[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Promoter Effect of Platinic Chloride on Raney Nickel. III. Hydrogenation of the Nitrobenzoic Acids and the Nitrobenzene–Aniline Intermediates[1]

BY SOL S. SCHOLNIK,[2] JULIAN R. REASENBERG, EUGENE LIEBER AND G. B. L. SMITH

Introduction

The catalytic hydrogenation of many aromatic nitro compounds in the presence of Raney nickel takes place more rapidly if platinum is added as platinic chloride just before the reduction.[3] The same result has been observed for carbonyl compounds but in the case of these substances the presence of alkali enhances the rate of hydrogenation,[4] but in the case of the nitro aromatic compounds alkali is generally a poison.[3]

The present work was carried out in order to ascertain the effect of alkali and platinum on the reduction of the sodium salts and methyl and ethyl esters of the isomeric nitrobenzoic acids when hydrogenated in the presence of Raney nickel. Also a study of the comparable rates of reduction, in the presence of Raney nickel, of the nitrobenzene-aminobenzene intermediates was made in order to obtain an insight of the mechanism of reduction of the nitro group under these conditions.

Experimental

Procedure.—The apparatus and general procedure employed was similar to that previously described[3]; the hydrogen acceptor (0.05 mole) and Raney nickel[5] (4.5 g.) were added to a one pint citrate of magnesia bottle and the volume was made up to 150 ml. with 95% ethanol. In the case of azo- and hydrazobenzene only 0.025 mole was used. The promoter (0.375 millimole of chloroplatinic acid) and sodium hydroxide (3 millimoles) were added in that order in certain experiments. The rate of shaking was 190 oscillations per minute.

Reduction of Sodium Salts and Methyl and Ethyl Esters of the Nitrobenzoic Acids.—The rates of reduction (ml. of hydrogen per 100 sec.) of these compounds are tabulated in the first part (1–9) of Table I. The reductions with catalyst b (Raney nickel and platinum) were carried to completion and the amines were identified as the acetyl or benzoyl derivatives. Aniline formed by the reduction of the nitrobenzene–aniline intermediate was identified also as acetanilide. The yields were from 81 to 100%, and it may be assumed that the reactions are practically complete.

Sodium salts rather than the free acids were used because the acids are sufficiently strong to attack the nickel, and nickel ions poison Raney nickel.[3] All nine compounds reduced to amines, but in the case of *p*-nitrobenzoate with nickel alone only approximately $^2/_3$ (2 moles) of hydrogen was absorbed while with nickel and platinum the rate was small at the $^2/_3$ point. At first it was believed that the reduction was complete at this point, and possibly the product was the diazo compound. However, analysis of the reduction mixture indicated the presence of only *p*-aminobenzoic acid and the original *p*-nitrobenzoic acid. Since alkali inhibits the reduction (Table I), this result might be due to increase of basicity as sodium *p*-aminobenzoate was formed. The following two experiments verified this view: (1) at the $^2/_3$ point 0.05 mole (1 equiv.) of acetic acid was added, and the rate of absorption increased, and the reduction was completed; (2) 0.1 mole of ammonium chloride was added to the reduction mixture at the beginning of the experiment, and the rate of absorption remained high until the absorption was complete. These experiments are presented graphically in Fig. 1.

Reduction of Nitrobenzene–Aminobenzene Intermediates.—The rates of reduction of the nitrobenzene–aniline intermediates are tabulated in the last part of Table I (10–15). Since the rate of reduction of nitrobenzene is essentially constant during the entire period, and there are no downward breaks in the rate curve, it is evident that no

TABLE I

RATES OF HYDROGENATION IN THE PRESENCE OF RANEY NICKEL AND THE EFFECTS OF PLATINUM AND OF ALKALI

	Rates[a] of hydrogenation with catalysts			
Compd. reduced	*a*	*b*	*c*	*d*
Sodium *o*-nitrobenzoate	95.6	262	69.3	114
Sodium *m*-nitrobenzoate	19.5	256	4.0[b]	10.5[b]
Sodium *p*-nitrobenzoate	19.3	284	0.4[b]	203
Ethyl *o*-nitrobenzoate	118	378	128	364
Ethyl *m*-nitrobenzoate	118	447	182	339
Ethyl *p*-nitrobenzoate	3.9[b]	502	16.7	80.4
Methyl *o*-nitrobenzoate	149	459	181	462
Methyl *m*-nitrobenzoate	172	464	203	334
Methyl *p*-nitrobenzoate	4[b]	397	19.6	243
Nitrobenzene	195	344	20.5[b]	127
Nitrosobenzene	0	0	0	0
Azobenzene	42.1	135	95.2	199
Hydrazobenzene	31.2	227	1.08	228
Azoxybenzene	22.4	165	218	325
β-Phenylhydroxylamine	120	270	197	26

[a] The rates are expressed as ml. of hydrogen absorbed per 100 sec. Catalyst *a*, Raney nickel. Catalyst *b*, Raney nickel and platinum. Catalyst *c*, Raney nickel and alkali. Catalyst *d*, Raney nickel, platinum, and alkali.
[b] The average rate is probably less than that recorded.

---

[1] Presented before the Division of Organic Chemistry at the Cincinnati meeting of the American Chemical Society, April, 1940. Original manuscript received August 26, 1940.

[2] Abstract of part of the thesis submitted by Mr. Scholnik to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1940.

[3] Lieber and Smith, THIS JOURNAL, **58**, 1417 (1936); Reasenberg, Lieber and Smith, *ibid.*, **61**, 384 (1939).

[4] Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935); **202**, 995 (1936); *Bull. soc. chim.*, [5] **4**, 31 (1937).

[5] Adkins and Covert, THIS JOURNAL, **54**, 4116 (1932).

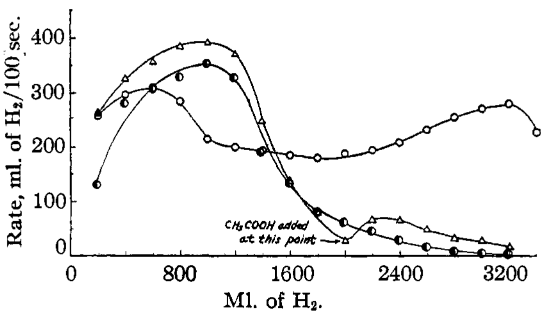

Fig. 1.—Effect of glacial acetic acid and ammonium chloride on the reduction of sodium *p*-nitrobenzoate: △, CH_3COOH; ○, NH_4Cl; ◐, Ni + $PtCl_4$.

intermediates having a reduction rate smaller than that of nitrobenzene (under these experimental conditions) likely are formed. However, an intermediate having a reduction rate greater than that of nitrobenzene is possible. The rates of the known intermediates of this system were determined, and the reduction curves of these compounds with Raney nickel are presented in Fig. 2. These curves show that nitrobenzene has the largest rate of reduction of all the compounds of the series.

Discussion

Platinum enhanced the rate of reduction in the presence of Raney nickel for every compound studied, and the largest relative promoting effect was obtained when the rates of hydrogenation with Raney nickel alone were small. In these experiments the effect of alkali was not so consistent. In the case of the nitrobenzene–aniline compounds only nitrobenzene was poisoned by alkali[3] while the others were definitely promoted. The rates of hydrogenation of the sodium nitrobenzoates were inhibited by alkali, while those of the esters were either not affected or were promoted. The reduction of sodium *p*-nitrobenzoate was poisoned during the course of the hydrogenation. This poisoning effect was counteracted by the addition of acetic acid or ammonium chloride (as a buffer), and these experiments indicate that alkalinity was the cause of the anomalous behavior of this compound on reduction in the presence of Raney nickel.

All the nitrobenzene–aniline intermediates have rates of hydrogenation smaller than that of nitrobenzene in the presence of Raney nickel. This indicates that none of these compounds form during the course of the reduction of nitrobenzene to aniline under the experimental conditions here employed.

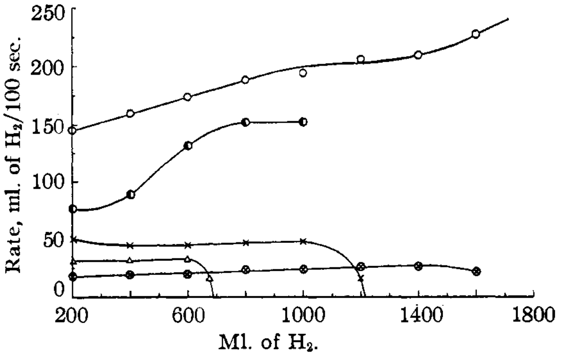

Fig. 2.—Reduction with Raney nickel of nitro-aminobenzene intermediates: ×, azobenzene; ⊗, azoxybenzene; △, hydrazobenzene; ○, nitrobenzene; ◐, β-phenylhydroxylamine.

Nitrosobenzene would not hydrogenate in the presence of any of the Raney nickel catalysts, but in the presence of Adams platinum oxide the hydrogenation proceeded smoothly and went to completion. When equimolar quantities of nitrobenzene and nitrosobenzene were placed in the reduction flask with Raney nickel, no absorption of hydrogen took place. It is evident, therefore, that nitrosobenzene is a poison for Raney nickel, and this is probably related to the property of the nitroso group to co-ordinate with nickel to form complexes.

Summary

1. Platinum added to Raney nickel catalyst accelerates the rate of hydrogenation under the conditions of these experiments of all the compounds studied.
2. Alkali (sodium hydroxide) is a poison in the hydrogenation of the isomeric sodium nitrobenzoates and nitrobenzene. It increases the rate of hydrogenation of the methyl and ethyl esters of nitrobenzoic acid, and of the nitrobenzene–aminobenzene intermediates.
3. The hydrogenation of nitrobenzene in the presence of Raney nickel under the conditions of these experiments proceeds directly to aniline.
4. Nitrosobenzene poisons Raney nickel catalyst.

BROOKLYN, N. Y.

RECEIVED FEBRUARY 10, 1941