JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 81 SEPTEMBER 1, 1959 NUMBER 16

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE JOHNS HOPKINS UNIVERSITY]

Kinetics of Catalytic Liquid Phase Hydrogenation. I. The Hydrogenation of Aromatic Nitrocompounds over Colloidal Rhodium and Palladium

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RECEIVED FEBRUARY 14, 1959

The liquid phase hydrogenation of the aromatic nitrocompounds over colloidal palladium and rhodium catalysts has been studied by kinetic methods. The experimental results indicate: (1) the catalytic behavior of palladium toward the compounds studied is essentially the same as that of rhodium; (2) the reaction is, in general, within the range of hydrogen pressure studied, first order with respect to the hydrogen pressure; (3) the reaction order with respect to the substrate has been found to vary with the nature of the solvent and also with respect to the amount of catalyst present; (4) the nature of the substrate can affect the reaction rate only when the reaction is first or fractional order with respect to the substrate; (5) for a given reaction the energy of activation is in the range 12 to 15 kcal. per mole when measurements are made under conditions leading to fractional or first order with respect to the substrate; the energy of activation is only a few kilocalories under conditions in which the rate is limited by diffusion of hydrogen through the solvent to the catalyst surface. A kinetic equation is derived based on these experimental results and found to be in good agreement with the kinetic characteristics of this reaction.

Introduction

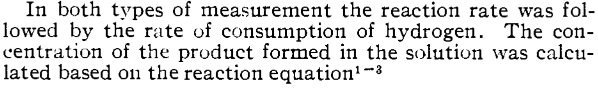
Hernandez and Nord[1,2] reported that for the catalytic hydrogenation of *para*-substituted nitrobenzene over colloidal rhodium the reaction rates were affected by the electron shifting property of the substituents and also increased by the presence of either acid or base in the solution; whereas, the reaction rates over colloidal palladium were affected by neither the nature of the substituents nor the acidity of the solution. The reactions were first order with respect to hydrogen pressure and zero order with respect to the substrate. The mechanism of the rhodium-catalyzed reaction was therefore interpreted as involving the formation of ionic hydrogen on the catalyst surface. The mechanism of the palladium-catalyzed reaction was believed to involve hydrogen atoms rather than protons.

In view of the similarity to be expected between these two noble metals, it seemed worthwhile to re-examine the catalytic hydrogenation of *para*-substituted nitrobenzene over both palladium and rhodium catalysts. The possible differences in the reaction kinetics and mechanisms over these two metals, the causes of the differences and the effects of the reaction environments such as the nature of the solvent are of particular interest.

Experimental and Results

Apparatus and Rate Measurements.—The experiments were carried out in two ways. In one, the rate was followed by measuring the change of hydrogen volume at constant pressure of one atmosphere. In the other, the rate was followed by measuring the change of hydrogen pressure at constant hydrogen. The apparatus used for both types of measurement consisted of a 300-ml. reaction flask which was inserted in a thermostated water-jacket and placed on a shaking machine. The temperature of the reaction flask was maintained constant within ±0.2°, and the shaking frequency was 280 per minute. In the constant pressure measurements, a conventional hydrogenation system[1] was used. For constant volume measurements the reaction was carried out in an enclosed system of which the maximum variation of volume due to change of mercury height in the manometer was about 4 ml.; this introduced an error of less than 2%.

In both types of measurement the reaction rate was followed by the rate of consumption of hydrogen. The concentration of the product formed in the solution was calculated based on the reaction equation[1-3]



The validity of this equation for the present case was verified for nitrobenzene and nitrophenol by the isolation and identification of the amine produced. The proportionality of 1:3 of nitrocompound used to the amount of hydrogen consumed is consistent with the kinetic results obtained.

Preparation of the Catalyst.—The colloidal rhodium and palladium catalysts were prepared using the procedures employed by Hernandez and Nord for preparing colloidal rho-

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(1) L. Hernandez and F. F. Nord, *J. Colloid Sci.*, **3**, 363 (1948).

(2) L. Hernandez and F. F. Nord, *Experientia*, **3**, 489 (1947).

(3) S. S. Scholnik, J. R. Reasenberg, E. Lieber and G. B. L. Smith, THIS JOURNAL, **63**, 1192 (1941).

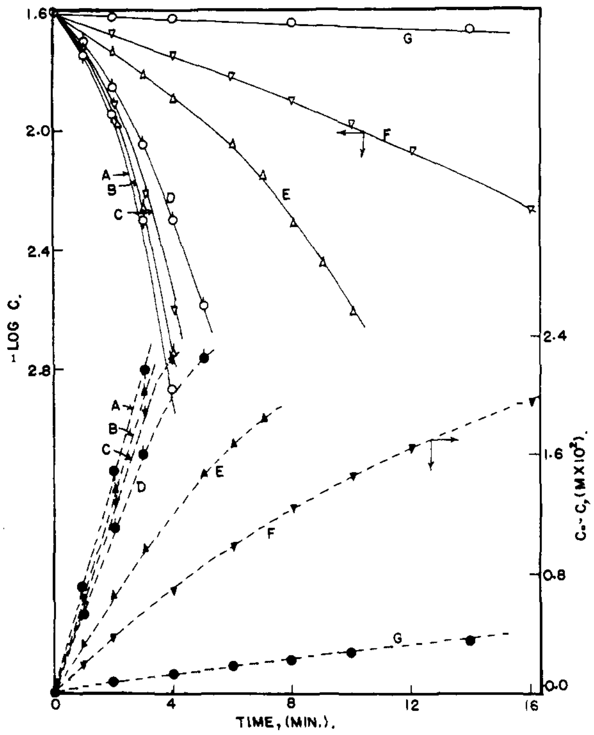

Fig. 1.—Hydrogenation of *p*-nitrophenol in 50% by wt. of ethanol aqueous solution at 25° with various amounts of palladium catalyst: A, 15 mg.; B, 10 mg.; C, 7.5 mg.; D, 5 mg.; E, 2.5 mg.; F, 1.5 mg.; G, 0.5 mg.

dium.[1] The only modification was that the calculated amount of alkali was used to neutralize the acid liberated in reduction; this eliminated the step of further neutralization of excess alkali by acetic acid. The solution obtained has a concentration of 0.5 mg. per ml. and each batch was used as a source of samples for three months without significant change of activity.

Determination of Reaction Order with Respect to Nitrocompound[4]: The rate measurements in this part were carried out under a constant hydrogen pressure of one atmosphere. The amount of nitrocompound used for each experiment was about 2.5 × 10^{-3} mole. In each series of experiments, the reaction was studied by varying only one particular factor and keeping the other conditions constant. The results demonstrated that the apparent reaction order with respect to the nitrocompound is controlled by the following factors.

1. **The Amount of Catalyst.**—The rates of hydrogenation of *p*-nitrophenol over various amounts of palladium and rhodium catalysts are plotted in Fig. 1 and Fig. 2, respectively, according to the zero-order and first-order reaction with respect to the nitrocompound. It is shown that the apparent reaction order with respect to the nitrocompound depends on the amount of catalyst. In both cases, the reaction is first order with respect to nitrocompound at low concentration of catalyst and approaches zero order with respect to nitrocompound as the amount of catalyst increases.

2. **The Nature of the Solvent.**—Two parallel series of rate measurements in water–ethanol and water–dioxane solutions of various compositions are plotted in Figs. 3 and 4, respectively, according to zero- and first-order kinetics with respect to the nitrocompound. The nitrocompounds used for this study are *p*-nitrophenol and *p*-nitroaniline. The results indicate that the solvent composition affects the reaction order in such a way that increasing the water content of both solvent systems shifts the reaction from first to zero order with respect to nitrocompound.

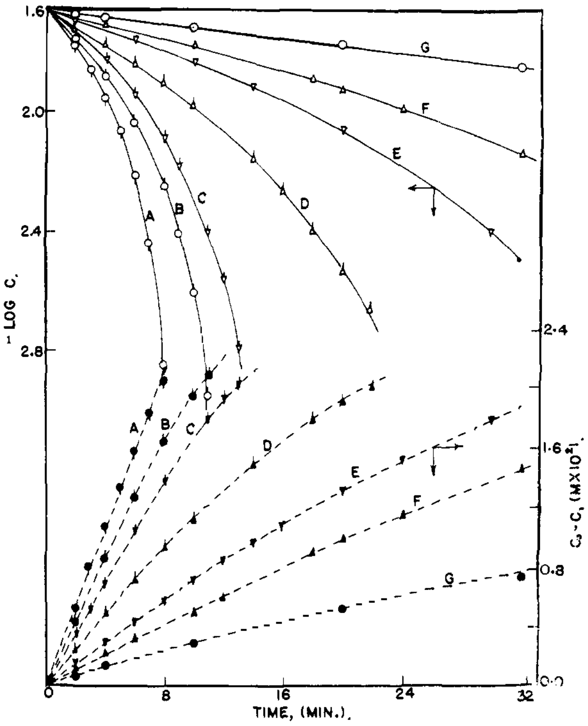

Fig. 2.—Hydrogenation of *p*-nitrophenol in aqueous solution at 25° with various amounts of rhodium catalyst: A, 15 mg.; B, 7.5 mg.; C, 5 mg.; D, 2.5 mg.; E, 1.5 mg.; F, 1 mg.; G, 0.5 mg.

3. **The Nature of Catalyst.**—Under the same experimental conditions and with the same amount of catalyst the rate of hydrogenation over palladium was found to be greater than that over rhodium. Also the reaction reaches zero order at lower amounts of catalyst for palladium than for rhodium. This is shown by comparing curve A of Fig. 4 and curve F of Fig. 6.

4. **The Acidity of the Solution.**—The effect of acidity of the solution on the reaction order depends partly on the amount and nature of the catalyst, the compositon of the solvent and the nature of the substrate. Under the conditions of first order with respect to nitrocompound, *i.e.*, in solvents of low water content and with low amounts of catalyst, the presence of acid or base (1 ml. of 70% $HClO_4$ or 3 ml. of 10% NaOH in 100 ml. of solution) increases the rate of hydrogenation and directs the reaction toward zero order with respect to the nitrocompound. This effect was observed for both palladium- and rhodium-catalyzed reactions. However, under the conditions of zero order with respect to nitrocompound, *i.e.*, in solutions of high water content and with large amounts of catalyst, the effect is negligible for palladium-catalyzed reactions yet is still appreciable in the case of rhodium. Typical curves of the rate of hydrogenation of *p*-nitrophenol in solutions of various acidities are shown in Figs. 5 and 6 for palladium- and rhodium-catalyzed reactions, respectively.

5. **The Nature of the Substrate.**—The rates of hydrogenation of six aromatic nitrocompounds over both palladium and rhodium catalysts have been determined under the same conditions. A typical set of curves for runs over palladium is shown in Fig. 7. The results show that the rate and order of reaction are dependent on the nature of the substituents on the aromatic nitrocompounds. In general, the compounds which react faster with hydrogen tend to have their hydrogenation reaction approaching zero order with respect to the substrate, while those which react slower will follow the first-order relation.

Determination of Reaction Order with Respect to the Hydrogen.—The rate measurements in this part were carried out at constant volume. The space occupied by hydrogen was kept at 230 ml. and an initial total pressure of about one atmosphere was used. In order to keep the concentration of the nitrocompound essentially constant during the rate

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[4] All of the organic nitrocompounds that were purchased as solids were purified by recrystallization; those that were obtained as liquids were purchased as pure compounds and were not further purified. However, care was taken to note the amount of hydrogen consumed during hydrogenation and to make sure that the total consumptions corresponded to that expected for the pure reactant.

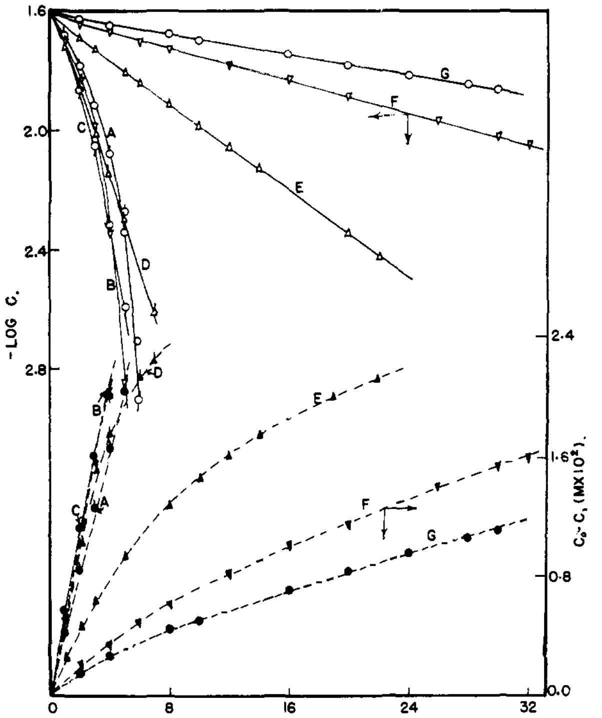

Fig. 3.—Hydrogenation of *p*-nitrophenol in aqueous solution of various amounts of ethanol over 5 mg. of palladium at 25°. The water content of the solvent (% by weight): A, 78; B, 61; C, 50; D, 40; E, 30; F, 20; G, 12.

measurement, a large excess of the nitrocompound of up to 0.04 mole per 100 cc. was used. In cases in which the solubility of the nitrocompound is limited the solution was kept saturated by suspending an excess of the nitrocompound in the solution. The range of pressure change was 750 to 150 mm. The reaction was first order with respect to the partial pressure of hydrogen but independent of the amount of catalyst used (over the range of 2 to 20 mg.) and the nature of the solvent.

Determination of Reaction Rate with Respect to the Amount of Catalyst.—The rate measurements in this part were made at constant pressure and under the same conditions as in the determination of reaction order with respect to the nitrocompound. The rate of reaction was found to increase with increasing amounts of catalyst when the amount of catalyst is low. The curves of initial rate *versus* amount of catalyst as shown in Fig. 8 leveled off when the catalyst reached a certain amount. The shape of the curves depended on the nature of the solvent and of the catalyst.

Determination of the Temperature Coefficients of Hydrogenation.—The rates of palladium- and rhodium-catalyzed hydrogenations were measured at temperatures of 25, 35 and 45° at constant pressure. The results as shown in Tables I and II indicate that the apparent activation energy depends strongly on the amount of catalyst and the nature of the solvent. For the reactions with low concentration of catalyst and solvent of high content of ethanol, E_a ranges from 13 to 16 kcal./mole; whereas with high concentrations of catalyst, E_a dropped to 0 to 1.5 kcal./mole. With an intermediate amount of catalyst, the rate of reaction increases with increasing temperature until it reaches a limiting value after which there is no further change observed.

Discussion

The experimental results obtained demonstrate the following similarities between the palladium and the rhodium catalyzed hydrogenation of aromatic nitrocompounds in liquid phase:

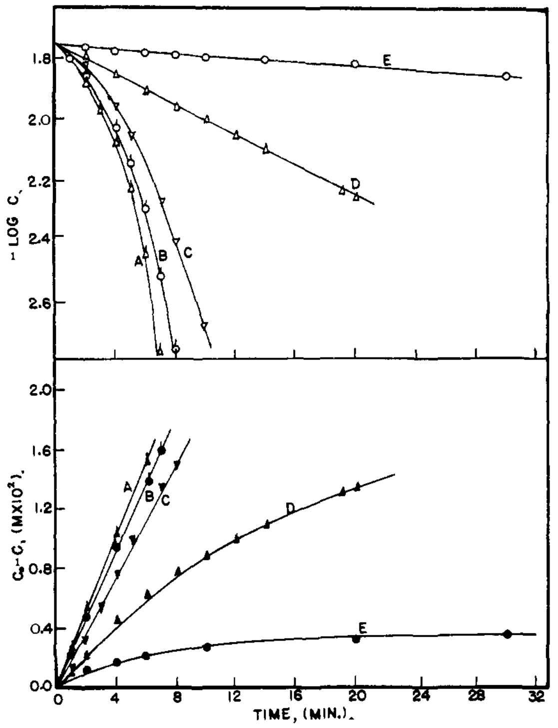

Fig. 4.—Hydrogenation of *p*-nitrophenol over 2.5 mg. of Pd in water–dioxane mixtures at 30°. The amount of dioxane in solvent (% by vol.): A, 0; B, 20; C, 40; D, 60; E, 70.

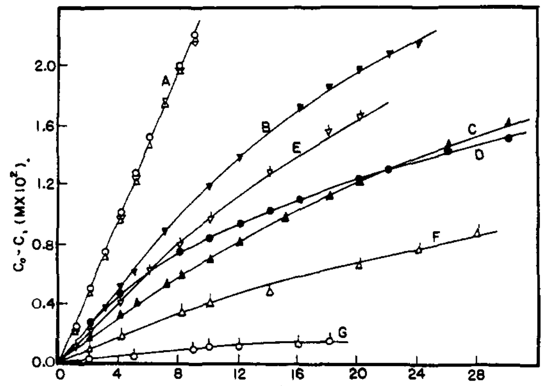

Fig. 5.—Acidity effect on the hydrogenation of nitrocompound over Pd. A, 2.5 mg. of Pd and 0.02359 mole of *p*-nitrophenol in acidic, neutral or alkaline solution at 30°. (In acidic solution the 100 ml. of solution contains 1 ml. of 70% $HClO_4$ and in alkaline solution the 100 ml. of solution contains 3 ml. of 10% NaOH.) B, 0.5 mg. of Pd and 0.02359 mole of *p*-nitrophenol in aqueous acidic solution at 30°. C, same conditions as B, except in alkaline solution. D, same conditions as B except in neutral solution. E, 2.5 mg. of Pd and 0.02604 mole of *p*-nitrotoluene in aqueous acidic solution containing 90% by vol. of ethanol at 25°. F, same conditions as E except in alkaline solution. G, same conditions as E except in neutral solution.

1. The rate of hydrogenation is dependent on the nature of the nitrocompound, the nature of the solvent and the amount of catalyst for both palladium and rhodium under the conditions that the reaction rate is relatively low and is first order or fractional order with respect to the nitrocompound. The reaction can be shifted toward zero

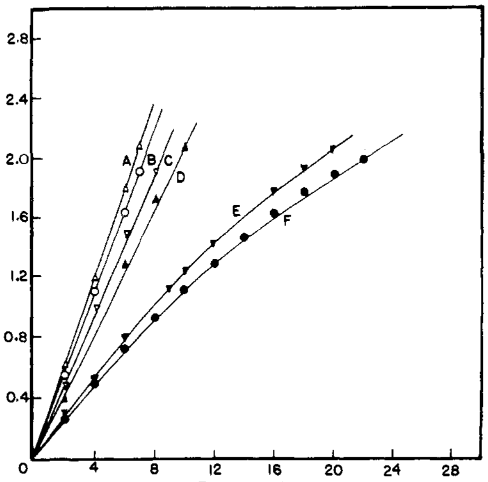

Fig. 6.—Acidity effect on the hydrogenation of *p*-nitrophenol in aqueous solution over rhodium at 30°. A, 20 mg. of Rh and 0.02359 mole of *p*-nitrophenol in alkaline solution. (In acidic solution the 100 ml. of solution contains 1 ml. of 70% $HClO_4$ and in alkaline solution it contains 3 ml. of 10% NaOH.) B, same conditions as A except in neutral solution. C, same conditions as A except in acidic solution. D, 2.5 mg. of Rh and 0.02359 mole of *p*-nitrophenol in alkaline solution. E, same conditions as D except in acidic solution. F, same conditions as D except in neutral solution.

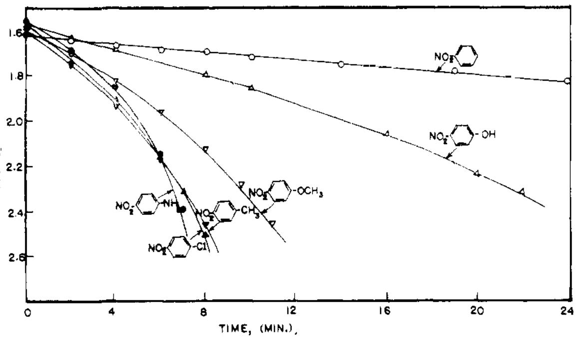

Fig. 7.—Rate curves of hydrogenation of nitrocompounds at 25° over 1 mg. of Pd in 100 ml. of aqueous solution containing 70% by vol. of ethanol and 1 ml. of 70% $HClO_4$.

order with respect to the nitrocompound by increasing and toward first order by decreasing the water content of the solvent, the amount of catalyst or the reaction temperature.

2. Generally, over the pressure range studied (150 to 750 mm.) the reaction is first order with respect to the hydrogen pressure.

3. With low amounts of catalyst, the reaction is essentially first order with respect to the amount of catalyst. As the amount of catalyst increases to a certain value the reaction rate becomes independent of the amount of catalyst. The amount of catalyst required to attain the limiting rate is higher for rhodium than that for palladium. The conditions under which the reaction changes from a fractional order to zero order with respect to nitrocompound also makes the reaction rate independent of the amount of catalyst.

4. The substituents of nitrobenzene affect the reaction rate over either palladium or rhodium only when the reaction is first order or fractional order with respect to the nitrocompound. When the reaction reaches zero order, no appreciable effect of the substituents was found.

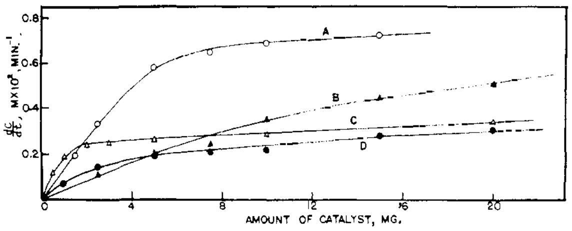

Fig. 8.—The correlation of initial rate of hydrogenation and the amount of catalyst. A, Pd and 0.0484 mole of *p*-nitrophenol in 50% by wt. of ethanol solution at 25°. B, Rh and 0.02604 mole of *p*-nitrotoluene in 50% by vol. of isopropyl alcohol solution at 30°. C, Pd and 0.02567 mole of *p*-nitrophenol in aqueous solution containing 1 ml. of 70% HClO at 30°. D, Rh and 0.02180 mole of *p*-nitrophenol in aqueous solution at 30°.

TABLE I

KINETIC DATA OF HYDROGENATION OF NITROCOMPOUNDS WITH LOW AMOUNTS OF CATALYST[a]

Catalyst, mg.	Nitrocompound	*T*, °C.	ab^b (min.$^{-1}$)	*E*a, kcal.
Pd, 2.5	*p*-Nitrophenol	25	0.0081	
	p-Nitrophenol	35	.0185	15.2
	p-Nitrophenol	45	.0420	
Pd, 2.5	*p*-Nitrotoluene	25	.0177	
	p-Nitrotoluene	35	.0406	16.6
	p-Nitrotoluene	45	.1044	
Pd, 2.5	*p*-Nitroaniline	25	.0711	
	p-Nitroaniline	35	.146	12.4
	p-Nitroaniline	45	.264	
Rh, 5	*p*-Nitrophenol	25	.0080	
	p-Nitrophenol	35	.0157	13.2
	p-Nitrophenol	45	.0326	
Rh, 5	*p*-Nitrotoluene	25	.0057	
	p-Nitrotoluene	35	.0097	13.7
	p-Nitrotoluene	45	.0198	
Rh, 5	*p*-Nitroaniline	25	.0126	
	p-Nitroaniline	35	.0234	12.8
	p-Nitroaniline	45	.048	

[a] Conditions of reaction: solvent, for reactions with 2.5 mg. of catalyst containing 5 ml. of water and 95 ml. of 95% alcohol; for reactions with 5 mg. of catalyst containing 10 ml. of water and 90 ml. of 95% alcohol; total volume 100 ml. [b] *ab* value is the constant of equation 9.

Based on these reaction characteristics and also on the fact that a large difference was found in apparent activation energies between the one obtained from the reactions of high amounts of catalyst and the other obtained from that of a low amount of catalyst, a kinetic equation has been derived to explain the experimental results.

According to the Langmuir–Hinshelwood type of mechanism for the reaction between two adsorbed reactants on the catalyst surface, the rate equation is

$$-\frac{\mathrm{d}C_A}{\mathrm{d}t} = kW\theta_A\theta_B \qquad (1)$$

where *W* is the weight of the catalyst in grams and θ_A and θ_B are the fractional surface coverages by

TABLE II

KINETIC DATA OF HYDROGENATION OF *p*-NITROPHENOL WITH HIGH AMOUNTS OF CATALYST[a]

Catalyst, mg.	*T*, °C.	*a* (mole min.$^{-1}$)	E_a, kcal.
Pd, 10	25	0.0027	
	35	.0035	.....
	45	.0037	
Pd, 20	25	.0035	
	35	.0035	0 to 1.5
	45	.0038	
Rh, 15	25	.0026	
	35	.0033	.....
	45	.0035	
Rh, 10	25	.0026	
	35	.0031	.....
	45	.0033	

[a] Conditions: solvent, water; total volume, 100 ml.

the reactants A and B, respectively, as given by the equations

$$\theta_A = \frac{\alpha C_A}{1 + \alpha C_A + \beta C_B + \gamma_1 C_{S_1} + \gamma_2 C_{S_2}} \quad (1a)$$

$$\theta_B = \frac{\beta C_B}{1 + \alpha C_A + \beta C_B + \gamma_1 C_{S_1} + \gamma_2 C_{S_2}} \quad (1b)$$

where α, β, γ_1 and γ_2 are the adsorption coefficients of the reactants A, B and solvents S_1, and S_2, respectively. The corresponding concentrations of the constituents in the solution are C_A, C_B, C_{S_1} and C_{S_2}. In liquid phase, where the surface of the catalyst is probably fully covered by the molecules of the reactants and solvents, 1 is negligible compared to the other terms in the denominator. If the concentrations of solvents are much larger than those of the reactants, it becomes probable that $\alpha C_A + \beta C_B << \gamma_1 C_{S_1} + \gamma_2 C_{S_2}$ and (1a) and (1b) can be simplified to

$$\theta_A = \frac{\alpha C_A}{\gamma_1 C_{S_1} + \gamma_2 C_{S_2}} \quad (1c)$$

$$\theta_B = \frac{\beta C_B}{\gamma_1 C_{S_1} + \gamma_2 C_{S_2}} \quad (1d)$$

Substituting (1c) and (1d) into (1) and replacing the notations C_A and C_B with C and C_{H_2}, the concentration of the nitrocompound and of hydrogen, respectively, the rate equation for the hydrogenation of nitrocompounds can be simply expressed as

$$-\frac{dC}{dt} = k_0 W C_{H_2} C$$

where

$$k_0 = k\frac{\alpha\beta}{(\gamma_1 C_{S_1} + \gamma_2 C_{S_2})_2} \quad (2)$$

Thus, the rate of hydrogen consumption on the catalyst surface due to the reaction will be

$$-\frac{d}{dt} C_{H_2} = -3\frac{dC}{dt} = 3k_0 W C_{H_2} C \quad (3)$$

Equations 2 and 3 can also be derived for the mechanism that one of the reactants is adsorbed on the catalyst surface and reacts with the other directly from the solution. If this is true, then

$$k_0 = k\frac{\alpha}{\gamma_1 C_{S_1} + \gamma_2 C_{S_2}} \text{ or } k_0 = k\frac{\beta}{\gamma_1 C_{S_1} + \gamma C_{S_2}}$$

Considering the reaction system as a whole, the amount of hydrogen entering the solution from the gas phase should be instantaneously equal to the sum of hydrogen escaping from the solution to the gas phase and the hydrogen consumed on the surface of catalyst due to reaction. This idea can be represented by the equation

$$k_1 P_{H_2} \exp^{(-\Delta Ft^\circ/RT)} = k_2 C_{H_2} \exp^{(-\Delta Fe_0/RT)} + 3k_0 C_{H_2} WC \quad (4)$$

where $\Delta F_t{}^0$ is the free energy of activation for the transfer of the hydrogen from the gas phase into the solution and $\Delta F_e{}^0$ is the free energy of activation for the escape of the hydrogen from the solution into the gas phase. The left-hand side of equation 4 represents the rate of transfer of hydrogen from the gas phase into the solution; the first term of the right side gives the rate of escape of hydrogen from the solution to the gas phase, and the second term expresses the rate of hydrogen consumption due to reaction on the catalyst surface.

By combining (2) and (4) and eliminating C_{H_2}, the kinetic expression is converted into

$$-\frac{dC}{dt} = \frac{k_0 k_1 WCP_{H\ 2}\exp(-\Delta F_t{}^0/RT)}{k_2\exp(-\Delta Fe^0)/RT + 3k_0 WC} \quad (5)$$

or

$$-\frac{dC}{dt} = \frac{(k_0 k_1/k_2)WCP_{H_2}\exp(\Delta F^0{}_{sol}/RT)}{1 + 3(k_0/k_2)WC\exp(\Delta F_e{}^0/RT)} \quad (6)$$

where $\Delta F^0{}_{sol}$ is the standard free energy of solution of hydrogen $= \Delta F_e{}^0 - \Delta F_t{}^0$

According to equation 6 the catalytic hydrogenation is first order with respect to hydrogen pressure and fractional order with respect to both substrate and catalyst. At constant pressure and temperature, P_{H_2} is constant and equation 6 can be simplified to

$$-\frac{dC}{dt} = \frac{abC}{1 + bC} \quad (7)$$

where a and b are constants at constant temperature and pressure, and

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

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

Integration of equation 7 gives

$$\frac{1}{b}\ln\frac{C_0}{C} + (C_0 - C) = at \quad (8)$$

where C_0 is the initial concentration of the nitrocompound in the solution in moles per liter. Knowing the initial concentration of the substrate, one can calculate the constants a and b from two points, (C_1, t_1 and C_2, t_2), on the rate curve. Application of (8) to the experimental results is shown in Fig. 9. This linear relationship has been obtained in all the results measured at constant pressure and temperature, thus indicating the validity of equation 7.

When b is so small[5] (which can be brought about by reducing the amount of the catalyst and the water content of the solvent) that $bC << 1$, equation 7 becomes

$$-\frac{dC}{dt} = abC = \frac{k_0 k_1}{k_2}\exp\left(\frac{\Delta F^0\text{sol}}{RT}\right)P_{H_2} WC \quad (9)$$

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(5) The b value of equation 7 can vary from $b < 1$ to $b > 1000$ depending on the amount of catalyst and the nature of the solvent.

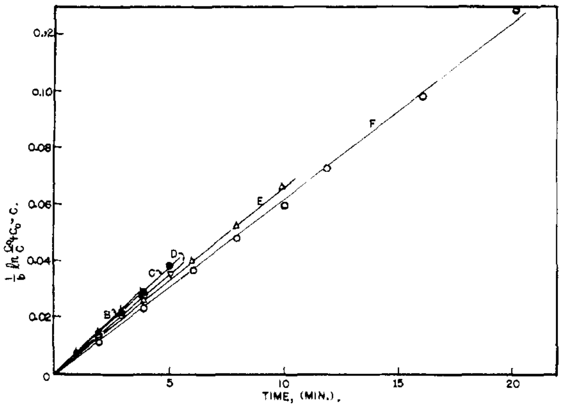

Fig. 9.—Replot of Fig. 1 with $1/b \ln C_0/C + C_0 - C$ against time. B, C, D, E and F are the same as those in Fig. 1.

The reaction is thus first order with respect to the hydrogen pressure, nitrocompound and the catalyst. When b is large and $bC >> 1$, then equation 7 can be simplified to

$$-\frac{dC}{dt} = a = \frac{1}{3} k_1 P_{H_2} \exp(-\Delta F_t^0/RT) \qquad (10)$$

In this case, the reaction rate is first order with respect to the hydrogen pressure but zero order with respect to the nitrocompound and catalyst.

Thus, a study of the a and b values and their dependence on the various reaction conditions would be useful in understanding the reaction kinetics and the mechanism. Typical sets of a and b values under various reaction conditions are shown in Tables III and IV.

TABLE III

HYDROGENATION OF *p*-NITROPHENOL IN AQUEOUS SOLUTION OF 50% BY WT. OF ETHANOL AT 25° OVER VARIOUS AMOUNTS OF PALLADIUM CATALYST

Amount of Pd, mg.	b^a	$a \times 10^3$, mole min.$^{-1}$
10.0	..	6.6
7.5	340	6.8
5.0	184	6.8
2.5	52	6.6
1.5	20	6.0

[a] Values a and b are constants of equation 7.

TABLE IV

PALLADIUM-CATALYZED HYDROGENATION OF *p*-NITROPHENOL IN WATER-ETHANOL SOLUTION

Reaction conditions: temp., 25°; total vol., 100 ml.; Pd, 5 mg.

% b wt. of ethanol	b	$a \times 10^3$, mole min.$^{-1}$
20	..	4.6
40	530	5.6
50	184	6.9
60	115	7.1
70	39	7.1

Constant a represents one-third of the rate of transfer of hydrogen from gas phase into the liquid and its value will apparently be dependent on the hydrogen pressure and the nature of the solvent. When the amount of catalyst is large and the solvent contains a high amount of water the reaction rate follows equation 10 and is therefore limited by the rate of transfer of hydrogen. This limiting rate of reaction with high amounts of catalyst appears not only in the hydrogenation of nitrocompounds over rhodium and palladium but also was found for the liquid phase hydrogenation of other reactions over various catalysts. Watt and Walling[6] interpreted this phenomenon by suggesting an empirical equation as

$$R_0 = \frac{AWP_{H_2}}{1 + BW} \qquad (11)$$

where R_0 is the rate of zero order reaction with respect to the substrate, W is the amount of catalyst, P_{H_2} is the hydrogen pressure, and A and B are constants. However, in this equation the dependence of the reaction order with respect to the substrate on various reaction conditions was ignored. Therefore, equation 11 cannot be adequately applied to the results of this study. Recently Price and Schiewetz[7] gave two possible explanations for the limiting rate in the hydrogenation of cyclohexene to cyclohexane in solution over a platinum catalyst. One is that the hydrogenation rate could be limited by the rate of diffusion of hydrogen from gas phase into the liquid. The other is that the rate could also possibly be limited by the ability of the solution to hold the catalyst particles in suspension, since only the suspended particles are catalytically active. The latter one is not applicable in the hydrogenation over a catalyst of colloidal form which can be held in good suspension even when the reaction reaches the limiting rate. The former one, however, is in agreement with the expression given in equation 10, which interprets the reaction rate as being limited by the rate of diffusion of hydrogen.

The effect of the solvent on the a values is shown in Tables IV, V and VI. The addition of an organic solvent into water generally increases the a values. Figure 10 shows the variation of a values, the amount of decrease in surface tension and the solubility of hydrogen with the composition of

TABLE V

PALLADIUM-CATALYZED HYDROGENATION OF *p*-NITROANILINE WATER-DIOXANE SOLUTION

Reaction conditions: temp., 30°; total vol., 100 ml.; Pd, 2.5 mg. The constants a and b are from equation 7.

% by vol. of dioxane	b	$a \times 10^3$, mole min.$^{-1}$
20	99	2.9
30	50	3.2
40	25	3.0
50	20	3.2

TABLE VI

THE VARIATION OF a VALUE WITH AMOUNT OF ETHANOL IN THE AQUEOUS SOLUTION OF *p*-NITROPHENOL

Reaction conditions: temp., 30°; total vol., 100 ml.; Pd, 10 mg. The constant a is from equation 8.

% by vol. of ethanol	0	1	2	5	10	20	50
$a \times 10^3$, mole, min.$^{-1}$	3.2	3.7	3.9	4.6	5.0	5.1	6.2

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(6) G. W. Watt and M. T. Walling, *J. Phys. Chem.*, **59**, 7 (1955).

(7) R. H. Price and D. B. Schiewetz, *Ind. Eng. Chem.*, **49**, 807 (1957).

water–ethanol mixture.[8,9] The close resemblance of the curves B and C suggests that surface tension of the solution has a great effect on the rate of transfer of hydrogen from the gas phase into the liquid.

The drop of apparent activation energy from 15.2 kcal. (nitrophenol) to 1.5 kcal. when both the amount of catalyst and the water content of the solvent increases gives further evidence to support the theory that the rate determining step is changed from the reaction on the surface of the catalyst to the transfer of hydrogen from the gas phase into the liquid. The activation energy for the transfer of hydrogen into water is 2.7 kcal.[10] which is in agreement with the lower value of apparent activation energy of hydrogenation (0 to 1.5 kcal.) within the experimental error.

Constant b equals $3(k_0/k_2)W \exp(\Delta F_e^\circ/RT)$. Its value is therefore proportional to the amount of catalyst and the value of k_0. The latter should, in turn, include the specific rate constant and the absorption coefficients of the reactants and the solvents on the catalyst. As equation 7 indicates, the increasing of the b value will result in the change of reaction to zero order with respect to the nitrocompound. Figures 3 and 4 and also Tables IV and V demonstrate that an increase of water content in solvent results in a large value of b. This probably is due to the increase of polarity of the solvent which can increase the b value by increasing the adsorption coefficients of the reactants, by reducing the activation energy of reaction between the reactants and by increasing the free energy of activation of the hydrogen escaping from the solution. The details of such effects are not known.

The effect of *para*-substituents of nitrobenzene on the reaction rates becomes obvious when the reaction is first order with respect to substrate. Tables I and VIII list the ab values from the first order rate equation 9. The b values in Table VIII are calculated by dividing the ab values by the a value taken from the B curve of Fig. 10.

TABLE VII

THE VARIATION OF *a* VALUE WITH THE ADDITION OF ORGANIC SOLVENT TO THE AQUEOUS SOLUTION OF *p*-NITROPHENOL

Reaction conditions: same as those in Table III. The constant a is from equation 8.

Organic solvent	Amount added, ml.	$a \times 10^{-3}$, mole min.$^{-1}$
Dioxane	1	3.1
Dioxane	5	3.2
Dioxane	10	3.2
Methanol	10	4.0
1-Propanol	10	6.0

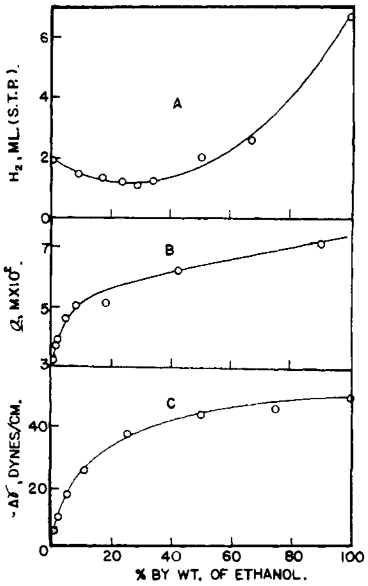

Fig. 10.—The effect of reaction medium: A, the solubility of hydrogen at 20° *vs.* composition of ethanol–water mixture. B, a value at 25° *vs.* composition of ethanol–water mixture. C, the decrease of surface tension at 30° *vs.* composition of ethanol–water mixture.[9,10]

In the first and fractional order ranges the reaction rate is accelerated by the addition of acid or base to the reaction solution. This occurs for the reactions over both palladium and rhodium catalysts. The effect can be caused by one or more of several reasons, such as the change of interaction strength between nitrocompound or hydrogen with the surface of the catalyst, change of surface activity, change of the true activation energy, etc. Further investigation in this respect is needed in order to get a better understanding of this point.

TABLE VIII

HYDROGENATION OF NITROCOMPOUNDS IN AQUEOUS SOLUTION OF 90% BY VOLUME OF ETHANOL AT 25°

Nitrocompound	ab,[a] min.$^{-1}$ (2.5 mg. of Pd)	b	ab,[a] min.$^{-1}$ (5 mg. of Rh)	
p-Nitronitrile	0.099	14.1	0.094	13.4
p-Nitroaniline	.071	10.1	.013	2.0
p-Nitrobenzoic acid	.035	5.0	.065	9.3
p-Nitrotoluene	.018	2.6	.006	0.9
p-Nitrophenol	.008	1.1	.008	1.1

[a] ab value is the constant of equation 9.

In conclusion, the kinetic characteristics have demonstrated so far that the mechanisms of hydrogenation of the nitrocompound over palladium and rhodium catalysts are quite similar. A comparison based on the weight amount of catalyst indicates that the palladium is more reactive than the rhodium. This may be due to either higher surface area or higher catalytic activity of the palladium. Hernandez and Nord's observation[1,2] that the hydrogenation of the aromatic nitrocompound over palladium was not affected by the nature of the substituents and also the acidity of the solution whereas the same reaction over rhodium was affected by both of them, probably is due to the difference of activity of these two catalysts. With

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(8) C. D. Hodgman (Editor-in-chief), "Handbook of Chemistry and Physics," 34th Ed., Chemical Rubber Publishing Co., Sandusky, Ohio, 1948.

(9) A. M. Comey, "A Dictionary of Chemical Solubilities," Vol. 2, The Macmillan Co., New York, N. Y., 1921, p. 379.

(10) The activation energy of transfer of hydrogen into water is calculated from the data of diffusion coefficients at 10, 16 and 21°; Hufuer, *Z. physik. Chem.*, **27**, 227 (1898).

the same amount (10 mg.) of catalyst in 50% ethanol solution the palladium-catalyzed reaction can be following the rate equation 10 whereas the rhodium-catalyzed reaction is following either equation 7 or equation 9. Such variation is consistent with the rate equation (equation 6) derived from this study. The effect of the substituents of nitrobenzene on the reaction rate exists in both the palladium- and rhodium-catalyzed reactions. Judging from the different orders of magnitude of *b* values for the same series of *p*-substituted nitrobenzene over different catalysts (Table VIII), one may conclude that the substituent group at the *para*-position may not only affect the true activation energy of the reaction of the adsorbed reactants but also probably the adsorption coefficient of the reactants over the different catalysts.

Although this investigation gives a gross mechanism of the liquid phase hydrogenation of aromatic nitrocompounds, the detailed features about the stepwise reaction on the surface of the catalyst and the chemical structure of the adsorbed species such as whether the adsorbed hydrogen is in an atomic or ionic form still cannot be stated.

Acknowledgment.—The authors wish to thank the National Science Foundation for supporting this research.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Nickel, Copper and Some of their Alloys as Catalysts for Ortho–Parahydrogen Interconversion[1]

BY PHOEBE B. SHALLCROSS[2] AND W. WALKER RUSSELL

RECEIVED JANUARY 21, 1959

The activity of nickel, copper and some of their alloys as catalysts for the ortho–parahydrogen interconversion at −196° and at several temperatures near room temperature has been studied. The dependence of catalyst activity upon catalyst composition is qualitatively the same for both the low temperature and higher temperature conversions. While alloying a few per cent. of copper or nickel with nickel or copper sharply decreases and increases catalyst activity, respectively, over the rest of the alloy composition range, catalytic activity changes relatively little. Experiments with preadsorbed hydrogen lead to the conclusion that in the alloy composition range from 5 to over 90% copper, compensation is operating between the effects of fixed hydrogen so that the reactivity of the adsorbed hydrogen which is more or less actively participating in the surface reaction remains little changed. The various types of adsorbed hydrogen must reflect in turn the influence of alloy composition.

Introduction

In a further study of the catalytic properties of the copper–nickel system the ortho–parahydrogen interconversion has been employed. The catalysts have been prepared by hydrogen reduction of the metal carbonate rather than the metal oxide precipitate[3] in order to avoid any separation of oxide phases.[4] However, X-ray diffraction measurements on the present catalysts show no significant differences from those on the earlier catalysts[3] or from careful measurements on massive nickel-copper alloys by others,[5,6] so it is concluded that the present alloy catalysts were well alloyed and highly homogeneous. This conclusion is supported by magnetic measurements made upon present catalysts both in the finely divided and in the massive state.

The ortho–parahydrogen interconversion appeared to be desirable as a measure of catalyst activity because only hydrogen is involved yet a magnetic mechanism[7] has been found operative at very low temperatures while chemical mechanisms[7] prevail over a wide range of temperatures if suitable chemisorption occurs. Since in the temperature range here employed the nickel–copper system changes from ferromagnetic to paramagnetic to diamagnetic as copper concentration increases, further information about the importance of the magnetic properties of the catalysts was hoped for. However, it appears that adsorbed hydrogen, by modifying its own environment, can partially mask the effect of the electronic structure of the catalyst. Thus even for an apparently simple reaction the electronic structure of the catalyst appears to influence catalysis somewhat indirectly through several types of hydrogen adsorption, which largely dictate the rates of the ortho-parahydrogen interconversion.

Experimental

Apparatus and Purification of Gases.—The hydrogen, helium and nitrogen employed were very pure gases which were further purified by passage over Ascarite, reduced copper at 400°, an active nickel-kieselguhr catalyst at 350°, Anhydrone, and finally through a charcoal trap at liquid nitrogen temperature, except for the nitrogen for which this trap was cooled with Dry Ice. While this train was also suitable for preparing the liquid nitrogen temperature equilibrium ortho–parahydrogen mixture, the hydrogen was next passed over an active nickel catalyst at room temperature when the room temperature equilibrium mixture was required for the reaction velocity measurements. The all glass apparatus consisted essentially of the above purification system, catalyst tubes, thermal conductivity cell, flow meter, B.E.T. system, McLeod gauge, mercury diffusion pump, cold traps, etc. Two connecting, vertical

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[1] This paper is based on a portion of a thesis presented by Phoebe B. Shallcross in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1958.

[2] Jesse Metcalf Fellow, 1954–1955, and Edwin P. Anthony Fellow, 1955–1958.

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