Catalytic Hydrogenation of Aromatic Nitriles

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Catalytic hydrogenation of various aromatic nitriles has been investigated using nickel-copper-kieselguhr catalyst in vapor phase. An earlier study has been made by P. Sabatier[1], but it was only reported that benzonitrile was reduced to toluene and ammonia, while a different result was presented by A. Frébault[2]. Systematic study in this field has never been made and the mechanism of hydrogenation of nitriles has not yet been thoroughly established, although some views have been presented during the past half century[3]. In this paper, results of a systematic study on the catalytic hydrogenation of various aromatic nitriles are presented. The effect of various substituents in aromatic ring is discussed, along with the factor of promotion and retardation in hydrogenation. Further, the mechanism of the hydrogenation of nitriles has been investigated and some views are presented.

1) **Hydrogenation of Aromatic Nitriles in Vapor Phase.**—It was previously reported that nitrile is hyrogenated to methyl compound and ammonia in vapor phase[1] (1), whereas to amines in liquid phase[3] (2).

$$RCN \xrightarrow{H_2} RCH_3+NH_3 \qquad (1)$$

$$RCN \xrightarrow{H_2} RCH_2NH_2,\ (RCH_2)_2NH \qquad (2)$$

The original purpose of the present study was to investigate whether or not aromatic nitriles of any kind undergo hydrogenolysis to methyl compounds in vapor phase. Various aromatic nitriles listed in Table I have been hydrogenated. The vapor of nitrile, mixed with an excess of hydrogen, was passed over a catalyst in a reaction tube, which was heated to an appropriate temperature between 200 ~350°C in an electric furnace. The catalyst, which consists of 60% of reduced nickel and 40% of reduced copper, was prepared according to Sabatier's method[1], and supported on purified kieselguhr. Representative experimental results of the hydrogenations are summarized in Table I. As seen in the table, it has been proved that aromatic nitriles are generally hydrogenated to the corresponding methyl compounds according to Formula 1 except for some special cases. However, it is important to note that this cleavage reaction of the nitrile group could not be complete unless sufficient condition for hydrogenation was given[4].

It is now apparent that the reaction temperature at which the hydrogenolysis is effectively carried out is governed by the nature of the compound to be hydrogenated. A well defined range of temperature for the efficient cleavage reaction was found for each compound. It has been found that, in general, a scission of C–C bond between nitrile group and

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[1] P. Sabatier and J. B. Senderens, *Compt. rend.*, **135**, 226 (1902); **165**, 309 (1917); **140**, 482 (1905).

[2] M. A. Frébault, ibid., **140**, 1036 (1905).

[3] C. Paal and J. Gerum, *Ber.*, **42**, 1153 (1909); G. Mignonac, *Compt. rend.*, **171**, 114 (1920); J. v. Braun et al., *Ber.*, **56**, 1988 (1923); K. W. Rosenmund et al., ibid., **58**, 51 (1925); K. Kindler, *Ann.*, **485**, 113 (1931); R. Juday and H. Adkins, *J. Am. Chem. Soc.*, **77**, 4559 (1955).

[4] M. Obata, K. Watanabe and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 116 (1957).

TABLE I. CATALYTIC HYDROGENATION OF AROMATIC NITRILES IN VAPOR PHASE

Catalyst: ca. 25 g (mixture of NiO and CuO (Ni 60%, Cu 40%) 11 g., purified kieselguhr 14 g., reduced at ca. 300°C before the hydrogenation experiment)

Flow velocity of hydrogen ca. 0.1 l./min.; Flow velocity of sample 0.05～0.1 g./min.

Expt. No.	Nitriles	Temp. (°C)	Time (hr.)	Methyl compounds and yields (%)	Yields of ammonia (%)	Other products (%)	Lit.
1.	Benzonitrile	250	1⅔	Toluene (87)	100		12
2.	Benzonitrile	358	3½	Toluene (29)	76	Benzene (39)	12
3.	α-Naphthonitrile	270	3	α-Methylnaphthalene (74)	97		1—3
4.	β-Naphthonitrile	240	3½	β-Methylnaphthalene (73)	74		4
5.	*p*-Tolunitrile	205	4	*p*-Xylene (72)			5
6.	*o*-Tolunitrile	240	3½	*o*-Xylene (87)	100		6, 17
7.	*p*-Nitrobenzonitrile	300	4⅓	*p*-Toluidine (43)	92	Aminonitrile (32)	7
8.	*m*-Nitrobenzonitrile	250	2⅓	*m*-Toluidine (56)	73	Aminonitrile (9)	8
9.	*o*-Nitrobenzonitrile	300	1¼	*o*-Toluidine (17)	79	Aminonitrile (20) Aniline (48)	9
10.	*p*-Aminobenzonitrile	330	3	*p*-Toluidine (80)	90	Aniline (5)	13
11.	*o*-Aminobenzonitrile	300	3	*o*-Toluidine (9)	94	Aniline (40)	13
12.	Ethyl *o*-cyanobenzoate	260	2	—	15	Phthalimidine (74)	10
13.	Ethyl *p*-cyanobenzoate	280	2	Ethyl *p*-toluate (70)	80		16
14.	*p*-Bromobenzonitrile	200～300	1½	—	0	Recovered nitrile	11
15.	*p*-Chlorobenzonitrile	250～350	1½	Toluene (small quantities)	35～60	Recovered nitrile	11
16.	Benzyl cyanide	240	3	Ethylbenzene (34)	69	Toluene (12) β-Phenylethylamine (18)	14
17.	*p*-Hydroxybenzonitrile	453	2¼	*p*-Cresol (75)	100	Toluene (10)	15
18.	Salicylonitrile	363	6½	*o*-Cresol (68)	80	Phenol (11)	18
19.	*p*-Methoxybenzonitrile	240	1⅓	*p*-Cresyl methyl ether (70)	100		22
20.	*o*-Methoxybenzonitrile	300	2¼	*o*-Cresyl methyl ether (73)	100		19
21.	2,6-Dimethoxybenzonitrile	300	4	—	86	1,3-Dimethoxybenzene (55) Recovered nitrile (13)	23
22.	*p*-Cyanobenzaldehyde	280	2½	*p*-Xylene (28)	60	Toluene (12)	24
23.	Terephthalonitrile	304	2⅓	*p*-Xylene (46)	81	*p*-Tolunitrile (11)	20
24.	Phthalonitrile	310	1½		78	*o*-Tolunitrile (15) Polymerization	20
25.	Acetylmandelic acid nitrile	250	4½	Ethylbenzene (70)	74	Acetic acid (68)	21
26.	2,4,6-Trimethyl benzonitrile	240	2½	Isodurene (ca. 50)	60	Recovered nitrile (34)	25
27.	Cinnamonitrile	260	2½	Propylbenzene (90)	100		26

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1) K. Hata, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **23**, 224 (1944). 2) K. Hata, ibid., **23**, 296 (1944). 3) K. Hata, ibid., **24**, 1 (1945). 4) K. Hata, ibid., **24**, 34 (1945). 5) K. Hasegawa and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 54, (1951). 6) Y. Tanaka and K. Hata, ibid., **73**, 85 (1952). 7) K. Watanabe, ibid., **76**, 391 (1955). 8) K. Watanabe, ibid., **76**, 395 (1955). 9) K. Watanabe, ibid., **76**, 398 (1955). 10) K. Watanabe, ibid., **76**, 888 (1955). 11) J. Mukai, K. Watanabe and K. Hata, ibid., **76**, 1354 (1955). 12) M. Tanaka, K. Watanabe and K. Hata, ibid., **76**, 1392 (1955). 13) K. Watanabe, ibid., **77**, 221 (1956). 14) K. Watanabe, ibid., **77**, 977 (1956). 15) M. Tanaka, K. Watanabe and K. Hata, ibid., **77**, 980 (1956). 16) K. Watanabe, ibid., **77**, 1272 (1956). 17) M. Obata, K. Watanabe and K. Hata, ibid., 78, 116 (1956). 18) M. Tanaka, ibid., 78, 1385 (1957). 19) F. Iwamoto, K. Watanabe and K. Hata, ibid., **78**, 1390 (1957). 20) M. Tanaka, ibid., **79**, 1302 (1958). 21) M. Tanaka, ibid., **79**, 1318 (1958). 22—26) Unpublished.

aromatic ring occurs as shown in Formula 3, when the hydrogenation is carried out at higher temperature (e. g., Experiment No. 2).

$$RCN \xrightarrow{H_2} RH + CH_3NH_2{}^* \qquad (3)$$

The data given in Table I, are the results of the hydrogenation which give the best yield of the methyl compound among several experiments carried out under various conditions, especially under various reaction temperatures (except for Experiment No. 2). On the other hand, ammonia, which was liberated from the nitrile group during hydrogenation, was introduced to normal sulfuric acid solution and was determined by a titration with baryta water. The yield of ammonia suggests the degree of the cleavage reaction of the nitrile group. When the condition of hydrogenation is changed, somewhat different results can be observed for each compound. It is significant that the cleavage of the nitrile group is largely dependent upon the kinds and the positions of substituents in the aromatic ring.

Besides the normal cleavage reaction of nitriles, various side reactions were observed. For example, reductive cyclization was remarkable in the reaction of ethyl *o*-cyanobenzoate⁵⁾. Sometimes, the side reaction was so complicated that the products could not be identified.

1) Effect of Substituents in Aromatic Ring on the Hydrogenation of Nitriles.—It is very difficult to estimate the effect of substituents on the hydrogenation of the nitrile group, because catalytic reaction is complicated with many factors. Nevertheless, it is conceivable that the relative reactivity of the cleavage reaction may be estimated by comparing the yields of the products, although a vapor phase hydrogenation is carried out ordinarily under such a drastic condition that it may cause undesirable side reactions. In general, it has been proved that a substituent in the aromatic ring exhibits both electronic and steric effects on the hydrogenation of the nitrile group. Any substituent seems to depress the hydrogenation of the nitrile group.

As for the electronic effect, electron-releasing substituents give less effect, while electron-attracting substituents such as nitro, cyano, ethoxycarbonyl and aldehyde groups restrain the hydrogenation of the nitrile group remarkably. However, the effect due to the electronic characteristics of the substituent is not always observed clearly since the catalytic hydrogenation is also governed by many other complicated factors.

In the catalytic reaction, it is the first requisite for the initiation of the reaction that the compound should be adsorbed on the surface of the catalyst. This consideration has led to the inference that the nitrile group will be unfavorably hydrogenated, if another substituent in the same ring undergoes competitive hydrogenation or interferes with the adsorption of the nitrile group on the catalyst by steric effect. As for the steric effect, it is expected that the nearer the substituent to the nitrile group is, the larger is its effect. This effect is observed distinctly about nitro, amino, cyano, hydroxyl and ethoxycarbonyl groups, and may be expressed in terms of "ortho effect" in hydrogenation. When two substituents are introduced in both ortho positions beside the nitrile group, a greater steric effect is observed (Table I, Experiments No. 21 and 26). This "ortho effect" could not be obviously observed in the previous studies of hydrogenation in liquid phase. Further investigation of this effect should be made in connection with a mechanism of the reaction on the surface of catalyst.

A special interfering effect of the nitro and amino groups on the hydrogenation of the nitrile group, has been studied in particular⁶⁾. It was first pointed out in the liquid phase hydrogenation by H. Rupe⁷⁾, that the nitro group has an interfering effect on the hydrogenation of the nitrile group, and it was shown extensively that the nearer the nitro group is to the nitrile group, the greater is the effect. Hydrogenation of nitro and aminobenzonitriles in vapor phase also gave less yield of the hydrogenolysis products (Table I, Experiments No. 7—11). In order to solve this problem, some experiments on mixed hydrogenation were made. The vapor of benzonitrile was mixed with that of nitrobenzene, aniline or water, and the mixture was hydrogenated as usual. On the other hand, benzonitrile was hydrogenated on the catalyst which had been previously used for the hydrogenation of nitrobenzene or aniline. The results of the experiments

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* Methylamine may be further hydrogenated to methane and ammonia in high reaction temperature.

5) K. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 888 (1955).

6) K. Watanabe, ibid., **77**, 225, 1741 (1956).

7) H. Rupe et al., *Helv. Chim. Acta*, **8**, 832, 838 (1925).

TABLE II. MIXED CATALYTIC HYDROGENATION OF AROMATIC NITRILES

Expt. No.	Method	Compounds (g.)	Temp. (°C)	Time (hr.)	Main products and yields (%)	Other products*
1.	A	Benzonitrile (7) Nitrobenzene (7)	250	3½	Toluene (61)	Aniline (74%)
2.	B	Benzonitrile (6)	250	2¼	Toluene (60)	
3.	A	Benzonitrile (8) Water (3)	250	2	Toluene (59)	Amines (+) Recovered nitrile
4.	A	Benzonitrile (6) Aniline (6)	250	3	Toluene (62)	Recovered aniline
5.	C	Benzonitrile (6)	250	2	Toluene (39) Dibenzylamine (18)	Benzylamine (+) Tribenzylamine (+) Recovered nitrile (18%)
6.	A	*p*-Aminobenzonitrile (6.6) Water (3)	330	2	*p*-Toluidine (59)	Recovered nitrile (15%) Aniline (+)

Method A: The mixture of two substances was hydrogenated.

Method B: Catalyst that was used beforehand for the hydrogenation of nitrobenzene (5 g.) was used successively.

Method C: Catalyst that was used beforehand for the hydrogenation of aniline (5 g.) was used successively.

* Products marked with (+) were detected in small quantities.

TABLE III. CATALYTIC HYDROGENATION UNDER INSUFFICIENT CONDITIONS

Expt. No.	Catalyst (g.)	Compounds (g.)	Temp. (°C)	Flow velocity of sample (g./hr.)	Products and yields (%)					Recovered sample (%)
					Methyl compds.	Prim. amine	Sec. amine	Tert. amine	Ammonia	
1.	30	*o*-Tolunitrile (6.7)	240	3	87	—	—	—	100	—
2.	10	〃 (5.9)	260	2	70	1	4	—	91	10
3.	10	〃 (6.0)	〃	6	37	3	8	—	64	37
4.	2	〃 (4.0)	〃	4	16	4	12	—	44	45
5.	0.7	〃 (5.1)	〃	2.5	0	9	11	—	17	61
6.[a]	25	〃 (6.3)	〃	3	62	2	3	—	63	22
7.	10	Benzonitrile (3.0)	260	5	52	2	14	2	68	8
		(12.0)	〃	5	47	7	17	3	70	17
		(5.0)	〃	6	32	6	25	5	64	18
8.	2	〃 (4.0)	〃	4.5	34	7	24	—		18
9.[b]	2	Benzylamine (5.6)	260	6	27	—	27	—		30

a) Flow velocity of hydrogen was diminished to 1.3 l./hr.: in other experiments, excess of hydrogen was used (flow velocity 5∼6 l./hr.)

b) Cf. Table V, Experiment No. 6.

are shown in Table II. From these results, it is inferable that the nitro group is first reduced to the amino group and suppresses the hydrogenation of the nitrile group by a competitive reaction. It is further proved that the amino group produced from the nitro group acts poisonously for the catalytic activity (cf. Section 4). However, the hydrogenolysis of *p*-aminobenzonitrile could not be affected by the *p*-substituted amino group. This can be interpreted by the steric ineffectiveness of the *p*-substituted amino group as a poison for the catalyst.

3) Investigation of Hydrogenation Mechanism of Nitriles.—The investigation of the behavior of various nitriles in the hydrogenation has led to the study of hydrogenation mechanism of nitriles, which is complicated owing to the presence of secondary products. Generally, it has been known[3] that the main process of the hydrogenation of nitriles may be shown as follows:

$$\mathrm{RCN} \rightarrow \mathrm{RCH{=}NH} \rightarrow \mathrm{RCH_2NH_2} \rightarrow \mathrm{RCH_3} + \mathrm{NH_3} \qquad (4)$$

$$\mathrm{RCH{=}NH} + \mathrm{RCH_2NH_2} \rightarrow \mathrm{RCH{=}NCH_2R} \rightarrow \mathrm{(RCH_2)_2NH} \qquad (5)$$

$$3\,\mathrm{RCH{=}NH} \rightarrow \mathrm{RCH(N{=}CHR)_2} \rightarrow \mathrm{RCH{=}NCH_2R} \rightarrow \mathrm{(RCH_2)_2NH} \qquad (6)$$

It is conceivable that the course of the

TABLE IV. HYDROGENATION OF BENZYLAMINE AND DIBENZYLAMINE

Expt. No.	Compounds (g.)		Temp. (°C)	Time (hr.)	Products and yields[b] (%)		Other products
1.	Benzylamine	(7.3)	250	2	Toluene	(66)	Oil of high boiling point
2.	Benzylamine	(10.0)	360	3	Toluene	(46)	Benzene (9%)
3.[a]	Benzylamine	(7.2)	250	1⅔	Toluene	(81)	
4.	Dibenzylamine	(6.0)	300	2½	Toluene Benzylamine	(34) (+)	Unidentified by-product
5.	Dibenzylamine	(7.3)	350	3½	Toluene Benzylamine	(44) (+)	Unidentified amine
6.	{Benzylamine {Benzonitrile (Mixture)	(4.0) (4.2)	250	3¼	Toluene (4.3 g.) Benzylamine Dibenzylamine	(68)[c] (+) (+)[d]	Recovered nitrile

a) Before the hydrogenation, 5 mg. of thiophene dissolved in 0.1 g. of benzene was vaporized and passed over the catalyst (cf. Table V, Experiment No. 6).

b) (+) denotes detectable but unestimated.

c) The yield of toluene from benzylamine is also calculated as the yield from benzonitrile.

d) Very small amount: When benzonitrile was hydrogenated with the catalyst treated with benzylamine beforehand, about the same amount of dibenzylamine was obtained (Table V, Experiment No. 10).

TABLE V. EFFECT OF THIOPHENE AND SOME BASES ON THE HYDROGENATION OF NITRILES

Expt. No.	Compounds (g.)		Additional compounds[a] (g.)		Temp. (°C)	Time (hr.)	Products and yields (%)			Recovered sample (%)	Remarks[b]
							Methyl compds.	Prim. amine	Sec. amine		
1.	Benzonitrile	(8)	None		250	1⅔	88	—	—	—	Catalyst 25 g.
2.	〃	(5)	Thiophene	(0.003)	250	2	82	+	—	—	Catalyst 10 g.
3.	〃	(5)	〃	(0.2)	250	2	14	—	—	84	Catalyst 10 g.
4.	〃	(7)	〃	(2.0)	250	1½	28	—	—	67	
5.	〃	(7)	〃	(0.005)	350	2	30	+	—	7	Benzene (42%)
6.	Benzylamine	(6)	〃	(0.003)	250	1½	66	—	21	12	Catalyst 10 g.
7.	Benzonitrile	(7.7)	Ammonia		250	2½	69	+	+	—	
8.[c]	〃	(7.1)	〃		250	2	14	14	13	43	
9.	〃	(6)	Aniline	(5)	250	2	39	+	18	18	Tribenzylamine
10.	〃	(7.4)	Benzylamine	(6.4)	250	3	66	+	+	+	
11.	〃	(10.8)	Dibenzylamine	(7.5)	250	2¼	18	14	30	19	
12.	〃	(7)	〃	(2.0)	355	2½	16	11	—	11	Benzene (47%)
13.	〃	(7)	Pyridine	(1.0)	250	2⅓	78	+	+	—	

a) The nickel catalyst was previously treated with the vapor of these compounds, and then the nitrile was hydrogenated.

b) 25 g. of catalyst was used except for Experiments No. 2, 3 and 6.

c) The mixture of benzonitrile and ammonia was hydrogenated.

reaction is nearly the same whether in liquid phase or in vapor phase although some differences are found. Some factors in the hydrogenation may forcibly control the process of these reactions. The normal process of the hydrogenation of nitrile in vapor phase follows the course shown in Formula 4, and other side reactions or interruption of the process 4 may be caused by inadequate conditions of the hydrogenation. Such a hydrogenation under insufficient conditions may give ample facilities for the study of hydrogenation mechanism. Therefore, some hydrogenation experiments were tried intentionally under insufficient conditions (quantity of catalyst, feeding velocity of sample and hydrogen, etc.)[4]. It has been shown that the course of the reaction can be controlled in the expected way according to the condition of the hydrogenation. The examples of these experimental results are summarized in Table III.

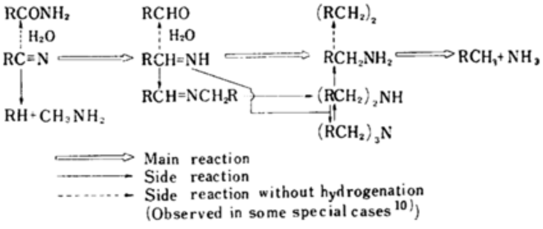
In the hydrogenation of *o*-tolunitrile (Experiments No. 1—5), the yield of the methyl compound through course 4 decreased according to the decreasing quantity of catalyst used, alternatively yielding the increasing quantity of primary and secondary amines. When a small amount of hydrogen was fed during the hydrogenation, a similar result was obtained (Experiment No. 6). In Experiment No. 7, benzonitrile was hydrogenated in three portions successively on the same catalyst, and the products were collected separately for every portion. The components of the reaction products were varied according to the proceeding of the reaction, whereby the changing feature of the reaction was observed.

To ascertain the hydrogenation mechanism, the investigation of the behavior of the intermediate compounds in the process is useful. Thus, the further hydrogenation of amines, which have been found to be intermediate of the process, was carried out[8]. The results of the experiments are summarized in Table IV. When benzylamine was hydrogenated, toluene was obtained and no dibenzylamine was found. But the yield of toluene from benzylamine by the hydrogenation was less than that from benzonitrile, and a small quantity of unidentifiable by-product was obtained from benzylamine. It has been found that benzylamine was smoothly hydrogenated and toluene was obtained in good yield, when a small quantity of thiophene was added to the catalyst (Experiment No. 3). On the other hand, when dibenzylamine was hydrogenated, toluene was obtained in considerable yield, along with a small amount of benzylamine and other unidentified by-product.

It was reported previously by v. Braun[3] that the secondary amine is formed by interaction between a primary amine and an aldimine when aromatic nitrile is hydrogenated in liquid phase (process 5). According to the present investigation in vapor phase, it is evident that dibenzylamine can scarcely be obtained by the hydrogenation of benzylamine, or of the mixture of benzonitrile and benzylamine. It is assumed subsequently that the formation of dibenzylamine in the hydrogenation under insufficient conditions, proceeds through hydrobenzamide and Schiff base as an intermediate according to Formula 6.

It has been found that, when aromatic nitriles are hydrogentated in vapor phase at a higher temperature, the ordinary hydrogenation to methyl compound (reaction 1) is generally accompanied with the hydrogenolysis of C–C bond between the nitrile group and aromatic ring (reaction 3). It has been proved that this cleavage of C–C bond occurs mainly before the hydrogenation of C–N bond does[9]. This cleavage reaction also occurs even at a temperature not so high, when the hydrogenation of the nitrile group happens to be interfered with by the effect of other substituents (Table I, Experiments No. 9 and 11). The cleavage of this type is observed especially in some ortho-substituted benzonitriles (Table I, Experiments No. 21 and 26).

Considering the results of these experiments, the hydrognation mechanism of aromatic nitriles in vapor phase is assumed to be as follows:



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[8] K. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1478 (1957).

[9] M. Tanaka, K. Watanabe and K. Hata, ibid., **76**, 1392 (1955).

[10] K. Watanabe, ibid., **76**, 391, 398 (1955); K. Watanabe, ibid., **77**, 1272 (1956); K. Hasegawa and K.Hata, ibid., **72**, 54 (1951).

TABLE VI. EFFECT OF THIOPHENE ON THE HYDROGENATION OF NITRILE IN LIQUID PHASE

Catalyst: U-Ni-B; Sample: Benzonitrile (7.2 g.); Solvent: 99% Ethanol; Room temperature

Expt. No.	Weight of thiophene (g.)	Hydrogen absorbed (%)	Time (hr.)	Products and yields (%)		
				Prim. amine	Sec. amine	Aldehyde
1.	0	90	1⅔	47	23	11
2.	0.007	93	2⅙	61	13	11
3.	3.5	89	11	56	11	15

4) Factors for Promotion and Retardation in Hydrogenation of Nitriles.—It has been widely known that the result of the hydrogenation reaction varies according to the character of the catalyst, which can be controlled by the addition of appropriate promoter or poisonous matter. The promotion or retardation of the hydrogenation was also observed in aromatic nitriles. The effect of various substances on the character of the nickel catalyst has been investigated[8], and the results of these experiments are summarized in Table V. When benzonitrile was hydrogenated with nickel catalyst which was previously treated with a small amount of thiophene, toluene was obtained in high yield, little by-product being found (Experiment No. 2). On the contrary, when the catalyst was previously treated with ammonia, amine or pyridine, the formation of toluene was suppressed and considerable amounts of by-products were obtained (Experiments No. 7—13). In some experiments, the mixture of benzonitrile and some other basic substances was hydrogenated with the ordinary nickel catalyst, and the results were similar to those in Table V (except the experiment with ammonia, cf. Experiments No. 7 and 8). A similar effect of thiophene has been observed in the liquid phase hydrogenation of benzonitrile (shown in Table VI)[11].

As the result of these experiments, the addition of basic substances (such as amine) has been found to cause retardation of the hydrogenation of nitrile. On the other hand, it has been found that the addition of a small quantity of thiophene causes promotion and increases the yield of the methyl compound, whereas the formation of secondary products is considerably suppressed. Thus, it is evident that the suitable amount of thiophene on the catalyst retards the side reaction of nitriles (e. g., the formation of secondary amine). This effect was especially remarkable in the case of hydrogenation under insufficient conditions. For example, toluene was obtained in high yield from benzonitrile, even when a small quantity of the catalyst was used (Experiment No. 2, compared with Experiment No. 7 in Table III). On the contrary, a large amount of thiophene acts as poison for all the various sorts of the reaction: a large quantity of the nitrile was recovered unchanged (Experiments No. 3 and 4).

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[11] T. Okazawa, K. Watanabe and K. Hata, unpublished.