

fit by  $\text{Cl}^-$  in the same way as is the reaction between  $\text{Co}(\text{NH}_3)_6^{+++}$  and  $\text{Cr}^{++}$ . A careful quantitative study of the catalysis by anions as a function of temperature may however lead to a means of distinguishing between the two kinds of activated complexes. Newton<sup>7</sup> has suggested that there may be a systematic difference in the entropies of activation for reactions having the activated complexes  $[\text{M}_1\text{X M}_2]_{\text{aq}}^{+p}$  and  $[\text{M}_1(\text{H}_2\text{O})_n (\text{H}_2\text{O})_m \text{M}_2\text{X}]^{+p}$  (both referred to reactants in the same state) and the point is well worth a detailed investigation.

The mechanism of reaction of  $\text{V}_{\text{aq}}^{++}$ , which seems more closely to approximate to the outer sphere than to the bridged activated complex, must in the last analysis be explicable on electronic grounds. "The" electron which is transferred from  $\text{V}_{\text{aq}}^{++}$  resides in a  $t_{2g}$  orbital; d orbitals of this symmetry type maximize along axes perpendicular to the faces of the coordination octahedron. Thus, sigma overlap of reductant orbitals with the acceptor orbital (presumably the  $d_z^2$  orbital of  $\text{Co}(\text{III})$ ) is facilitated by attack of the ligand of the oxidant most "permeable" to electrons at a face of the coordination octahedron of the reductant. With  $\text{Cr}_{\text{aq}}^{++}$  as reductant, the electron which is to transfer resides in an  $e_g$  orbital, say  $d_z^2$ , and a bridged

(7) T. W. Newton, private communication.

activated complex is required to provide sigma overlap with the  $d_z^2$  orbital of the oxidant.

It is interesting (and it may be productive) to speculate on the origin of the scatter in the rate measurements for the system  $\text{V}_{\text{aq}}^{++} + \text{Co}(\text{NH}_3)_5\text{OH}_2^{+++}$ . The factor of 2 in scatter can be explained by the reaction sequence

1.  $\text{Co}^{\text{III}}(t_{2g}^6) + \text{V}^{\text{II}}(t_{2g}^3) \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g) + \text{V}^{\text{III}}(t_{2g}^2)$
2.  $\text{Co}^{\text{II}}(t_{2g}^5e_g) + \text{Co}^{\text{III}}(t_{2g}^6) \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g^2) + \text{Co}^{\text{III}}(t_{2g}^6e_g)$
3.  $\text{Co}^{\text{III}}(t_{2g}^5e_g) + \text{V}^{\text{II}}(t_{2g}^3) \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g^2) + \text{V}^{\text{III}}(t_{2g}^2)$
4.  $\text{Co}^{\text{II}}(t_{2g}^5e_g) + \text{M} \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g^2)$
5.  $\text{Co}^{\text{III}}(t_{2g}^5e_g) + \text{M} \longrightarrow \text{Co}^{\text{III}}(t_{2g}^6)$

If reaction 1 is rate-determining in all cases, and either reaction 4 or 5, de-excitation by some adventitious impurity, is much faster than reaction 2 and 3, the observed rate will be the rate of 1. Contrarywise, if reactions 2 and 3 are rapid compared to the de-excitations 4 and 5, the observed rate will be twice that of 1. Scatter is to be understood on the basis of a competition between de-excitation and energy transfer leading to reaction.

**Acknowledgment.**—This work was supported by the Atomic Energy Commission under Contract AT(11-1)-378.

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## Kinetics of Liquid Phase Hydrogenation. II. Hydrogenation of Aromatic and Aliphatic Nitrocompounds Over A Colloidal Platinum Catalyst

BY HSIEN-CHENG YAO AND P. H. EMMETT

RECEIVED JUNE 20, 1960

The rate of hydrogenation of para-substituted nitrobenzene over colloidal platinum obeys the same kinetic equation found applicable to the hydrogenation over colloidal rhodium and palladium catalysts.<sup>1</sup> The hydrogenation of aliphatic nitrocompounds seems to be poisoned by the reaction products. Another difference is that with the addition of acid or base the rate of hydrogenation of aromatic nitrocompounds increases whereas the rate for aliphatic nitrocompounds decreases.

### Introduction

In the first part of this kinetic study of liquid phase hydrogenation,<sup>1</sup> the reaction characteristics of the hydrogenation of aromatic nitrocompounds over colloidal rhodium and palladium catalysts have been described. A kinetic equation was derived and found to be in good agreement with all the results found in the reactions studied. The present investigation is designed to extend the same kinetic study to hydrogenation reactions over colloidal platinum. For the reaction substrate, aromatic nitrocompounds and a few aliphatic nitrocompounds were used.

### Experimental and Results

**Apparatus and Procedures.**—The same apparatus and experimental procedures as that described previously<sup>1</sup> were used.

**Preparation of the Catalyst.**—The solution of platinum chloride containing 0.5 mg. of Pt per ml. of solution was prepared by dissolving either platinum chloride or 10% solution of  $\text{H}_3\text{PtCl}_6$  in 1% polyvinyl alcohol (PVA) aqueous solution.

(1) Hsien-Cheng Yao and P. H. Emmett, *THIS JOURNAL*, **81**, 4125 (1959).

To 500 ml. of this solution, 3 ml. of 10% NaOH solution was added; the solution was then brought to a boil for a few minutes. After the solution was cooled down to 0° in an ice bath, 0.2–0.3 ml. of hydrazine hydrate was added. The solution was then shaken and gradually warmed to room temperature. The brown solution did not change appearance in the first few minutes; then the color became darker followed by a sudden change to a black color with evolution of gas. It was then boiled for 10 minutes and stored for use.

**Determination of Reaction Order with Respect to Aromatic Nitrocompounds.**—The rates of hydrogenation of aromatic nitrocompounds were determined under constant pressure of hydrogen. The following factors which were found to affect the order of reaction were studied by varying only one particular factor and maintaining the other conditions constant in each series of experiments.

1. **The Amount of Catalyst.**—In a series of seven experiments only the amount of catalyst used was varied. The amount of Pt in 100 ml. of aqueous solution containing 0.002322 mole of *p*-nitrophenol ranged from 0.5 to 20 mg. The results of a series of experiments in neutral solutions are plotted according to zero order kinetics with respect to the substrate in Fig. 1. Similar results were obtained in a parallel series of experiments under the same conditions but in solutions made acidic by the addition of 1 ml. of 70%  $\text{HClO}_4$ . It was found that the reaction order with respect to the nitrocompound changes from first to zero order with increasing amount of catalyst. The amounts of platinum at

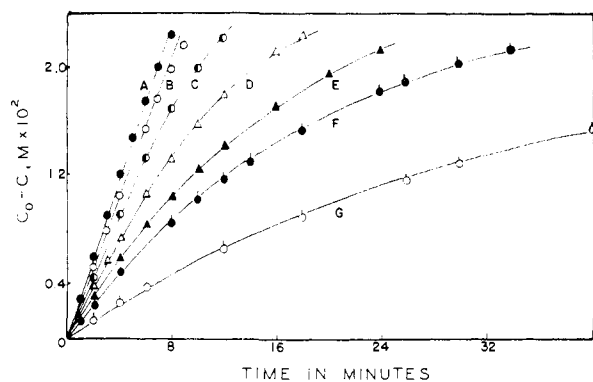


Fig. 1.—Rate curves for the hydrogenation of *p*-nitrophenol in 0.0232 molar aqueous solution at 25° over various amounts of platinum: A, 20 mg.; B, 10 mg.; C, 5 mg.; D, 2.5 mg.; E, 1.5 mg.; F, 1 mg.; G, 0.5 mg.

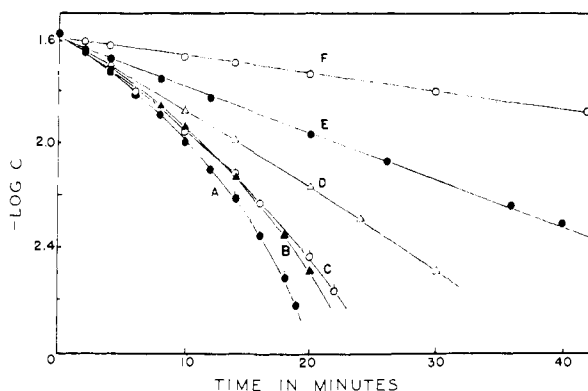


Fig. 2.—Rate curves for the hydrogenation of *p*-nitrophenol over 2.5 mg. of platinum in 0.02685 molar aqueous solution containing various amounts (% by vol.) of ethanol: A, 15; B, 30; C, 40; D, 50; E, 60; F, 70.

which the reaction becomes zero order are 10 and 5 mg. for the neutral and acidic solutions, respectively.

2. **The Nature of the Solvent.**—A series of six runs was made using as solvents water-ethanol mixtures with composition varying from 15 to 70% by volume of ethanol. There were 2.5 mg. of platinum and 0.002685 ml. of *p*-nitrophenol in each 100 ml. of the solution, and the determinations were carried out at 25°. The results, as shown in Fig. 2, indicate that the reaction changes from fractional order to first order with respect to the *p*-nitrophenol substrate as the content of ethanol in the solvent increases; actually, for ethanol concentrations of 50% or higher by volume, the reaction under the specified reaction conditions was found to be first order with respect to the *p*-nitrophenol concentration.

3. **The Nature of the Nitrocompounds.**—The dependence of the reaction rate and reaction order with respect to substrate on the nature of the aromatic nitrocompounds is shown in Table III.

4. **The Acidity of the Solution.**—The rates of hydrogenation of *p*-nitrophenol at 25° were measured in neutral, acidic and alkaline solutions. In each of these measurements 100 ml. of the solution was used containing 0.002685 mole of *p*-nitrophenol, 60% by volume of ethanol and 2.5 mg. of platinum catalyst. The acidic solution was made by adding 1 ml. of 70% HClO<sub>4</sub> and making the solution up to 100 ml.; the alkaline solution, by adding 3 ml. of 10% of NaOH solution. The time for half conversions were 3, 17 and 17 minutes, respectively, for acid, alkaline and neutral solutions. It appears that addition of acid to the solution is much more effective in increasing the rate of hydrogenation of *p*-nitrophenol than the addition of alkali.

**Determination of Reaction Order with Respect to Aliphatic Nitrocompounds.**—The results for hydrogenation of nitromethane and nitroethane over colloidal platinum are

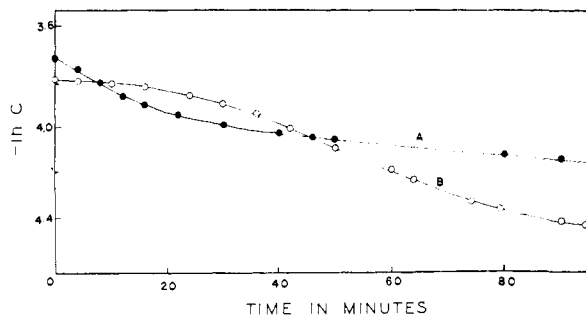


Fig. 3.—Rate curves of hydrogenation of nitromethane (A,  $C_0 = 0.0247 M$ ) and nitroethane (B,  $C_0 = 0.0225 M$ ) in 15% by vol. of ethanol aqueous solution over 2.5 mg. of Pt at 25°.

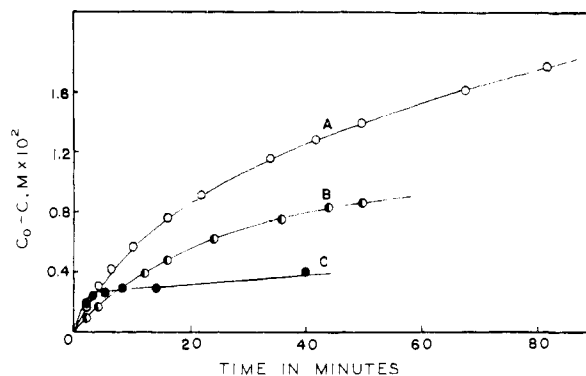


Fig. 4.—Rate curves for the hydrogenation of excess amount of nitromethane over 5 mg. of Pt at 25°: A, 100 ml. of aqueous solution; B, 100 ml. of aqueous solution containing 3 ml. of 10% NaOH; C, 100 ml. of aqueous solution containing 1 ml. of 70% HClO<sub>4</sub>.

plotted in Fig. 3 according to first order with respect to the nitrocompounds. The rate curves show that the reaction order with respect to the substrate is greater than the first. In the hydrogenation of nitroethane the reaction is delayed at the beginning. If excess amount of nitromethane was used to maintain the substrate concentration essentially constant, the rate was found to decrease as the reaction proceeds as shown in Fig. 4. This differs from the behavior observed for aromatic nitrocompounds for which pseudo-zero order reaction prevails under similar conditions. The effect of acidity of the solution on the reaction rate is also shown in Fig. 4. Both acid and alkali reduce the rate of hydrogenation of nitromethane, whereas acid greatly enhances the reaction rate of *p*-nitrophenol as described above.

**Determination of Reaction Order with Respect to Hydrogen Pressure.**—To study the pressure dependence the rates of hydrogenation of aromatic and aliphatic nitrocompounds were measured under constant volume conditions. Excess amount of nitrocompound was used to keep its concentration essentially constant during the rate measurements. It is found that the hydrogenation of *p*-nitrophenol over colloidal platinum is first order with respect to hydrogen. For nitromethane, the reaction order with respect to hydrogen pressure could not be determined by the same method due to the fact that reaction rate decreases as the reaction proceeds even at the constant pressure of hydrogen. By comparison of the initial rates of three runs under the same conditions except different hydrogen pressures, it is shown in Table I that the rate of hydrogenation of nitromethane increases with an increase in the pressure of hydrogen.

## Discussion

In the previous study of liquid phase hydrogenation of aromatic nitrocompounds over colloidal palladium and rhodium catalysts,<sup>1</sup> the kinetic

TABLE I

THE VARIATION OF INITIAL RATE WITH INITIAL PRESSURE OF HYDROGEN IN THE HYDROGENATION OF EXCESS AMOUNT<sup>a</sup> OF NITROMETHANE OVER PLATINUM AT 25°

Amount Pt, mg.	Time, min.	Initial pressure hydrogen, mm.	Methylamine formed, $M \times 10^4$
5	6	122	0.77
5	6	391	0.91
5	6	736	2.0

<sup>a</sup> 2 ml. of nitromethane in 100 ml. of water.

equation was derived for the rate of change in the concentration of the substrate with time

$$-\frac{dC}{dt} = \frac{(k_0 k_1 / k_2) W C P_{H_2} \exp\left(\frac{\Delta F_{sol}^0}{RT}\right)}{1 + 3(k_0 / k_2) W C \exp\left(\frac{\Delta F_e^0}{RT}\right)} \quad (1)$$

$W$  is the weight of catalyst and  $P_{H_2}$ , the partial pressure of hydrogen. The other symbols have the same meaning as those designated previously.<sup>1,2</sup> Equation 1 can be simplified to

$$-\frac{dC}{dt} = \frac{abC}{1 + bC} \quad (2)$$

where

$$a = \frac{1}{3} k_1 P_{H_2} \exp\left(\frac{-\Delta F_e^0}{RT}\right)$$

and

$$b = 3(k_0 / k_2) W \exp\left(\frac{\Delta F_e^0}{RT}\right)$$

At constant temperature and pressure,  $a$  and  $b$  are constants. When  $bC \gg 1$ , equation 2 becomes

$$-\frac{dC}{dt} = a \quad (3)$$

and the apparent order of the reaction becomes zero. When  $bC \ll 1$ , equation 2 becomes

$$-\frac{dC}{dt} = abC \quad (4)$$

the rate then being apparent first order with respect to the original reactant. Integration of (2) gives

$$\frac{1}{b} \ln \frac{C_0}{C} + (C_0 - C) = at \quad (5)$$

Knowing the initial concentration of the substrate,  $C_0$ , one can calculate constants  $a$  and  $b$  from any two points on the rate curve. By the application of equation 5 to the experimental results obtained for the hydrogenation of *p*-nitrophenol over colloidal platinum the values of  $a$  and  $b$  were calculated; they are listed in Table II. Plotting  $1/b$

TABLE II

HYDROGENATION OF *p*-NITROPHENOL IN WATER ( $C_0 = 0.0232 M$ ) OVER PLATINUM AT 25°<sup>a</sup>

Amount Pt,	$a \times 10^3$	$b$
10	2.8	640
5	2.7	296
2.5	2.8	108
1.5	2.8	50
1	2.7	34
0.5	3.1	10

<sup>a</sup> Values of  $a$  and  $b$  are constants of equation 2 and 5.

(2)  $\Delta F_{sol}^0$ , the standard free energy change for the solution of hydrogen equals  $\Delta F_e^0 - \Delta F_s^0$  where  $\Delta F_e^0$  and  $\Delta F_s^0$  are the standard free energies of activation for the escape of hydrogen from the solution and the transfer of hydrogen to the solution, respectively.

$\ln C_0 + (C_0 - C)$  vs.  $t$ , yields a linear relationship for all the data in Fig. 1. This result and the fact that the reaction is first order to hydrogen pressure indicate that equation 1 is valid in the present case. The reaction order with respect to substrate was again found to vary with the amount of catalyst and the nature of the solvent in the same fashion as that found in the hydrogenation of aromatic nitrocompounds over colloidal palladium and rhodium. The "a" value in Table II for the reaction in the same solution but with different amounts of catalyst is essentially constant; however, the  $b$  value which shows an increase with increasing amount of catalyst affects the reaction order with respect to the nitrocompound. The average value of "a"  $2.8 \times 10^{-3} M/\text{min.}$  is of the same magnitude as obtained for the hydrogenation by palladium or rhodium under the same conditions. With a large amount of catalyst and a high water content in the solvent, the reaction is zero order with respect to both the substrate and the catalyst. In this case, the reaction follows equation 3. The "a" values calculated from experiments under conditions described in footnote of Table III are shown in Table III.

TABLE III

THE HYDROGENATION OF NITROCOMPOUNDS OVER PLATINUM

Nitrocompounds	Initial conc., $M \times 10^2$	$a \times 10^3$ , <sup>a</sup> molc min. <sup>-1</sup>	$ab \times 10^3$ , <sup>b</sup> min. <sup>-1</sup>
Nitrobenzene	2.438	5.9	1.4
<i>p</i> -Nitrobenzoic acid	2.524	6.2	5.8
<i>p</i> -Chloronitrobenzene	2.440	6.2	9.4
<i>p</i> -Nitrophenol	2.685	6.1	1.2
<i>p</i> -Nitraniline	2.740	5.7	3.1
<i>p</i> -Nitrotoluene	2.160	6.0	3.2

<sup>a</sup> Conditions in this series of reactions are: temp., 25°; Pt, 7.5 mg; solution vol., 100 ml.; the solution contains 1 ml. of 70% HClO<sub>4</sub> and 60% by vol. of ethanol.  $a$  value is for equation 3. <sup>b</sup> Conditions in this series of reactions are: temp., 25°; Pt, 2.5 mg.; solution vol., 100 ml.; the solution contains 70% by vol. of ethanol and 1 ml. of 70% HClO<sub>4</sub>.  $ab$  value is for equation 4.

Under these conditions, it is shown that the reaction rate is independent of the nature of the substrate. When the amount of catalyst is small and the water content of the solvent is lower, the reaction appears to be first order with respect to the nitrocompound and follows equation 4. The  $ab$  values calculated from equation 4 are listed in the last column of Table III. The effect of the nature of parasubstituents of the aromatic nitrocompounds on the hydrogenation rate under these conditions becomes great.

The rate of hydrogenation of aliphatic nitrocompounds was found to be slower than that of the aromatic nitrocompounds. In such a slow rate range, the reaction would be expected to be first order with respect to the nitrocompound if rate equation 1 were valid. However, the experimental results at constant pressure for both nitromethane and nitroethane indicate that the apparent reaction order is greater than first order with respect to substrate. As the reaction proceeds, the rate becomes much less than expected for a first order reaction. When a large excess of nitrocompound was used to keep the concentration of the substrate essentially constant, the reaction rate still decreased with in-

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<sup>3</sup> 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.

**Acknowledgment.**—We want to thank the National Science Foundation for its financial support of this work.

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

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RECEIVED JUNE 20, 1960

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<sup>1</sup> 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<sup>2</sup> 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<sup>3</sup> 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<sup>4</sup> and platinum catalysts,<sup>5</sup> 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.<sup>3,4</sup> 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.<sup>-1</sup>. The theoretical consumption of hydrogen is 32 cc. S.T.P. for 0.16 g. of PtO<sub>2</sub>. 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<sub>2</sub> 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<sub>4</sub>) or basic (3 cc. of 10% NaOH). One experiment with nitromethane was carried out in glacial acetic acid. About 0.16 g. of PtO<sub>2</sub> 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