[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MARYLAND]

Kinetics of Liquid Phase Hydrogenation. IV. Hydrogenation of Nitrocompounds Over Raney Nickel and Nickel Powder Catalysts

BY HSIEN-CHENG YAO AND P. H. EMMETT

RECEIVED AUGUST 28, 1961

Successive runs on the rate of hydrogenation of *p*-nitrophenol over a Raney nickel catalyst at 25° show rates that decrease steadily with an increase in the removal of hydrogen (or aluminum) from the Raney nickel catalyst. The rate of hydrogenation of nitrophenol over degassed Raney nickel catalyst is first order with respect to hydrogen and zero order with respect to nitrophenol. The same kinetics are observed for the hydrogenation of nitrobenzene except that a sharp increase in the zero order rate change occurs at the point at which the nitrobenzene is converted to azoxybenzene. Over nickel powder, formed by the decomposition of nickel formate, the rate of hydrogenation of nitrophenol like that previously observed for colloidal Pt, Pd and Rh is first order with respect to the nitrophenol at low catalyst concentration and zero order at high amounts of catalyst. The apparent energy of activation for nitrophenol hydrogenation is 1.7 kcal. per mole over degassed Raney nickel and 9.8 kcal. over Ni powder.

Introduction

In previous studies of liquid phase hydrogenation of nitrocompounds a kinetic equation was derived and found to be in good agreement with the experimental results for colloidal rhodium,[1] palladium[1] and platinum catalysts[2] and for platinum formed by the reduction of platinum oxide.[3] In the present investigation, the kinetic study is extended to the reduction of nitrocompounds over Raney Nickel and nickel powder catalysts.

The work on Raney Nickel was included in this study in the hope that it might throw further light on the influence of the hydrogen content of these catalysts on their catalytic activity. It is well known that Raney Nickel catalysts on being heated from room temperature to about 400° evolve 50 to 200 cc. of hydrogen per gram of nickel. Evidence also has existed for a long time that a Raney catalyst prior to being heated can act as a reducing agent by furnishing its own supply of hydrogen.[4] A few years ago Smith and co-workers[5] reported that the activity of a Raney Nickel catalyst for the hydrogenation of benzene decreased as hydrogen was removed. Such a decrease in activity with removal of hydrogen was also noted by Kokes and Emmett[6] for the hydrogenation of ethylene at −78° and for the conversion of *ortho* to *para* hydrogen. The hydrogenation of nitro compounds at 25° over Raney Nickel, accordingly, gave promise of contributing information as to the hydrogenating effectiveness of the hydrogen content and the influence of this hydrogen content on the activity of the nickel for the hydrogenation of aromatic nitro-compounds.

After the experimental work on this paper was completed, a paper by Mars, Scholten and Zwietering[7] interpreted the hydrogen evolution from Raney Nickel catalysts as being due to the interaction of water with aluminum diffusing out of the nickel crystals. Accordingly, throughout the present paper any general statement as to "hydrogen furnished by the Raney Nickel" will mean hydrogen either held in the lattice by the mechanism suggested by Kokes and Emmett[8] or formed by the reaction of water with aluminum diffusing out of the nickel as proposed by Zwietering, *et al.*[7]

Experimental

Preparation of Catalysts.—The Raney Nickel catalyst was prepared following the methods of Covert and Adkins[9] from nickel–aluminum alloy purchased from the Central Scientific Company. The catalyst was further washed with alcohol and water and stored in water. The surface area of the catalyst thus prepared was 84 m.^{2}/g. as measured by nitrogen adsorption at −195°.

The "degassed Raney Nickel" catalyst was prepared by heating the dried Raney Nickel at 300° under continuous pumping for three hours. According to previous work such treatment should cause over 90% of the hydrogen evolution from the catalyst to take place. The surface area of the catalyst decreased on degassing to 63.5 m.^{2}/g.

The nickel powder catalyst was prepared by thermal decomposition of nickel formate following the procedures used by Allison, Comte and Fierz-David.[10] The catalyst was

TABLE I

HYDROGENATION OF *p*-NITROPHENOL IN AQUEOUS SOLUTION OVER RANEY NICKEL AT 25°

Exp. no.	Wt. of catalyst, g.	Time of standing without H_2 after Raney Ni was mixed with *p*-nitrophenol soln. at room temp.	H_2 taken from the gas phase ml.	H_2 furnished by the Raney Ni ml.[b]	Reaction rate[a] $\frac{dc}{dt}$, $M \times 10^{-3}$ min.$^{-1}$
1	1.01	10 min.	114.6	34.4	2.83
2	..	10 min.	136.7	12.3	2.31
3	..	30 min.	139.3	9.7	1.58
4	..	30 min.	142.0	7.0	1.37
5	..	60 min.	144.7	4.3	1.36
6	..	Over night	137.7	11.3	0.95
7	..	5 hr.	144.5	4.5	.90
8	..	Over night	138.5	10.5	.73
9	..	10 min.	149	0	.78
10	..	1.5 hr.	147	2	.79
11	..	Over night	144	5	.58
12	..	2 hr.	148	1	.62
13	..	About 36 hr.	149	0	.59
14	0.942	2 hr.	149	0	.56

[a] As shown in Fig. 1, the reaction rate is not always a constant in each experiment. In such cases, the maximum rates are used. [b] The total hydrogen coming from the Raney Nickel was 102 ml.

---

[1] Hsien-Cheng Yao and P. H. Emmett, *J. Am. Chem. Soc.*, **81**, 4125 (1959).

[2] Hsien-Cheng Yao and P. H. Emmett, *ibid.*, **83**, 796 (1961).

[3] Hsien-Cheng Yao and P. H. Emmett, *ibid.*, **83**, 799 (1961).

[4] L. Kh. Freidlin and N. I. Ziminova, *Doklady Akad. Nauk S. S. S. R.*, **74**, 955 (1950); *C. A.*, **45**, 1836 (1951).

[5] H. A. Smith, A. J. Chadwell, Jr., and S. S. Kirslis, *J. Phys. Chem.*, **59**, 820 (1955).

[6] R. J. Kokes and P. H. Emmett, *J. Am. Chem. Soc.*, **82**, 4497 (1960).

[7] P. Mars, J. J. F. Sholten and P. Zwietering, Second International Catalysts Congress, Paris 1960.

[8] R. J. Kokes and P. H. Emmett, *J. Am. Chem. Soc.*, **81**, 5032 (1959).

[9] L. W. Covert and H. Adkins, *ibid.*, **54**, 4116 (1932).

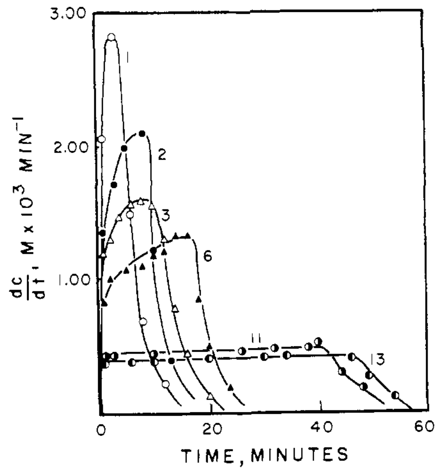


Fig. 1.—The variation of reaction rate in the hydrogenation of p-nitrophenol over Raney nickel catalyst. Numbers 1, 2, 3, 6, 11 and 13 are the same reaction numbers as listed in Table I. Data for the ordinate are based on the rate of hydrogen consumption from the gas phase.

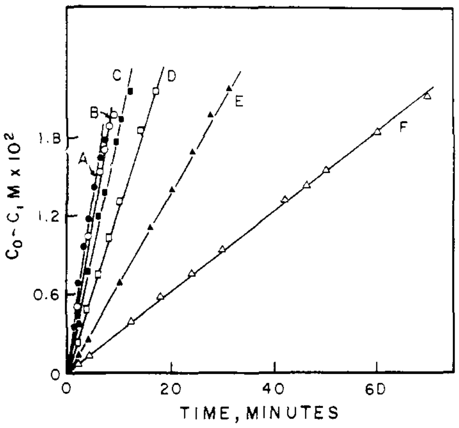


Fig. 2.—Rate curves for the hydrogenation of p-nitrophenol over various amounts of degassed Raney nickel: A, 2.15 g.; B, 1.01 g.; C, 0.679 g.; D, 0.342 g.; E, 0.171 g.; F, 0.0574 g.

then washed with benzene, alcohol and water, and stored in water. The surface area of the nickel powder as measured by nitrogen adsorption at −195° was 22 m.^{2}/g.

Apparatus.—The apparatus and methods of rate measurements at hydrogen pressure of one atmosphere or less have already been described.[1] For the reaction under a high pressure of hydrogen, a high-pressure reaction vessel of 600 cc. capacity was used.

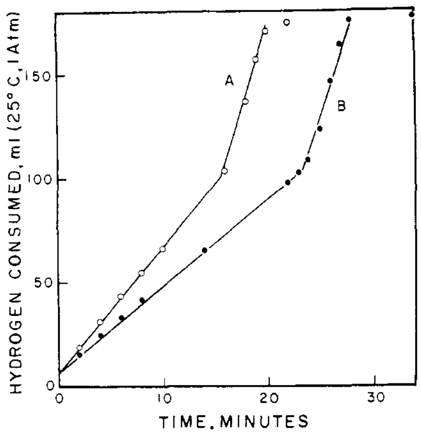


Fig. 3.—Rate curves for the hydrogenation of nitrobenzene over various amount of degassed Raney nickel: A, 0.343; B, 0.226 g.

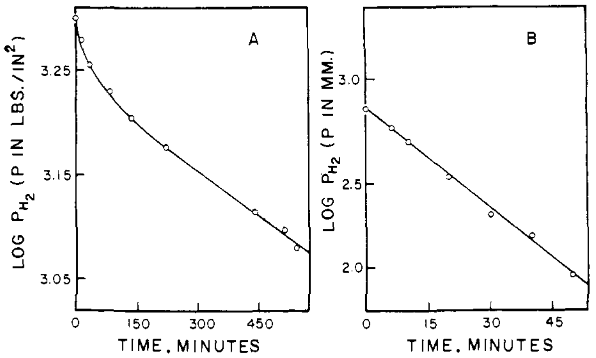


Fig. 4.—Rate curves for the hydrogenation of p-nitrophenol over degassed Raney nickel with respect to the hydrogen pressure: A, 1200–2000 lb./in.^{2}; B, 77–726 mm.

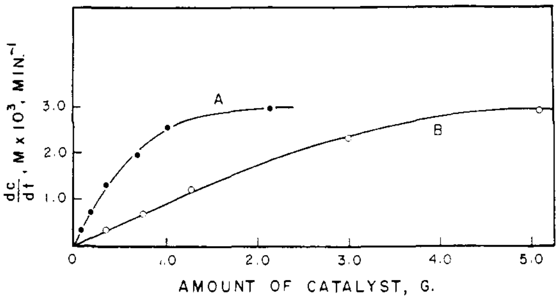


Fig. 5.—The initial rate of hydrogenation of p-nitrophenol in aqueous solution over A, degassed Raney nickel and B, nickel powder.

Results

Hydrogenation of Nitrocompounds over a Raney Nickel Catalyst.—At the start of the work, a series of p-nitrophenol hydrogenation rate measurements was made over a single sample of Raney Nickel catalyst. For each run 100 ml. of aqueous solution of nitrophenol (C_0 = 0.0235 M) was used. After each run, the reaction mixture was allowed to stand for about 20 minutes. The solution was then removed from the catalyst by careful decantation and the catalyst was further washed with water. After the water was decanted, the catalyst was used for the succeeding rate measurements. The catalyst was weighed in a 2 ml. specific gravity bottle both before the first run and after the last run of the series. The difference in weight of nickel is presumably due to loss in decantation; this amounted to 6.8% for a catalyst of 1.01 grams after 14 successive rate measurements. The results of these rate measurements are shown in Fig. 1 and Table I.

Rate of Hydrogenation of Nitrocompounds over Degassed Raney Nickel Catalyst.—Rate measurements carried out under constant hydrogen pressure of one atmosphere for the hydrogenation of p-nitrophenol and nitrobenzene are shown in Figs. 2 and 3, respectively. The reaction order is inde-

(10) F. Allison, J. L. Comte and H. E. Fierz-David, *Helv. Chim. Acta*, **34**, 818 (1951).

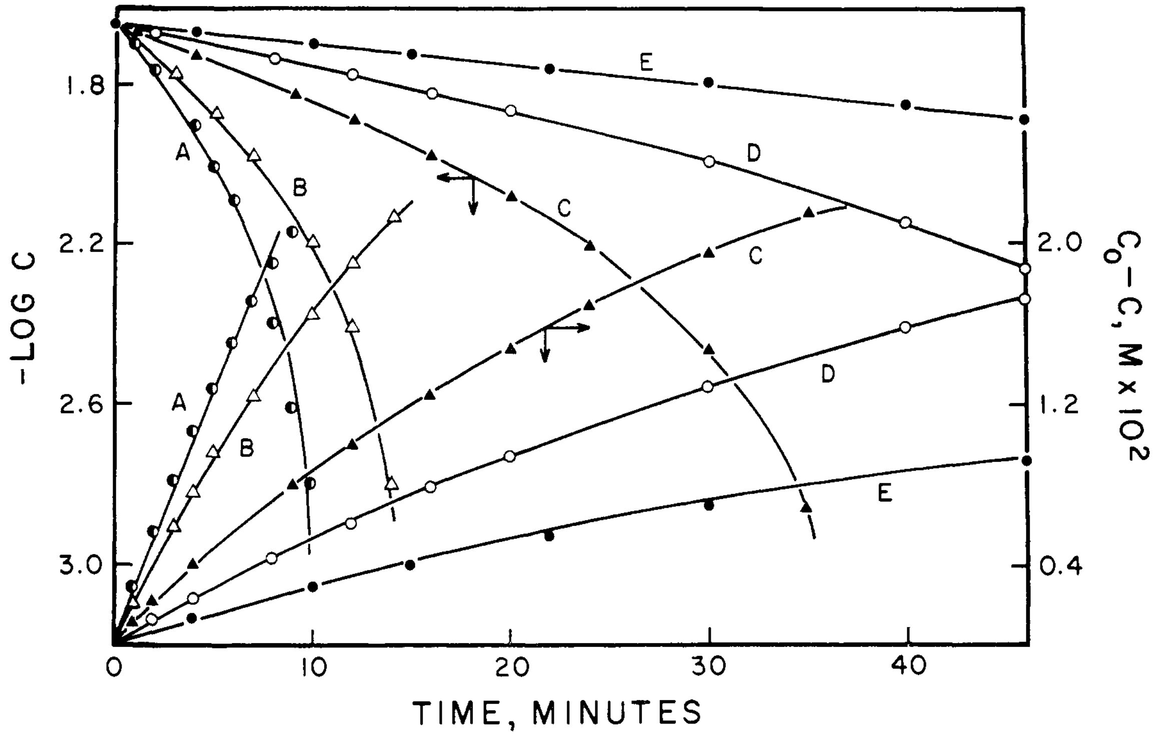


Fig. 6.—Rate curves for the hydrogenation of *p*-nitrophenol over various amount of nickel powder: A, 5.10 g.; B, 2.97 g.; C, 1.27 g.; D, 0.74 g.; E, 0.345 g.

pendent of the amount of catalyst and is zero order with respect to the nitrocompounds for both reactions. In the case of *p*-nitrophenol, the reaction rate remained constant up to 90% completion, whereas a sharp increase of rate to a new zero order reaction rate was observed for nitrobenzene at the point at which approximately half of the theoretical amount of hydrogen was consumed.

TABLE II

APPARENT ACTIVATION ENERGY FOR THE HYDROGENATION OF *p*-NITROPHENOL OVER DEGASSED RANEY NICKEL AND NICKEL POWDER

Catalyst	Amount of catalyst, g.	Temp., °C.	Specific rate × 10^3 M min.$^{-1}$ g.$^{-1}$	App. E_a kcal./mole
Degassed	0.220	25	3.46	
Raney Ni	.217	35	3.86	1.7
	.170	45	4.16	
Nickel	1.225	25		
Powder	1.168	35	0.76	9.8
	1.275	45	1.23	

Measurements of the reaction order with respect to hydrogen for the hydrogenation of *p*-nitrophenol were carried out under constant volume conditions. The results are shown in Fig. 4. The reaction is first order with respect to hydrogen pressure in the low pressure range and appears to become greater than first order at higher pressure.

As shown in Fig. 5 (curve A), the rate of hydrogenation increases with increasing amount of catalyst and eventually levels off. The reaction rate are shown in Table II. The apparent activation energy for hydrogenation of *p*-nitrophenol over degassed Raney Nickel is found to be 1.7 kcal./mole in spite of the fact that the measurements were made with small amounts of catalyst under conditions in which the rate is certainly not controlled by the rate of solution of hydrogen in the liquid phase.

Rate Measurements over Nickel Powder.—The reaction order with respect to the nitrocompounds was determined by experiments under constant one atmosphere pressure. The results are shown in Fig. 6. The reaction order with respect to the nitrocompound is affected by the amount of catalyst in the same manner as that over colloidal Pd, Rh, Pt and reduced Adams Catalyst, that is, the reaction order changes from first order to zero order with increasing amount of catalyst.

Rate measurements at constant volume and with excess amount of *p*-nitrophenol showed that over the pressure range 373 to 826 mm., the hydrogenation reaction is first order with respect to the partial pressure of hydrogen.

The variations of the reaction rate with respect to the amount of catalyst is shown as curve B of Fig. 5. The results again indicate that reaction rate increases with increasing amount of catalyst and levels off as the latter becomes large.

The reaction rates measured at constant pressure of hydrogen and under the conditions that the solution of hydrogen is not the rate-controlling step are listed in Table II. The apparent activation energy is 9.8 kcal./mole.

Identification of Reaction Products.—The reaction products of the hydrogenation of nitrobenzene and *p*-nitrophenol were isolated and identified by melting point determination of the compounds or their derivatives. The aniline was determined by conversion to acetanilide. The *p*-aminophenol

TABLE III

REACTION PRODUCTS IN VARIOUS REACTION SYSTEMS

Catalyst	Catalyst amount, g.	Nitrocompd.	Solvent	Hydrogen pressure	Theor. amt. of H_2 consumed,[a] %	Product isolated
Raney Ni	2.52	1.19 g. nitrobenzene	100 ml. of 95% alc. soln.	0	..	Aniline and nitrobenzene
Degassed Raney Ni	0.633	0.556 g. *p*-nitrophenol	100 ml. of 70% alc. soln.	1 atm.	50	*p*-Aminophenol *p*-Nitrophenol
	.744	4.45 g. *p*-nitrophenol	100 ml. of 70% alc. soln.	1 atm.	40	*p*-Aminophenol *p*-Nitrophenol
	.556	0.556 g. *p*-nitrophenol	100 ml. of 70% alc. soln.	1 atm.	100	*p*-Aminophenol
	.134	15.79 g. *p*-nitrophenol	300 ml. of 90% ethanol	1200–2000 lb./in.^{2}	40	*p*-Nitrosophenol *p*-Azophenol *p*-Nitrophenol
	.68	2.706 g. nitrobenzene	100 ml. of 95% alc. soln.	1 atm.	30	Nitrobenzene Azoxybenzene
	.583	0.27 g. nitrobenzene	100 ml. of 95% alc. soln.	1 atm.	56	Azoxybenzene
	.346	.27 g. nitrobenzene	100 ml. of 95% alc. soln.	1 atm.	100	Aniline
Nickel powder	.792	.541 g. nitrobenzene	100 ml. of 95% alc. soln.	1 atm.	50	Nitrobenzene Aniline
	1.07	.541 g. nitrobenzene	100 ml. of 95% alc. soln.	1 atm.	100	Aniline
	1.02	.556 g. *p*-nitrophenol	100 ml. of 95% alc. soln.	1 atm.	50	*p*-Nitrophenol *p*-Aminophenol

[a] Theoretical amount of hydrogen denotes the amount of hydrogen which will be required for complete hydrogenation of the nitrocompound to the corresponding aminocompound.

was isolated by evaporating the alcoholic solution under vacuum and then converting to *p*-hydroxyacetanilide with acetic anhydride. Nitrosophenol, azophenol and azoxybenzene were isolated as pure compounds. A summary of the reaction products formed under various experimental conditions is given in Table III.

Discussion

The results for the catalytic hydrogenation of *p*-nitrophenol over Raney Nickel are shown in Fig. 1 and Table I. The amounts of hydrogen taken from the gas phase to react with the same amount of *p*-nitrophenol are different among experiments of the same series; that is, the later experiments consume more hydrogen from the gas phase than the initial ones. In addition, the rate of hydrogen consumption in the first few experiments (see curves in Fig. 1) increases until the reaction is nearly complete, whereas in the later experiments the rate appears to be constant and independent of the concentration of the *p*-nitrophenol. The reaction product of both the earlier and later runs was found to be the same, *p*-aminophenol, regardless of the difference in the amount of measured hydrogen uptake.

The following explanations of the above observations are proposed:

(1) The hydrogen used for the reaction comes not only from the gas phase but also in part from the catalyst itself. The relative amount of hydrogen taken from these two sources is shown in Table I.

(2) After the hydrogen originally present on or near the catalyst surface is used up, the contribution of hydrogen from the catalyst may be controlled by the diffusion of hydrogen or aluminum from the bulk of the catalyst toward the surface. This slow diffusion process is responsible for the fact that hydrogen from the catalyst cannot be exhausted during the first experiment of the series.

(3) If the hydrogen being furnished by the catalyst actually comes from the interaction of water with residual aluminum as postulated by Zwietering, *et al.*,[7] it would seem necessary to postulate that the reaction between water and aluminum dissolved in the nickel occurs at a fast rate only in the presence of a hydrogen acceptor. It is well known that Raney Nickel stored in water does not lose more than one-third of its hydrogen producing potential in the course of a year.[8] Possibly a layer of chemisorbed hydrogen inhibits the attack by water.

(4) The initial rise in the rate of consumption of hydrogen from the gas phase may reasonably be interpreted to mean that the initial reaction of hydrogen from the Raney Nickel depletes the supply of nitrophenol at the catalyst surface. The rise in rate of hydrogen consumption would then be due to the gradual restoration of nitrophenol to the region around the catalyst particles when shaking begins at the start of an experiment.

(5) The drop in maximum activity between runs 1 and 13 in Fig. 1 could, as suggested by Kokes and Emmett,[6] be due to a decrease in the number of electrons contributed to the nickel either by hydrogen in the lattice or by aluminum. It could also be caused by the building up of a film of hydrated alumina around the catalyst particles if the hydrogen comes from the reaction of aluminum with water.[7] It may be noted that the decrease in rate per unit amount of hydrogen furnished by the catalyst is fairly constant as judged by the data in Table I.

For a Raney Nickel catalyst which has been degassed at high temperature, the readily available dissolved hydrogen or the excess aluminum near the surface have been largely removed. The measured rate of hydrogen consumption over such a catalyst would therefore be close to the true rate of hydrogenation. The results as plotted in Fig.

2 indicate that the hydrogenation of para-nitrophenol over such a nickel catalyst is zero order with respect to the substrate. These kinetic characteristics persist even though the rate is far below the limiting value that can be obtained with a large excess of catalyst. In contrast, the same reaction over colloidal Pd, Rh and Pt are fractional or first order with respect to the substrate when the rate is below the limiting value. Furthermore, the temperature coefficient of the reaction even with small amounts of catalyst is less for the degassed Raney Nickel (1.7 kcal. per mole) than for colloidal Pd,[1] Rh[1] or Pt.[2] The results are consistent with the hypothesis that the slow step in the reaction over the degassed Raney Nickel is the diffusion of hydrogen through a layer of adsorbed nitrobenzene or nitrophenol on the catalyst and possibly through any layer of hydrated alumina that may be present. Such a diffusion control would account for the rate being proportional to hydrogen, independent of the concentration of organic reactant and characterized by a low temperature coefficient.

At room temperature the hydrogen present in the Raney Nickel catalyst converts nitrobenzene directly to aniline; but, under the same conditions over degassed Raney Nickel, the hydrogen from the gas phase reacts with nitrobenzene to give azoxybenzene as a reaction intermediate. The rate curves over the degassed Raney Nickel as shown in Fig. 3 consists of two zero order steps; a sharp increase of rate occurs at a point where approximately half of the theoretical amount of hydrogen is consumed. Isolation of the products indicates that azoxybenzene was formed during the first half of the reaction. In contrast, nitrophenol in experiments at atmospheric pressure gave only aminophenol as a reaction product.

It is interesting to note that the occurrence of azoxybenzene during the catalytic hydrogenation of nitrobenzene over degassed Raney Nickel has its analogy in the chemical and electrochemical reduction of nitrobenzene.[11] In the latter cases azoxybenzene can be obtained under carefully chosen conditions presumably through the condensation of the primary reduction intermediates nitrosobenzene and phenylhydroxylamine or through the disproportionation of phenylhydroxylamine. In line with the catalytic results on *para*-nitrophenol (Table III), no formation of azoxyphenol occurs from either *ortho* or *para* nitrophenol by chemical or electrochemical reduction even though azoxycompounds are obtained from nitrobenzene or from *meta*-nitrophenol.

Sokolskii and Shmonina[12] studied the hydrogenation of nitrobenzene and found that platinum catalyst and Raney Nickel promoted by rhodium or palladium give direct conversion of nitrobenzene to aniline. However, over unpromoted Raney Nickel, a stepwise increase of reaction rate was found at 25 and 40° due to the formation of an intermediate. These authors believe that the intermediate is nitrosobenzene as their results indicate no reduction of nitrosobenzene in the presence of nitrobenzene. This is in agreement with the results obtained in this Laboratory that, of all the catalysts studied (colloidal Pd, Rh, Pt and Raney Nickel), only degassed Raney Nickel gives a stepwise rate curve. However, in our experiments the intermediate product was isolated and shown to be azoxybenzene rather than nitrosobenzene.

In the hydrogenation of *p*-nitrophenol over degassed Raney Nickel, it was found that direct conversion to *p*-aminophenol occurs at hydrogen pressure of one atmosphere; whereas at high pressures up to 2000 lb./in.,^{2} the same catalyst gives *p*-nitrosophenol and *p*-azophenol as reaction intermediates. Without further study, the reason for such pressure dependency is not certain. It should be noted, however, that the experiment leading to *p*-nitrosophenol and *p*-azophenol was not only at high pressure but was carried out in 90% ethanol rather than the usual 70% and at a very high ratio of nitrophenol to catalyst.

The dependence of reaction rate on the amount of degassed Raney Nickel used is the same as that found for colloidal palladium, rhodium and platinum catalysts. As shown in Fig. 5, the reaction rate increases with increasing amount of the catalyst and eventually becomes constant.

The kinetic equation

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{abC}{1 + bC} \qquad (1)$$

has been derived and proved to be valid in the previous study on hydrogenation of nitrocompounds over colloidal Pd,[1] Rh[1] and Pt.[2] C is the concentration of nitrocompound in solution, t is the time in minutes, a is proportional to the partial pressure of hydrogen and b is proportional to the weight of catalyst used. When the amount of catalyst used is so large that the reaction rate approaches a constant, equation 1 becomes

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = a \qquad (2)$$

The "a" values obtained for the reaction over colloidal Pd, Rh and Pt at one atmosphere pressure in aqueous solutions are 0.0032 M/min., 0.0031 M/min. and 0.0028 M/min., respectively. The limiting rate for the reaction over degassed Raney Nickel under the same conditions is 0.0029 M/min. Therefore, the rate of hydrogenation over a large amount of degassed Raney Nickel appears to be controlled by the rate of solution of hydrogen in the same manner as that in the reactions catalysed by colloidal Pd, Rh and Pt.

The hydrogenation of nitrocompounds over nickel powder prepared from nickel formate is different from that observed over Raney Nickel but is quite similar to that over colloidal Pd, Rh and Pt catalysts reported previously. The reaction varies from first order to zero order with respect to the substrate as the amount of nickel

---

(11) I. L. Finar, "Organic Chemistry," Vol. I, Longman Greene and Co., London, 1959, pp. 535–537. M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Co., New York, N. Y., 1958, pp. 49–55. E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIA, Elsevier Publishing Co., Amsterdam, 1954, p. 312.

(12) D. V. Sokolskii and V. P. Shmonina, *Sbornik Statei po Obshchei Khim., Akad. Nauk S.S.S.R.*, **2**, 1186–1194 (1953); *cf.*, *C. A.*, **49**, 3632 (1955). V. P. Shmonina and D. V. Sokolskii, *Kataliticheskoe Gidrirovanie i Okislenie, Akad. Nauk Kazakh. S.S.R., Trudy Konf.*, 100 (1955); *cf.*, *C. A.*, **50**, 12618 (1956).

TABLE IV

"a" AND "b" VALUES FOR THE HYDROGENATION OF p-NITROPHENOL OVER NICKEL POWDER IN AQUEOUS SOLUTION

Amount catalyst, g.	a, M/min.	b
0.345	0.0030	4.5
0.74	.0030	10.5
1.27	.0029	23.8
2.97	.0030	95.5
5.10	.0029	1273.0

catalyst increases and is first order with respect to hydrogen pressure. The rate of reaction also increases with increasing amount of catalyst and then levels off. No reaction intermediate other than the final products was isolated. The apparent activation energy for hydrogenation of p-nitrophenol is 9.8 kcal./mole as compared to 15.2 kcal./mole and 13.2 kcal./mole obtained for the same reaction over Pd and Rh, respectively.

The integrated form of equation 1 is

$$\frac{1}{b}\ln\frac{C_0}{C} + (C_0 - C) = at \qquad (3)$$

Application of this equation to results of Fig. 6 is shown in Fig. 7. The linearity obtained indicates the validity of the equation for the hydrogenation of nitrocompound over the nickel powder catalyst. The "a" and "b" values calculated from the results are listed in Table IV.

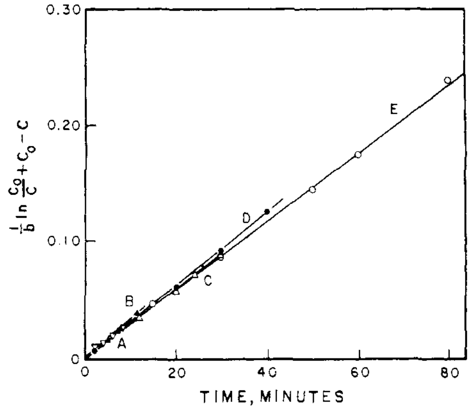


Fig. 7.—Replot of results in Fig. 6 with $\frac{1}{b}\ln\frac{C_0}{C} + C_0 - C$ *vs.* time: A, B, C, D, E, are the same as those in Fig. 6.

Acknowledgments.—The authors wish to thank the National Science Foundation for financing this work. They are also indebted to Dr. Hans Schaefer for helpful discussions.

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

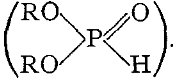
The Oxidation of Diethylphosphonate. Kinetics and a Kinetic Isotope Effect

BY B. SILVER AND Z. LUZ

RECEIVED JULY 17, 1961

The mechanism of the acid catalyzed formation of the phosphite tautomer of diethylphosphonate has been studied. The dependence on acidity of the oxidation reaction of diethylphosphonate was determined from 0.05 N to 4.5 N HCl, and a decrease was observed in the apparent acid catalysis constant with increasing acidity. A comparison was made between the oxidation rates of normal and deuteriated $(EtO)_2PO{\cdot}D$, diethylphosphonate, a value of 4 being found for the kinetic isotopic effect (k^H/k^D) on the acid catalyzed reaction. A change in solvent from H_2O to D_2O increases the rate of the acid catalyzed oxidation reaction. The results are interpreted in terms of a pre-equilibrium protonation on the phosphoryl group followed by the rate-determining fission of the phosphorus hydrogen bond.

Introduction

The structure of dialkyl phosphonates has been shown[1] to involve a hydrogen atom directly bonded to the phosphorus atom of the phosphoryl group, . There are many chemical reactions of these compounds which imply the existence of a tautomeric equilibrium between the normal or phosphonate form and an "active" or phosphite form,[2] *i.e.*, $(RO)_2PO{\cdot}H \rightleftarrows (RO)_2P{\cdot}OH$. However, physical measurements have failed to prove the existence of the phosphite form.[2] The chemical evidence is mainly based on kinetic data, for example Nylen[3] found the oxidation of phosphonates to phosphates by halogens to be independent of the concentration of oxidizing agent at high halogen concentrations. This led him to suggest the existence of the above tautomerism in which the phosphite form is the active species, undergoing oxidation. Recently Luz and Silver[4] have studied the kinetics of the acid catalyzed exchange of the phosphorus bonded hydrogen in several dialkyl phosphonates. It was found that the exchange reaction follows the same rate law as that found for oxidation, *i.e.*

$$k = \frac{R}{[\text{phosphonate}]} = k_w + k_H[H^+] \qquad (1)$$

where R is the reaction rate. The values of k_w and k_H for exchange were found to be similar to those given by Nylen for the oxidation reaction. The results are best interpreted in terms of the above tautomeric equilibrium. Fox[5] also has used such an equilibrium to explain his results for hydrogen exchange of dibutylphosphonate in butyl alcohol.

On the basis of the above evidence a general scheme was suggested[4] to describe the mechanism of both the acid catalyzed exchange and oxidation reactions.

---

[1] J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, Chap. 7.

[2] G. O. Doak and L. D. Freedman, *Chem. Revs.*, **61**, 31 (1961).

[3] P. Nylen, *Z. anorg. u. Allgem. Chem.*, **235**, 161 (1938).

[4] Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961).

[5] R. B. Fox, NRL Report 5242, January 8, 1959.