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The Ruthenium-Catalyzed Hydrogenation of Aromatic Amines Promoted by Lithium Hydroxide

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The effects of the addition of various alkaline substances on the ruthenium-catalyzed hydrogenation of aromatic amines have been investigated at raised temperature and pressure. The addition of lithium hydroxide was shown to be the most effective for rapid and selective hydrogenation of aromatic amines. The effect of various solvents on the hydrogenolysis of carbon-nitrogen bonds has also been studied in the hydrogenation of *m*-xylene-α,α′-diamine and *N,N*-dimethyl-*p*-phenylenediamine. Generally, the hydrogenation was fast and the amount of the hydrogenolysis was small in secondary alcohols. Typical examples of the syntheses of alicyclic amines are given.

It was previously shown that the ruthenium-catalyzed hydrogenation of aniline is promoted by the addition of small amounts of alkalies which not only depress the formation of dicyclohexylamine but also eliminate a strong inhibitory action of the ammonia produced along with the secondary amine.[1]

Subsequently, the effect of the addition of various alkaline substances has been compared in the hydrogenation of some aromatic amines over ruthenium catalysts, and it has been found that the addition of lithium hydroxide in fairly large amounts is the most effective for rapid and selective hydrogenation of aromatic amines. The effect of solvents on the hydrogenolysis of carbon-nitrogen bonds has also been studied in the hydrogenation of *m*-xylene-α,α′-diamine and *N,N*-dimethyl-*p*-phenylenediamine which are both known liable to the hydrogenolysis rather readily.[2,3]

Experimental

Materials. The aromatic amines hydrogenated were carefully purified by distillation at reduced pressure, if necessary, under the atmosphere of nitrogen. Aniline, bp 79°C/20 mmHg; *o*-toluidine, bp 90°C/18 mmHg; *N,N*-dimethylaniline, bp 85°C/19 mmHg; *N,N*-dimethyl-*p*-phenylenediamine, bp 143.5—144.5°C/21 mmHg, mp 36—37°C; *m*-xylene-α,α′-diamine, bp 130—131°C/4 mmHg, n_D^{20} 1.5707; *p*-xylene-α,α′-diamine, bp 157°C/21.5 mmHg, mp 52—54°C; 4,4′-methylenedianiline, bp 170—172°C/6 mmHg, mp 92—93°C. These amines were of commercial preparations except *p*-xylene-α,α′-diamine.

p-Xylene-α,α′-diamine was prepared by hydrogenation of terephthalonitrile (25 g) with rhodium hydroxide catalyst (0.3 g) and lithium hydroxide (0.4 g) in 100 m*l* ethanol at 85°C under the hydrogen pressure of 70—100 kg/cm² for 1.5 hr (70% yield).

Catalysts. The ruthenium hydroxide catalyst was prepared by adding a slight excess of lithium hydroxide solution to a hot aqueous ruthenium chloride. The ruthenium-carbon catalyst (5% Ru) was obtained from the Nippon Engelhard Co.

Hydrogenation. All hydrogenations were carried out in stainless steel bombs with stirrers driven magnetically. The catalyst, the additive, the substrate, and then the solvent, if necessary, were put into the bomb. Sodium and potasssium hydroxides were added in a 10% solution. The other alkaline substances were added in fine powder. The reaction temperature was controlled within 0.5°C by immersing the bomb in an oil bath maintained at a constant temperature.

Analysis of the Products. The hydrogenation product was analyzed directly by gas chromatography (column: PEG 6000-KOH on Chromosorb W). The product was also isolated by distillation after removing most of the catalyst by filtration, if necessary with addition of ether to the reaction mixture.

Results and Discussion

The effect of the addition of three alkalies is compared in Table 1 in the hydrogenation of aniline with ruthenium hydroxide catalyst. It is seen from the Table that aniline is hydrogenated most rapidly when lithium hydroxide was added in the amounts more than 30 mg (as monohydrate) to 65 mg of the catalyst. The stronger alkalies, sodium and potassium hydroxides, greatly depressed the rate of the hydrogenation even when added in the amount less than 10% of the weight of the catalyst. Aniline was hydrogenated fairly rapidly even when no alkali was added. This is probably due to the promotion by a small amount of the alkali which was contaminated into the catalyst during its preparation.[4]

Table 1. Effect of added alkalies on the hydrogenation of aniline[a)]

Alkali added	mg	Reac. time (hr)	Aniline hydrogenated (%)
None	—	2.5	90
$LiOH\cdot H_2O$	10	2.5	94
$LiOH\cdot H_2O$	30	2.5	99
$LiOH\cdot H_2O$	50	2.5	100
$LiOH\cdot H_2O$	100	2.5	99
NaOH	3	2.5	90
NaOH	6	2.5	73
KOH	6	2.5	30

a) Aniline (65 g) was hydrogenated with 65 mg of the ruthenium hydroxide catalyst at 110°C under the hydrogen pressure of 70—100 kg/cm².

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[1] S. Nishimura, T. Shu, T. Hara, and Y. Takagi, This Bulletin, **39**, 329 (1966).

[2] I. Hashimoto and M. Tashiro, *Yuki Gosei Kagaku Kyokai Shi*, **25**, 144 (1967).

[3] a) L. C. Behr, J. E. Kirby, R. N. MacDonald, and C. W. Todd, *J. Amer. Chem. Soc.*, **68**, 1296 (1946). b) M. Freifelder and G. R. Stone, *J. Org. Chem.*, **27**, 3568 (1962).

[4] Analysis of a specimen of the ruthenium hydroxide catalyst by the atomic absorption spectrophotometric method indicated that 0.45% of lithium (as metal) was contained in the catalyst.

Table 2. Effect of added alkali and alkaline-earth metal hydroxides and sodium carbonate on the hydrogenation of *o*-toluidine

Catalyst, mg	Additive, mg	Reac. time (hr)	*o*-Toluidine hydrogenated (%)	Secondary amine formed (%)[b]
Ru hydroxide, 30	None, —	4[c]	79.4	6.7
Ru hydroxide, 30	$LiOH \cdot H_2O$, 30	6	99.8	0.7
Ru hydroxide, 30	NaOH, 1.5	6	85.1	2.3
Ru hydroxide, 30	NaOH, 3.0	6	55.0	—
Ru hydroxide, 30	Na_2CO_3, 100	6	94.4	1.9
Ru hydroxide, 30	$Ca(OH)_2$, 80	6	96.4	2.4
Ru hydroxide, 30	$Ba(OH)_2 \cdot 8H_2O$, 100	6	90.6	2.7
5% Ru-carbon, 360	None, —	10.5	46.8	7.4
5% Ru-carbon, 360	$LiOH \cdot H_2O$, 120	10.5	99.7	0.3
5% Ru-carbon, 360	$LiOH \cdot H_2O$, 360	10.5	97.8	trace

a) *o*-Toluidine (25 g) was hydrogenated at 110°C under the hydrogen pressure of 70—100 kg/cm².
b) Based on the *o*-toluidine converted.
c) The hydrogenation almost stopped.

In Table 2 the effects of the addition of alkali and alkaline-earth metal hydroxides and sodium carbonate are compared in the hydrogenation of *o*-toluidine where differences in the effect are more clearly seen than in the case of aniline. The hydrogenation was also the most rapid in the presence of lithium hydroxide. The addition of lithium hydroxide is also the most effective to suppress the formation of secondary amine and accordingly 2-methylcyclohexylamine is formed in the highest yield under the promotion of lithium hydroxide. When other bases or no base were added, it was difficult to complete the hydrogenation within a reasonable time and the formation of secondary amine increased. The addition of lithium hydroxide was also effective in the hydrogenation over a ruthenium-carbon catalyst as seen in Table 2.

Table 3. Effect of added alkalies on the hydrogenation of *m*-xylene-α,α′-diamine (*m*-XD)[a]

Expt. No.	*m*-XD (g)	Alkali added, mg	Time for complete hydrogenation (hr)	Proportion of hydrogenolysis (mol%)[b]
1	4	None, —	1.8	10.2
2	4	$LiOH \cdot H_2O$, 6	0.7	8.3
3	4	$LiOH \cdot H_2O$, 20	0.7	2.1
4	4	$LiOH \cdot H_2O$, 50	0.7	1.3
5	4	$LiOH \cdot H_2O$, 100	0.6	2.8
6	4	NaOH, 0.75	1.7	2.3
7	4	NaOH, 1.5	1.0	3.3
8	4	NaOH, 3.0	1.3	1.9
9	4	NaOH, 6.0	1.5	1.4
10	4	KOH, 0.75	0.6	9.0
11	4	KOH, 1.5	0.6	2.4
12	4	KOH, 3.0	1.0	3.2
13	4	KOH, 6.0	1.6	3.1
14	12	$LiOH \cdot H_2O$, 50	2.0	2.1
15	12	KOH, 1.5	4.8	11.1

a) *m*-Xylene-α,α′-diamine was hydrogenated with 30 mg of the ruthenium hydroxide catalyst in 10 m*l* of isopropyl alcohol at 120°C under the hydrogen pressure of 70—100 kg/cm².
b) Given by mol (*m*-methylbenzylamine+1-aminomethyl-3-methylcyclohexane+2×*m*-xylene)×100/mol (*m*-XD converted).

The effect of three alkalies added in various amounts on the hydrogenation of *m*-xylene-α,α′-diamine (*m*-XD) is shown in Table 3. In contrast to the hydrogenation of aniline and *o*-toluidine, the addition of a small amount of potassium hydroxide was more effective in this hydrogenation than the addition of sodium hydroxide. The same tendency was also observed in the hydrogenation of benzylamine.[5] Figure 1 illustrates the decrease in the rate during the course of hydrogenation of *m*-XD as a function of conversion, when each alkali was added in its optimum amount. It is clearly seen that the decrease in the rate is the least in the presence of lithium hydroxide. This result becomes important when the hydrogenation is performed in a larger substrate to catalyst ratio (see Expts. 14 and

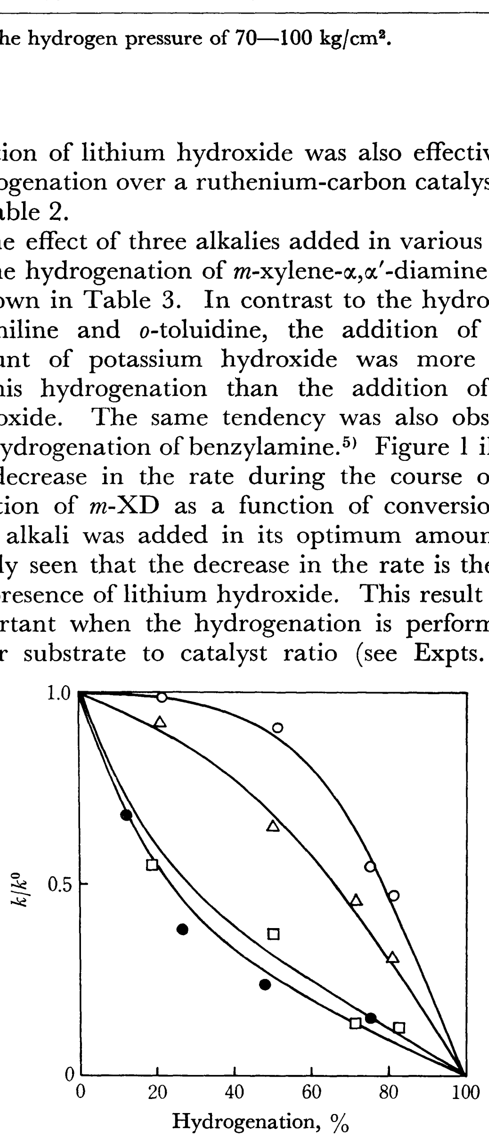

Fig. 1. Decrease in the rate during the hydrogenation of *m*-xylene-α,α′-diamine (*k*: rate at a given hydrogenation; k^0: rate at the initiation).
○: with addition of 50 mg $LiOH \cdot H_2O$
△: with addition of 1.5 mg KOH
□: with addition of 1.5 mg NaOH
●: without addition of alkali
(For reaction conditions, see Table 3)

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[5] unpublished observation.

and 15 in Table 3). The hydrogenation of *m*-XD may be accompanied by the hydrogenolysis of the benzyl-nitrogen bond, with formation of *m*-methylbenzylamine, 1-aminomethyl-3-methylcyclohexane and *m*-xylene.[2] The addition of alkalies was found also effective to suppress the hydrogenolysis as seen from the results shown in Table 3. In particular, the addition of lithium hydroxide is seen very effective for this purpose, since the amount of the hydrogenolysis was only 2.1% even in the hydrogenation of a larger amount of the substrate (Expt. 14 in Table 3). *N*,*N*-Dimethyl-*p*-phenylenediamine (DMP) is also known to be liable to an extensive hydrogenolysis of the dimethylamino group on hydrogenation.[3] Since the nature of the solvent may have a profound effect on the hydrogenolysis of a polar bond, as shown previously in the hydrogenation of *p*-anisidine,[6] the effect of various solvents on the hydrogenolysis of carbon-nitrogen bond has been studied on the hydrogenation of *m*-XD and DMP. The results are summarized in Table 4. It will be seen from the results in the table that the proportion of the hydrogenolysis is smaller in higher primary alcohols, secondary and tertiary alcohols and methylcyclohexane. Among these solvents, secondary alcohols appear the most preferred ones, as the rate of hydrogenation is in most cases larger in secondary alcohols than in the other solvents mentioned. In Fig. 2 initial rates of the formation of hydrogenolysis products[6] in the hydrogenation of *m*-XD are plotted *versus* the reciprocal of the dielectric constant of the solvents in which hydrogenations were carried out. A similar dependence of the rates on the polarity of the solvents as observed in the hydrogenation of *p*-anisidine can be seen also in this hydrogenation, but the effect is much less pronounced than in the case of *p*-anisidine. Since differences in the rates of hydrogenolysis are rather small among the solvents, the proportion of hydrogenolysis seems to depend more on the variation of the rates of the hydrogenation with the solvents as shown in Fig. 3.

TABLE 4. EFFECT OF SOLVENTS ON THE HYDROGENOLYSIS OF *m*-XYLENE-α,α'-DIAMINE (*m*-XD) AND *N*,*N*-DIMETHYL-*p*-PHENYLENEDIAMINE (DMP)[a]

Solvent	Hydrogenation of *m*-XD			Hydrogenation of DMP	
	React. time (hr)	Half-hydrogenation time (hr)	Amount of hydrogenolysis (mol %)	Reac. time (hr)	Amount of hydrogenolysis (mol %)
MeOH	3.5	0.38	9.5	4.3	29.3
EtOH	4.6	0.42	8.8	3.3	35.8
PrOH	2.8	0.17	5.4	3.7	15.4
i-PrOH	2.4	0.23	5.1	2.7	13.4
BuOH	—	—	—	3.0	14.7
s-BuOH	2.1	0.20	5.6	2.7	13.3
t-BuOH	2.6	0.23	7.0	3.0	15.9
t-PeOH	2.4	0.17	4.4	—	—
THF[b]	—	—	—	4.7	36.1
i-Pr_2O	6.2	0.47	11.7	4.3	18.3
Bu_2O	5.6	0.85	9.6	—	—
MCH[c]	3.0	0.23	5.7	3.3	10.1

a) *m*-XD and DMP (0.03 mol) were hydrogenated with 30 mg of the ruthenium hydroxide catalyst and 6 mg of $LiOH \cdot H_2O$ under 70—100 kg/cm² hydrogen pressure, in 20 m*l* solvent at 120°C for *m*-XD and in 10m*l* solvent at 130°C for DMP.
b) Tetrahydrofuran
c) Methylcyclohexane

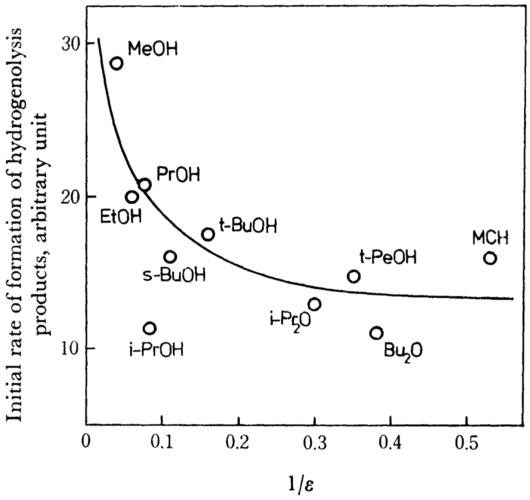

Fig. 2. Effect of solvents on the initial rates of formation of hydrogenolysis products as a function of the reciprocal of the dielectric constant of solvents (ε at 80°C) in the hydrogenation of *m*-xylene-α,α'-diamine with ruthenium hydroxide catalyst.

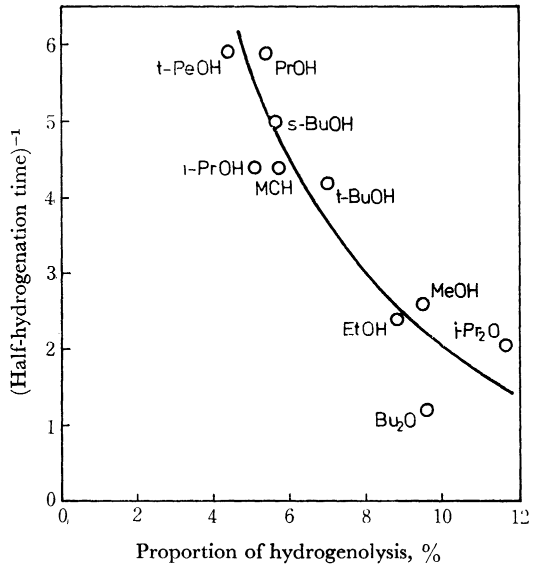

Fig. 3. Relation between proportion of hydrogenolysis and the rate of hydrogenation in the hydrogenation of *m*-xylene-α,α'-diamine with ruthenium hydroxide catalyst.

The results shown in Tables 1—3 and in Fig. 1 indicate that lithium hydroxide is the most effective promotor of the alkaline substances investigated in the ruthenium-catalyzed hydrogenation of aromatic amines. Since ruthenium is one of the most effective metals for the hydrogenation of aromatic amines,[7] the present im-

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[6] S. Nishimura and H. Yoshino, This Bulletin, **42**, 499 (1969).

[7] P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, Inc., New York (1967), p. 352.

Table 5. Hydrogenation of aromatic amines with ruthenium hydroxide catalyst promoted by lithium hydroxide[a]

Compound, g	Catalyst (mg)	$LiOH\cdot H_2O$ added (mg)	Solvent, m*l*	Reac. temp. (°C)	Reac. time (hr)	Yield of alicyclic amine (%)	
						By glpc.	By distil.
Aniline, 65	65	50	—	110	2.5	99.8	93[b]
o-Toluidine, 43	50	50	—	110	4.5	99.2	93[c]
N,*N*-Dimethylaniline, 61	61	50	—	110	2.0	99.7	97[d]
N,*N*-Dimethyl-*p*-phenylenediamine, 14	100	160	*i*-PrOH, 25	120	4.0	95.5	83[e]
m-Xylene-α,α′-diamine, 12	30	50	*i*-PrOH, 10	120	2.0	96.9	87[f]
p-Xylene-α,α′-diamine, 12	30	50	*i*-PrOH, 10	120	6.3	89.0	73[g]
4,4′-Methylenedianiline, 30	100	160	*i*-PrOH, 50	120	7.5	—	84[h]

a) Aromatic amines were hydrogenated under the hydrogen pressure of 70—100 kg/cm^2.
b) Bp 134.5—135.5°C; n_D^{25} 1.4558.
c) Bp 153—154°C; n_D^{25} 1.4564.
d) Bp 163—164°C.
e) Bp 98.5—100°C/22 mmHg; n_D^{25} 1.4785 [reported: bp 200—205°C/755 mmHg; n_D^{25} 1.4795, Ref. 3b].
f) Bp 120—121°C/17 mmHg; n_D^{20} 1.4939 [reported: bp 110.4°C/8 mmHg; n_D^{20} 1.4950 (*trans*); bp 85—86°C/2 mmHg; n_D^{20} 1.4917 (*cis*), J. C. Dubin, Fr. Pat. 1408314 (1965); *Chem. Abstr.*, **65**, 5637 (1966)].
g) Bp 140°C/34 mmHg; n_D^{20} 1.4919 [reported: bp 98—99°C/5 mmHg; n_D^{20} 1.4890 (*trans*); bp 79—79.5°C/2 mmHg; n_D^{20} 1.4959 (*cis*), A. Bell, J. G. Smith, and C. J. Kibler., *J. Polym. Sci., Part A-3*, 19 (1965)].
h) Bp 140°C/5 mmHg; n_D^{25} 1.5037 [reported: bp 128°C/1.2 mmHg; n_D^{25} 1.5051, A. E. Barkdoll, D. C. Engl, and H. W. Gray, W. Kirk, Jr., and G. M. Whitman., *J. Amer. Chem. Soc.*, **75,** 1156 (1953)].

provement of the hydrogenation by the addition of lithium hydroxide offers a very useful general method of the synthesis of alicyclic amines from aromatic amines. Typical examples of the hydrogenation in preparative scales are listed in Table 5. It is seen that in most cases hydrogenations were completed within a few hours with use of only small portions of the catalyst to the substrate (0.1—0.7% as Ru hydroxide or 0.06—0.4% as Ru metal) and the corresponding alicyclic amines were obtained in excellent yields.[8)]

The authors are indebted to the Mitsubishi Chemical Industries Co., Ltd., for the analysis of the lithium in the catalyst and also for providing some of the aromatic amines and terephthalonitrile.

[8)] Lithium hydroxide added to or contained in the catalyst was shown also effective in the rhodium-catalyzed hydrogenation of nitriles and aromatic amines.[1,9,10)] However, the simple addition of lithium hydroxide appears not always effective as noticed in the hydrogenation of *p*-anisidine.[10)]

[9)] Y. Takagi, S. Nishimura, K. Taya, and K. Hirota, *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), **61**, 114 (1967).

[10)] S. Nishimura, H. Uchino, and H. Yoshino, This Bulletin, **41**, 2194 (1968).