Rhodium-Platinum Oxide as a Catalyst for Hydrogenation. III⁽¹⁾. The Catalytic Hydrogenation of Aniline

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It has been reported in previous papers(1-7) that (3 : 1) or (7 : 3) rhodium-platinum oxide,

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1) Part II : S. Nishimura, This Bulletin, **34**, 1544 (1961).
2) S. Nishimura, ibid., **33**, 566 (1960).
3) S. Nishimura, T. Onoda and A. Nakamura, ibid., **33**, 1356 (1960).
4) S. Nishimura, ibid., **34**, 32 (1961).
5) S. Nishimura and H. Taguchi, ibid., **35**, 1625 (1962).
6) S. Nishimura and K. Mori, ibid., **36**, 318 (1963).
7) S. Nishimura and H. Taguchi, ibid., **36**, 353 (1963).

prepared by fusion of a mixture of rhodium chloride and chloroplatinic acid with sodium nitrate, is not only highly active, but also very selective as a catalyst in the hydrogenation of various organic compounds. Its high selectivity has already been shown in the hydrogenation of the compounds having C–O linkages liable to hydrogenolysis[1-4,6,7] and in the cis hydrogenation of substituted aromatic compounds[7].

This paper descibes another example of the high selectivity of the rhodium-platinum oxide revealed in the hydrogenation of aniline. Numerous catalysts have been used in the hydrogenation of aniline; of these, cobaltic oxide promoted with calcium oxide and ruthenium dioxide have been shown to give high yields of cyclohexylamine[8,9]. In an acidic medium, platinum catalyzes the hydrogenation even at room temperature, but so much dicyclohexylamine is produced that it is often more dominant than cyclohexylamine[10-12] (see Table I). As has already been reported[5], (7:3)rhodium-platinum oxide also catalyzes the hydrogenation in acetic acid at room temperature and gives a better yield of cyclohexylamine than platinum oxide. Table I summarizes the results of further investigations carried out in various solvents at an atmospheric or high pressure of hydrogen. With (7:3)rhodium-platinum oxide, aniline is hydrogenated most rapidly in acetic acid, and 16∼22% of dicyclohexylamine is obtained with cyclohexylamine as the main product in hydrogenation at room temperature. With ethanol as a solvent, aniline is hydrogenated rather rapidly at 50°C and gives cyclohexylamine exclusively[13]. The addition of a small amount of acetic acid to ethanol causes the formation of dicyclohexylamine to the extent of 12% at 50°C, and a longer time is required for the completion of the hydrogenation than in ethanol. In ethanol and acetic acid in the amount equivalent to that of aniline, the hydrogenation proceeds smoothly at room temperature, and less than half as much dicycloheylamine is formed as in acetic acid. It is obvious from these results that acetic acid greatly promotes the formation of the secondary amine. The high selectivity of cobalt and ruthenium catalysts is probably connected with their use in neutral or alkaline conditions. Figure 1 shows the effect of hydrogen pressure on the rate of the hydrogenation of aniline in

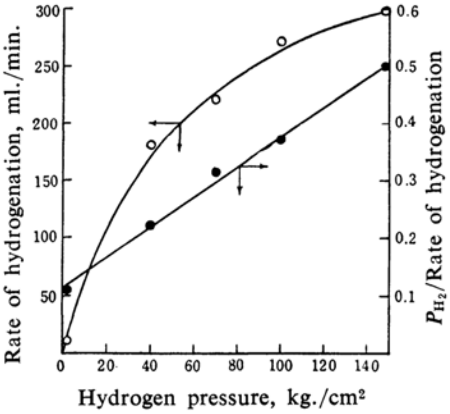

Fig. 1. Effect of hydrogen pressure on the rate of the hydrogenation of aniline with (7:3) rhodium-platinum oxide (0.1 g.) in acetic acid at 27°C.

TABLE I. CATALYTIC HYDROGENATION OF ANILINE WITH RHODIUM-PLATINUM AND PLATINUM CATALYSTS

Aniline g.	Catalyst g.	Solvent ml.	Temp. °C	H_2 press. kg./cm²	Time min.	% Product Cyclohexylamine	% Product Dicyclohexylamine
9.31	Pt oxide, 0.5	AcOH, 50	25	1.0	600	35	51
9.31	(3:1)Rh–Pt oxide, 0.5	AcOH, 50	25	1.0	480	65	20
4.66	(7:3)Rh–Pt oxide, 0.3	AcOH, 30	25	1.0	280	65	22
9.31	Pt oxide, 0.1	AcOH, 50	22	100∼72	55% Reduction/6hr.		
9.31	(7:3)Rh–Pt oxide, 0.1	AcOH, 50	26	70∼20	73	68	20
9.31	(7:3)Rh–Pt oxide, 0.1	AcOH, 50	27	149∼93	40	72	16
9.31	(7:3)Rh–Pt oxide, 0.1	EtOH, 50	50	90∼71	47	92	∼0
9.31	(7:3)Rh–Pt oxide, 0.1	EtOH, 50 +AcOH, 0.5	50	91∼78	100	75	12
9.31	(7:3)Rh–Pt oxide, 0.1	EtOH, 44 +AcOH, 6.2 g.	26	150∼130	60	84	6

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[8] C. F. Winans, *Ind. Eng. Chem.*, **32**, 1215 (1940).

[9] G. M. Whitman, U. S. Pat. 2606925 (1952); *Chem. Abstr.*, **47**, 3874i (1953). Cf. also L. C. Behr et al., *J. Am. Chem. Soc.*, **68**, 1296 (1946); A. E. Barkdoll et al., ibid., **75**, 1156 (1953); M. Freifelder and G. R. Stone, *J. Org. Chem.*, **27**, 3568 (1962).

[10] A. Skita and W. Berendt, *Ber.*, **52**, 1519 (1919).

[11] G. S. Hier and R. Adams, ibid., 59, 162 (1926).

[12] R. H. Baker and R. D. Schuetz, *J. Am. Chem. Soc.*, **69**, 1250 (1947).

[13] Cf. Abbott Laboratories, Brit. Pat. 881512 (1961); *Chem. Abstr.*, **56**, 11465f (1962).

acetic acid. The rate is approximately proportional to $P_{H_2}/(1+bP_{H_2})$, where b is a constant, in the range of 1 to 149 kg./cm^2 of hydrogen pressure, which is indicated by the straight line of P_{H_2}/rate versus P_{H_2} shown in Fig. 1. The rate of the hydrogenation at 149 kg./cm^2 is about thirty times as great as that at atmospheric pressure, but the yield of cyclohexylamine is increased only slightly by increasing the hydrogen pressure. The condensation reaction to give secondary amines seems to be rapid in acetic acid, not a rate-controlling step in the formation of dicyclohexylamine. The use of platinum oxide under high pressures is quite unsatisfactory because of the decrease of the activity during the hydrogenation, as has already been noticed by Baker and Schuetz$^{12)}$. The findings on the hydrogenation of various substituted anilines will be published later.

Experimental

The procedure for the preparation of catalysts and the hydrogenation apparatus at high pressure have been described previously$^{1,7)}$. Hydrogenations at atmospheric pressure were carried out in a 200 ml. glass bottle shaken at about 300 to 400 oscillations per minute.

The reaction mixture was allowed to stand in order to let most of the catalyst settle, and the upper layer was filtered. The catalyst was washed with acetic acid three times. After the addition of an excess of hydrochloric acid to the filtrate, the solvent was distilled off at reduced pressure. The residual solid was treated with aqueous sodium hydroxide and extracted with ether, and the ethereal solution was dried on solid potassium hydroxide. Distillation at atmospheric pressure followed by distillation at reduced pressure gave cyclohexylamine (b. p., 133∼136°C) and dicyclohexylamine (b. p., 129∼130°C/20 mmHg).

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