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The Hydroxide-Blacks of Ruthenium and Rhodium as Catalysts for the Hydrogenation of Organic Compounds. II.[1] The Effects of Solvents and Added Alkalis in the Hydrogenation of Aniline

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The hydrogenation of aniline with the hydroxide-black catalysts of ruthenium and rhodium was investigated, using various alcohols as solvents. The formation of dicyclohexylamine increased in the following order with respect to the solvents: *t*-butyl alcohol$\cong$isopropyl alcohol$\ll$ ethyl alcohol$<$methyl alcohol. It was shown that the addition of a small amount of alkali greatly hinders the formation of dicyclohexylamine. The effects of added ammonia and dicyclohexylamine were also investigated. The addition of ammonia retarded the rhodium-catalyzed hydrogenation much more seriously than the hydrogenation with ruthenium, but it was found that in the presence of alkali the hydrogenation with rhodium was not inhibited by the addition of ammonia.

In the preceding paper,[1] it was reported that the hydroxide-blacks of ruthenium and rhodium are catalysts excellent in activity and selectivity in the hydrogenation of aromatic compounds. The method of the preparation of the hydroxides is very simple; ruthenium hydroxide is much more

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[1] Part I: Y. Takagi, T. Naito and S. Nishimura, This Bulletin, **38**, 2119 (1965).

active than the ruthenium dioxide prepared by the method of Pichler and Buffleb,[2] and rhodium hydroxide is nearly as active as the rhodium oxide of the Adams type.[3] It was further suggested that the hydroxides, though they were precipitated with a strong alkali, contained much less alkali than the oxides mentioned above. This paper will deal with the hydrogenation of aniline and the effects of solvents and added alkalis on the reactions using the hydroxide-black catalysts of ruthenium and rhodium.

Usually the hydrogenation of aniline to cyclohexylamine is accompanied by the formation of dicyclohexylamine, and it has been known that the addition of metal oxides of a basic character, such as the oxides of calcium and magnesium, is effective in depressing the formation of the secondary amine in the hydrogenations with cobalt and nickel catalysts.[4-7] It has recently been accepted that ruthenium is the most effective of the platinum metals for the hydrogenation of aromatic amines to alicyclic amines.[8-14] Ruthenium dioxide has often been used for this hydrogenation.[8-10,12,13] More recently, rhodium and rhodium-platinum catalysts have been used successfully for the hydrogenation of aniline.[14-16] However, no detailed study of the effects of added alkalis and solvents seems to have been done in the hydrogenation of aniline, especially with ruthenium and rhodium catalysts. Only the effects of added ammonia and dicyclohexylamine have recently been studied with reference to ruthenium and rhodium catalysts supported on carbon.[14]

Experimental

Catalysts.—The hydroxides of ruthenium and rhodium were prepared in a method described previously.[1] Ruthenium dioxide was prepared by the method of Pichler and Buffleb.[2] Rhodium oxide was prepared by a modification of Adams' method described in a previous paper.[3]

Hydrogenation.—A 200 ml. autoclave of an electromagnetically-stirring type was charged with 0.1 g. of the catalyst, 0.1 mol. of aniline, and 50 ml. of the solvent at an initial hydrogen pressure of 80 kg./cm^2. The temperature was raised to 80°C under stirring and maintained constant during the hydrogenation. After the completion of the hydrogenation, the hydrogen pressure dropped to 45 kg./cm^2 at 80°C. For the addition of ammonia, ammonia gas was led into the solvent through a soda-lime tube; the amount of ammonia dissolved was determined by the titration method. Probably some loss of the ammonia occurred during loading and purging operations. Sodium hydroxide and lithium hydroxide were added as a 10% aqueous solution. The products were analyzed directly by means of gas chromatography using a column containing PEG-6000.

Results and Discussion

The Effects of Solvents.—An acidic medium is often used with platinum catalysts to avoid poisoning by nitrogen bases, but it has been shown that the use of acetic acid increases the formation of dicyclohexylamine in hydrogenation with a (7 : 3) rhodium-platinum catalyst, although the rate is the greatest in the acid.[16] In this study, the effects of various alcohols on the selectivity of the hydrogenation of aniline were investigated, using ruthenium hydroxide as the catalyst. From the results shown in Table I, it may be seen that the formation of dicyclohexylamine increases in the following order with respect to the solvents: *t*-butyl alcohol$\cong$isopropyl alcohol$\ll$ethyl alcohol $<$methyl alcohol. The formation of dicyclohexylamine was observed to be very little in *t*-butyl and isopropyl alcohols, whereas it was much larger in ethyl and methyl alcohols. This order of selectivity indicates that the more basic the alcohol used as the solvent, the more unfavorable it is for the formation of dicyclohexylamine;[17] this is in line with the previous observation that acetic acid increases the formation of dicyclohexylamine.

When the hydrogenation was carried out using alcohols as the solvents, the hydrogenation with ruthenium hydroxide proceeded rather rapidly to completion, whereas the hydrogenation with rhodium hydroxide was almost completely inhibited after about 80 to 90% of aniline had been hydrogenated. These results suggest that the rhodium catalyst is much more easily poisoned by nitrogen bases than is the ruthenium catalyst.

The Effects of Added Alkalis.—The addition of ammonia has been shown to suppress the formation of secondary amines in the hydrogenation of nitriles[18] and aniline[4]. However, the presence

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[2] H. Pichler and H. Buffleb, *Brennstoff-Chem.*, **21**, 257 (1940).
[3] S. Nishimura, This Bulletin, **34**, 1544 (1961).
[4] C. F. Winans, *Ind. Eng. Chem.*, **32**, 1215 (1940).
[5] A. I. Naumov, Z. G. Lapteva and M. M. Shumilina, U. S. S. R. Pat. 114260 (1958) [*Chem. Abstr.*, **53**, 14026 (1959)].
[6] P. Richter, J. Pasek, V. Ruzicka and L. Jarkovsky, Czech. Pat. 98263 (1959) [*Chem. Abstr.*, **56**, 12771 (1962)].
[7] H. Hagihara and E. Echigoya, *Catalyst* (*Shokubai*), **6**, 345 (1964); This Bulletin, **38**, 2094 (1965).
[8] L. C. Behr, J. E. Kirby, R. N. MacDonald and C. W. Todd, *J. Am. Chem. Soc.*, **68**, 1296 (1946).
[9] G. M. Whitman, U. S. Pat. 2606925 (1952) [*Chem. Abstr.*, **47**, 3874 (1953)].
[10] A. E. Barkdoll, D. C. England, H. W. Gray, W. Kirk, Jr., and G. M. Whitman, *J. Am. Chem. Soc.*, **75**, 1156 (1953).
[11] G. M. Illich, Jr., and R. M. Robinson, German Pat. 1106319 (1958) [*Chem. Abstr.*, **56**, 2351 (1962)].
[12] M. Freifelder and G. R. Stone, *J. Am. Chem. Soc.*, **80**, 5270 (1958).
[13] M. Freifelder and G. R. Stone, *J. Org. Chem.*, **27**, 4568 (1962).
[14] H. Greenfield, ibid., **29**, 3082 (1964).
[15] Abbott Laboratories, Brit Pat. 881512 (1961) [*Chem. Abstr.*, **56**, 11465 (1962)].
[16] S. Nishimura and H. Taguchi, This Bulletin, **36**, 873 (1963).
[17] It is of interest that similar effects of solvent alcohols were reported on the selectivity of the hydrogenation of benzyl alcohol using a platinum oxide catalyst (Y. Ichinohe and H. Ito, This Bulletin, **37**, 887 (1964)).
[18] E. J. Schwoegler and H. Adkins, *J. Am. Chem. Soc.*, **61**, 3499 (1939).

Table I. Hydrogenation of aniline with ruthenium and rhodium catalysts in various alcohols[a]

Catalyst	Solvent	Time for hydrogenation hr.	Yield of product,[b] %			
			Cyclohexylamine	Dicyclohexylamine	Cyclohexanol	Aniline unreacted
Ru hydroxide	MeOH	3.0	87.5	11.9	0.6	0.0
Ru hydroxide	EtOH	3.2	91.4	6.9	1.7	0.0
Ru hydroxide	*i*-PrOH	1.0	100.0	trace	0.0	0.0
Ru hydroxide	*t*-BuOH	1.5	99.7	0.3	0.0	0.0
Rh hydroxide	*i*-PrOH	1.5[c]	79.1	3.5	0.0	17.4
Rh hydroxide	*t*-BuOH	1.5[c]	90.0	2.0	trace	8.0

a) Aniline (0.1 mol.) was hydrogenated with 0.1 g. of the hydroxide in 50 ml. of the solvent at 80°C and 80 kg./cm^2 of initial hydrogen pressure.

b) Yields are given in weight per cent of the products.

c) Hydrogenation was strongly inhibited in the course of the reaction and not completed.

Table II. Effects of added alkalis on the hydrogenation with ruthenium and rhodium catalysts[a]

Catalyst	Solvent	Additive mg.	Time for hydrogenation hr.	Yield of product,[b] %			
				Cyclohexylamine	Dicyclohexylamine	Cyclohexanol	Aniline unreacted
Ru hydroxide	EtOH[c]	NaOH, 4	1.6	97.7	1.7	0.6	0.0
Ru hydroxide	*i*-PrOH	NaOH, 4	0.6	100.0	0.0	0.0	trace
Ru hydroxide	*t*-BuOH	LiOH, 5	2.0	99.6	0.2	0.0	0.2
Ru hydroxide	*t*-BuOH	LiOH, 20	1.8	100.0	trace	0.0	0.0
Ru hydroxide	*t*-BuOH	NaOH, 4	1.3	100.0	0.0	0.0	0.0
Ru hydroxide	*t*-BuOH	NaOH, 7	2.0	98.6	0.0	0.0	1.4
Ru dioxide	*t*-BuOH	—	6.5	99.3	0.0	trace	0.7
5% Ru-C	*t*-BuOH	—	4.5	83.7	12.6	3.7	0.0
5% Ru-C	*t*-BuOH	NaOH, 7	5.0	84.8	10.2	5.0	0.0
Rh hydroxide	*t*-BuOH	LiOH, 20	0.7	99.8	0.2	trace	0.0
Rh hydroxide	*t*-BuOH	NaOH, 4	0.8	99.7	0.3	trace	0.0
Rh hydroxide	*t*-BuOH	NaOH, 7	0.7[d]	61.6	0.2	0.0	38.2
Rh oxide	*t*-BuOH	—	0.6	100.0	0.0	trace	0.0
5% Rh-C	*t*-BuOH	—	0.8	64.0	34.6	1.4	0.0

a) Aniline (0.1 mol.) was hydrogenated with 0.1 g. of unsupported catalysts or 1 g. of supported catalysts in 50 ml. of the solvent at 80°C and 80 kg./cm^2 of initial hydrogen pressure.

b) Yields are given in weight per cent of the products.

c) The use of carefully purified ethanol was necessary for rapid hydrogenation, otherwise the rate decreased markedly with the coloration of the solvent.

d) Hydrogenation was strongly inhibited in the course of the reaction and not completed.

of ammonia strongly retards the hydrogenation of aniline,[4] especially with rhodium and ruthenium catalysts.[14] Probably the most effective and simplest way to suppress the formation of secondary amines is to add a small amount of strong alkali to the reaction mixture.[19,20] Thus, it was found that the addition of only 4 mg. of sodium hydroxide or 20 mg. of lithium hydroxide per 100 mg. of the hydroxide catalyst extremely depresses the formation of dicyclohexylamine with ruthenium hydroxide and almost completely inhibits it with rhodium hydroxide (see Table II). It is noteworthy that, in the presence of the added alkali, the rhodium-catalyzed hydrogenation proceeded rapidly to completion, although the hydrogenation in the absence of alkali was strongly poisoned in the course of the hydrogenation. The addition of an excess amount of alkali (7 mg. of sodium hydroxide) prevented the hydrogenation with rhodium hydroxide from being completed, but not that with ruthenium hydroxide. Neither the ruthenium dioxide prepared by Pichler's method nor the rhodium oxide of the Adams type gave any dicyclohexylamine, even in the absence of added alkali.

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19) M. Fluchaire and F. Chambret, *Bull. Soc. Chim. France*, **11**, 22 (1944).

20) M. Taniyama, N. Sawa, T. Nagaoka and T. Takeda, Japanese Pat. 21353 (1963) [*Chem. Abstr.*, **60**, 2756 (1964)].

It is obvious that these oxide catalysts in themselves contain alkaline substances which were contaminated during preparation.[21] Commercial 5% ruthenium- and rhodium-on-carbon catalysts* gave considerable yields of dicyclohexylamine, even in *t*-butyl alcohol, and the addition of a small amount of alkali was of little effect in supressing the formation of the secondary amine (see Table II). Presumably the added alkali was adsorbed on carbon rather than on the catalyst metal.

From the fact that, without the addition of alkali, the hydrogenation with rhodium hydroxide was strongly inhibited before it could be completed, it was supposed that the ammonia and/or dicyclohexylamine produced during the hydrogenation may have poisoned the catalyst. Therefore, the effects of the addition of ammonia and of dicyclohexylamine were studied in isopropyl alcohol using rhodium hydroxide as the catalyst. As may be seen in Fig. 1, the addition of 0.06 mol. of dry ammonia inhibited the hydrogenation almost completely, whereas the addition of 0.05 mol. of dicyclohexylamine retarded the hydrogenation only to a little extent.[22] Thus it is obvious that it was ammonia rather than dicyclohexylamine which inhibited the hydrogenation seriously. The hydrogenation with ruthenium hydroxide was also retarded by the addition of ammonia, though to a much lesser extent. The decrease in the rate observed at the later stages of the hydrogenations in ethyl alcohol and in methyl alcohol, when compared with those in isopropyl and *t*-butyl alcohols, may be attributed to the action of the ammonia formed along with dicyclohexylamine in the course of the hydrogenation (see Fig. 2 and Table I). However, it has been found that, in the presence of a slight amount of added alkali, the hydrogenation with rhodium hydroxide proceeded rapidly to completion, even when 0.077 mol. of ammonia was added (Fig. 1)[23] It is probable that the added alkali eliminated the poisoning action of ammonia by preventing or weakening its adsorption on the catalyst. In connection with these findings, it is of interest to note that, in the synthesis of ammonia, the role of potassium oxide in the doubly-promoted iron catalysts may be explained by assuming that the alkali metal oxide eliminates the poisoning by adsorbed NH-NH_2- and NH_3-species, thus promoting the synthesis of ammonia.[24,25]

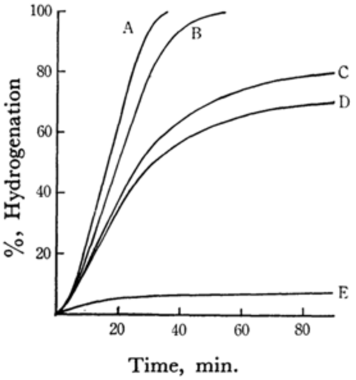


Fig. 1. Hydrogenation of aniline with rhodium hydroxide catalyst in isopropyl alcohol with addition of the following substances.

A LiOH, 10 mg.
B NH_3, 0.077 mol. + LiOH, 10 mg.
C None
D Dicyclohexylamine, 0.05 mol.
E NH_3, 0.063 mol.

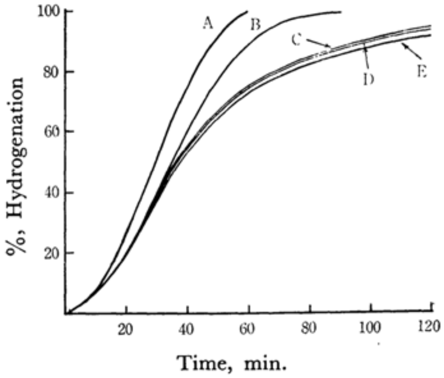
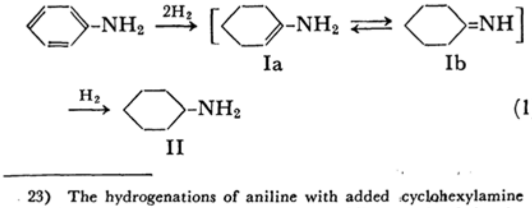


Fig. 2. Hydrogenation of aniline with ruthenium hydroxide catalyst in various solvents and the effect of added ammonia.

A	*i*-PrOH	B	*t*-BuOH
C	MeOH	D	*i*-PrOH + 0.06 mol. NH_3
E	EtOH		

The mechanism of the formation of dicyclohexylamine is probably the same as that proposed for the production of secondary amines in the hydrogenation of nitriles.[26] Dicyclohexylamine is probably formed by the following reaction sequence via enamine and imine intermediates.[14] However, it is not obvious which step of the reaction leading



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[21] Cf. Ref. 1 and C. W. Keenan, B. W. Giesemann and H. A. Smith, *J. Am. Chem. Soc.*, **76**, 229 (1954).

* Obtained from Engelhard Industries, Inc., Newark, New Jersey, U. S. A.

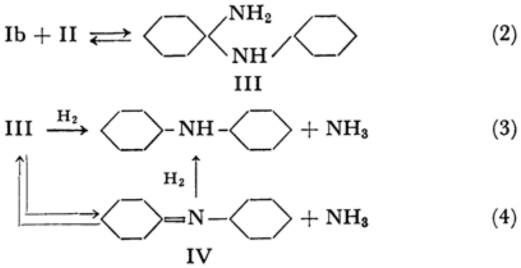
[22] Similar results have been reported with supported ruthenium and rhodium catalysts (Ref. 14).

[23] The hydrogenations of aniline with added cyclohexylamine and dicyclohexylamine were similarly rapidly completed in the presence of alkali.

[24] W. G. Frankenburg, "Catalysis," Vol. III, Reinhold Publishing Corp., New York (1955), p. 171.

[25] R. Krabetz and C. Peters, *Angew. Chem.*, **77**, 333 (1965).

[26] J. von Braun, G. Blessing and F. Zobel, *Ber.*, **56B**, 1988 (1923).



to the formation of dicyclohexylamine is retarded by alkali. It is probable that the elimination of ammonia by reaction 3 or by reaction 4 is depressed by the presence of alkali, but the present results also suggest another possibility, that the alkali prevents a longer stay of cyclohexylamine on the catalyst surface and thus depresses the addition of it to the Ib imine by reaction 2. In some cases, a small amount of cyclohexanol was obtained (see Tables I and II), the formation of which probably results from the hydrolysis of imine intermediates (Ib and IV). The formation of dicyclohexylamine from two moles of cyclohexylamine was not observed at all under the conditions used in this study, though the condensation is known to occur at higher temperatures.

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