layer of oxide, to the saturation of the solvent with dissolved hydrogen and to the adsorption of a hydrogen molecule by each surface atom of platinum. Further reduction of the inner layers of the oxide constitutes the decreasing branch of the rate curve.

After the platinum oxide was reduced by hydrogen, its catalytic properties in hydrogenation of the p-nitrophenol and also the nitromethane are similar to those of colloidal Pd, Rh and Pt catalysts in the hydrogenation of aromatic nitrocompounds. The reaction order with respect to the nitrocompound is dependent on the amount of catalyst and the nature of solvent as shown in Figs. 3 and 4. The reaction is first order with respect to the hydrogen

pressure within the pressure range studied. It is first order with respect to the concentration of both aromatic nitrocompounds and aliphatic nitrocompounds when the amount of catalyst, type of solvent and temperature are such as to produce a low enough reaction rate.

Smith and Bedoit[3] reported that in the hydrogenation of nitrocompounds over the platinum oxide catalyst the reaction orders with respect to the substrate are different for the reaction of an aromatic nitrocompound than for an aliphatic nitrocompound. The former was reported to yield a zero order reaction and the latter a first order reaction with respect to the concentration of the substrate. In view of the fact that the rate of hydrogenation of the aliphatic nitrocompounds is much lower than that of the aromatic nitrocompounds, such variation of reaction order under same reaction conditions is not unexpected. However, by increasing the amount of catalyst and the addition of acid into the solution the reaction rate of hydrogenation of nitromethane can be greatly increased and changed from first order to zero order with respect to the nitromethane as is evident from the data in Fig. 4.

The reaction of nitromethane over reduced platinum oxide catalyst differs from that over colloidal platinum[5] in one respect; there is no product poisoning effect observed over reduced platinum oxide. Adams and Shriner[7] reported that the platinum oxide prepared from the fusion of chloroplatinic acid and sodium nitrate contains some alkali ranging from 1.72 to 4.80% depending on the temperature of fusion. Smith and co-workers[2] analyzed the platinum oxide purchased from the American Platinum Works which is presumably the same type of sample used in the present study and reported 2.2% sodium. It is therefore suspected that the alkali present in the catalyst may be responsible for the absence of the poisoning effect of the aliphatic amine formed.

(6) L. E. Line. Jr., B. Wyatt and H. A. Smith. THIS JOURNAL. 74, 1808 (1952).

(7) R. Adams and R. L. Shriner. ibid.. 45, 2171 (1923).