BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 8—14 (1966)

Studies of Organic Catalytic Reactions. III.1) The Hydration Mechanism of Nitriles to Amides with Nickel Catalysts

By Ken-ichi WATANABE and Koji SAKAI

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received March 26, 1965)

Benzonitrile, benzyl cyanide, acetonitrile and 2-cyanopyridine give the corresponding amides by the hydration with nickel catalysts and water. The effect of pyridine and thiophene on the hydration has been investigated. In general, the yield of amides increases upon the addition of a suitable amount of pyridine. On the contrary, the reaction is distinctly suppressed by the addition of thiophene. This fact is in striking contrast to the effect on the hydrogenation of nitriles. The correlation of the catalytic functions in hydration and the hydrogenation of nitriles has been studied, and the hydration mechanism with nickel catalysts has been discussed.

Nitriles are hydrated to the corresponding amides by refluxing them with metal catalysts (a nickel catalyst is the best) in water1). In this novel reaction, neither acid nor alkali is necessary, and the reaction is generally stopped at the amide stage, especially in the reaction of aromatic nitriles. However, the reaction of aliphatic nitriles is somewhat complicated because of the side reactions with accompany the hydration. The present paper will deal with the mechanism of this catalytic hydration reaction of nitriles from the points of view of organic reaction and catalytic function.

It has been reported that a nickel catalyst acts in two different ways, exhibiting both acidic and basic functions. In this paper, this conception will be developed further by some experiments and discussed. In the hydration of benzonitrile, benzyl cyanide, benzamide and acetonitrile, when pyridine was used as a basic substance, it accelerated the hydration. While thiophene, when used as an acidic substance, suppressed the hydration. In addition, pyridine also suppressed side reactions. As a result of many facts mentioned below, the hydration mechanism of nitriles to amides with nickel catalysts will be presented.

The Hydration of Benzyl Cyanide, Acetonitrile and 2-Cyanopyridine with Nickel Catalysts.—Though Raney nickel is effective enough for this reaction,1) Urushibara nickel catalyst-B (U-Ni-B)1,2) was used in these experiments. Some results of the hydration of three nitriles are shown in Table I and in Figs. 1 and 2. In the hydration of acetonitrile, hydrogen cyanide was generated as well as ammonia. The formation of propionic acid, hydrogen cyanide and formic acid suggests that catalytic cleavages of acetonitrile and new bond formations take place in addition to the hydration reaction. It is of great interest that such reactions occur in the liquid phase around at 100°C.[*1] The effect of the electronegative character of the nitrogen atom in the pyridine nucleus was so predominant in the hydration of cyanopyridines that a remarkably good result was obtained in the case of 3-cyanopyridine (amide yield: 89%),1) while a nickel complex was obtained in the case of 2-cyanopyridine.

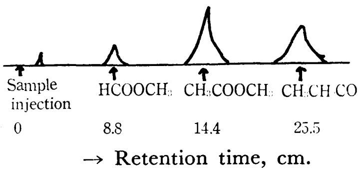


Fig. 1. Gas chromatographic chart of analysis of acids. (Acids were converted to methylesters respectively.)

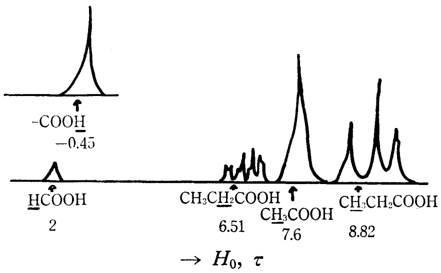


Fig. 2. NMR spectrum chart of acids.

[*1] The hydration of adiponitrile gave the corresponding amide in a poor yield (ca. 20%) and was accompanied by various kinds of side reactions. By the gas chromatographic analysis of the oily by-product, five components were detected. It seemed that an acidic substance was included in the oil. It can only be preumed that the reaction was much more complicated than that of acetonitrile.

1) Paper II: K. Watanabe, This Bulletin, **37**, 1325 (1964).

2) Y. Urushibara and S. Nishimura, This Bulletin, **28**, 466 (1955).

TABLE I. THE HYDRATION OF NITRILES TO AMIDES WITH U-Ni-B IN WATER

Exp. No.	Nitrile	g.	Catalyst g.	Water ml.	Reaction time hr.	Yield[1] of amide %	Recovered[2] nitrile	Other product	Remark
1	Benzyl cyanide	10	4	150	10	58	+	Phenylacetic acid, Phenethylamine, Benzaldehyde (?)	
2	Acetonitrile	7	4	100	5	28[3]	+	Acids,[4] Amine (+)	5)
3	Acetonitrile	7	4	100	7.5	47.2	+	Acids, Amine (+)	5)
4	Acetonitrile	7	8	100	5	49.6	+	Acids, Amine (+)	5)
5[6]	Acetonitrile	35	20	500	8	70	+	Acids, Amine (+)	5)
6	2-Cyanopyridine	7	4	100	10	ca. 40	—	Nickel complex	
7[7]	3-Cyanopyridine	7	4	100	10	89	—		

1) Yield of amide was calculated from the weight of amide obtained in pretty pure.
2) Recovered nitrile was analyzed by gas chromatography.
3) This is the highest yield of the reaction products by this condition.
4) Acids are propionic acid, acetic acid and a trace of formic acid.
5) Besides ammonia gas, hydrogen cyanide was detected.
6) The content was stirred with efficient stirrer during the refluxing.
7) Paper II.

TABLE II. THE HYDRATION OF BENZONITRILE TO BENZAMIDE WITH VARIOUS CATALYSTS

Exp. No.	Catalyst	g.	Weight of sample g.	Solvent (water) ml.	Reaction time hr.	Yield[1] of benzamide %
1	U-Ni-B	4	5	80	8	78
2	Stabilized-Ni (F50)	25	5	80	8	78
3	ZnO	4	5	80	8	—
4	$Cu-CrO_2$	4	5	80	8	20

1) Yield of amides was calculated from the weight of amides obtained.

Studies of Catalysts for the Hydration.—The effect of the nature of many catalysts on this hydration has been examined.[1] It has been found that the usual catalysts for hydrogenation are generally effective in the hydration of nitriles.

For this paper, some other catalysts have also been tested in the hydration of benzonitrile. The catalysts used were U-Ni-B, Stabilized-Ni (F50),[*2] zinc oxide, and copper chromium oxide. The results of representative experiments are shown in Table II. The highest yield of benzamide was given with U-Ni-B (Exp. No. 1), the other substances gave poor results as catalysts for the hydration.

The Effect of Ammonia Gas on the Hydration.—During the hydration of any nitrile, a small quantity of ammonia gas is gradually generated. The quantity of ammonia gas generated during the reaction with benzonitrile was examined every hour,[*3] this was also tried in the case of the hydrolysis of benzamide with U-Ni-B in water. The results of the measurements are shown in Fig. 3. It may easily be assumed that the ammonia gas generation was caused by the cleavage of the C–N bond of the nitrile groups. The quantitative analysis of all the ammonia gas generated from benzonitrile throughout the eight-hour reaction always gave constant results (ca. 20% yield), while benzamide was obtained in a 77 per cent yield. On the contrary, the hydrolysis of benzamide was much slower than that of benzonitrile, and no constant

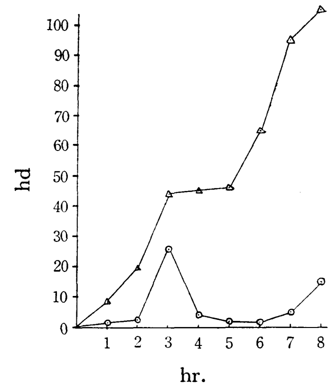


Fig. 3. The relative quantity of ammonia gas generated during the hydration with U-Ni-B.
—△— Benzonitrile —○— Benzamide

[*2] Obtained from the Nikko Scientiffic & Chemical Industry Co., Ltd., Tokyo, this was a kind of nickel catalyst on kieselguhr (50%) made from nickel formate, stabilized with inert gas.

[*3] The reaction apparatus was connected to a gas samplemetric tube of the gas chromatography, and the ammonia gas generated was introduced to the tube for just three minutes and then analyzed by the usual method. Gas chromatography: column, 30% Carbo-wax 1500 on Celite ca. 30—40 mesh; length, 2 m.; temp., 75°C; flow rate, 6/10 ml./sec.; carrier gas, H_2.

TABLE III. THE EFFECT OF AMMONIA ON THE HYDRATION OF BENZONITRILE

Exp. No.	Weight of sample g.	Catalyst g.	Ammonia added	Solvent ml.		Reaction time hr.	Yield of amide %
1	5	—	NH_4OH conc. 2—3 drops (pH 8.8—9.2)	Water	80	8	4.3
2	5	—	NH_4OH conc. 80 ml.	NH_4OHaq.	80	8	4.3
3	5	—	Constant flow of ammonia gas	Water	80	8	22.0
4	5	U-Ni-B, 4	—	Water	80	5	1)
5	5	U-Ni-B, 4	NH_4OH conc. 2—3 drops (pH 8.8—9.2)	Water	80	5	2)

1) Benzonitrile unreacted after the reaction for five hours; 19%.
2) Benzonitrile unreacted after the reaction for five hours; 12%.

TABLE IV. THE EFFECTS OF PYRIDINE AND THIOPHENE ON THE HYDRATION OF NITRILES TO AMIDES IN WATER WITHOUT NICKEL CATALYST

Exp. No.	Nitrile	Weight of sample g.	Admixture ml.	Water ml.	Reaction time hr.	Yield of amide	Generated ammonia gas	Recovered nitrile g.
1	Benzyl cyanide	10	—	150	10	Trace	—	7.20
2	Benzyl cyanide	10	Pyridine, 1	150	10	Trace	—	8.30
3	Benzyl cyanide	10	Thiophene, 1	150	10	Trace	—	8.10
4	Benzonitrile	5	—	80	8	Trace	—	4.10
5	Benzonitrile	5	Pyridine, 1	80	8	Trace	—	4.00
6	Benzonitrile	5	Thiophene, 1	80	8	Trace	—	3.85

TABLE V. THE HYDRATION OF BENZYL CYANIDE TO PHENYLACETAMIDE WITH U-Ni-B IN WATER1)

Exp. No.	Admixture	Yield of amide %	Recovered nitrile %	Other product
1 2)	—	58	6	Phenylacetic acid, Phenethylamine, Benzaldehyde (?)
2	Pyridine (1 ml.)	83	2.5	—
3	Pyridine (1.5 ml.)	51	7	—
4	Thiophene (1 ml.)	16	31	Amine
5 3)	Pyridine (0.5 g.)	72	2.3	—
6	Pyridine (1 g.)	69	2.9	—
7	Pyridine (1.5 g.)	49	6.5	—

1) 10 g. of benzyl cyanide, 4 g. of catalyst and 150 ml. of water were refluxed for ten hours in each run.
2) The catalyst prepared at one time was divided into four parts of the same quantity and they were used respectively in each run of Exp. No. 1—4 at the same time.
3) Same way with 2).

results were observed with regard to the ammonia generation. A part of the ammonia generated during the reaction may form an ammonium salt of the acid that is produced by the hydrolysis of nitriles. On the basis of the results of experiments with benzonitrile, however, it may be assumed that the ammonium salts are too unstable under these reaction conditions and that they are likely to decompose and free the ammonia gas. In order to establish whether ammonia gas itself behaves as a catalyst for the hydration of nitriles, some experiments were carried out. Benzonitrile was refluxed with water containing a few drops of concentrated ammonium hydroxide without a nickel catalyst or was refluxed with concentrated ammonium hydroxide without a catalyst.*4 In one case, ammonia gas was introduced constantly throughout the reaction in the absence of a nickel catalyst. The results of the experiments are shown in Table III. It has been proved that ammonia gas itself generally effective to some extent as a catalyst for the hydration.

The Effect of Pyridine and Thiophene on the Hydration of Nitriles.—The effect of pyridine and thiophene on the hydration of some nitriles was studied in detail in the examination of this

---

*4 Krewson and Couch reported that concentrated ammonium hydroxide was only effective for the hydrolysis of nicotinonitrile in the sealed-tube (at 108°C for twelve hours). C. F. Krewson and J. F. Couch, *J. Am. Chem. Soc.*, **65**, 2256 (1943).

catalytic reaction mechanism. Blank tests with pyridine and thiophene showed that neither of them had any influence upon the hydration of benzonitrile and benzyl cyanide without catalysts (Table IV). In the hydration of benzyl cyanide, benzonitrile and acetonitrile, however, pyridine had favorable effects, while thiophene had unfavorable effects. This effect of pyridine was observed conspicuously in the reactions of benzyl cyanide. As is shown in Table V, the yield of phenylacetamide increased a great deal upon the addition of a suitable amount of pyridine (ca. 20% of a nickel catalyst). Further, it is noteworthy that no by-product could be obtained.

The results of the experiments with benzonitrile are shown in Figs. 4 and 5. Figure 4 shows the amount of the diminution of benzonitrile during the reaction with pyridine. The most desirable amount of pyridine added was ca. 1 g. (ca. 25% of a nickel catalyst). As is shown in Fig. 5,*[5] it has been found that thiophene has a distinct effect in suppressing the reaction. The effect of pyridine on the hydration of acetonitrile was somewhat different from that of the other cases. Pyridine did not promote the hydration of acetonitrile, and the yield of acetamide was decreased. However, it was found that no propionic acid or formic acid was obtained, only acetic acid and acetamide were obtained by the addition of pyridine. Therefore, pyridine seemed to suppress the catalytic cleavages of acetonitrile. As for the effect of thiophene, it was as large as in the other cases. When acetamide was refluxed with a newly-prepared catalyst in water, the reaction hardly ever took place suprisingly. The reaction of acetonitrile may be assumed to be as shown in Fig. 6. Benzoic acid was obtained in a poor yield by the hydrolysis of benzamide,*[6] a small quantity of ammonia gas was hardly ever generated. The effect of pyridine and thiophene was also observed by the generation of ammonia, a generation which was of the same type as the hydration of benzonitrile.

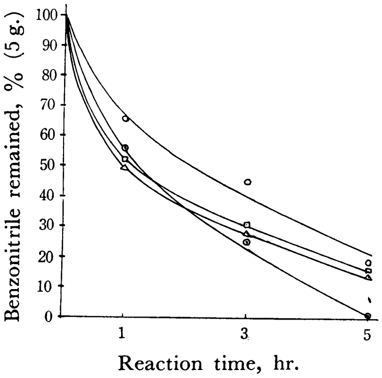


Fig. 4. Diminution of benzonitrile in the hydration with pyridine. (5 g. of benzonitrile and 4 g. of U-Ni-B were used in each run.)

Exp. No. 1 —○— Standard (without pyridine)
Exp. No. 2 —⊙— Addition of 1 g. of pyridine
Exp. No. 3 —△— Addition of 0.5 g. of pyridine
Exp. No. 4 —□— Addition of 2.5 g. of pyridine

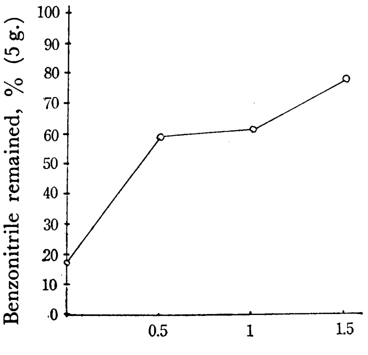


Fig. 5. Unreacted benzonitrile in the hydration with thiophene. (5 g. of benzonitrile and 4 g. of U-Ni-B were used in each run; reaction time, 5 hr.)

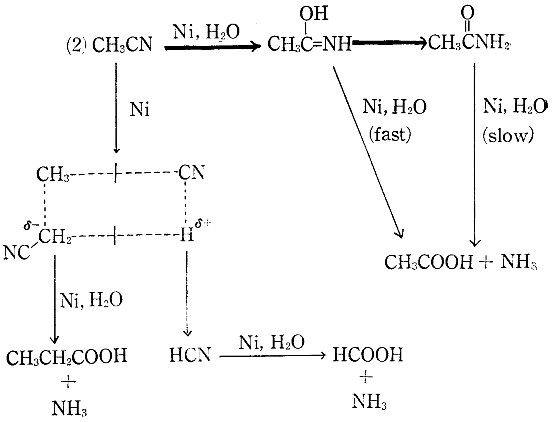


Fig. 6. Reactions of acetonitrile with nickel catalysts in water.

Discussion

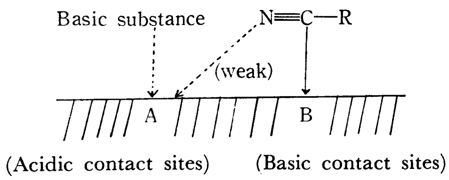
As the result of many experiments, it is apparent, in the hydration of nitriles with nickel catalysts in water, that pyridine and organic bases have favorable effects on the reaction, while that thiophene and organic acids have unfavorable effects. It has previously been shown[1)] that nitriles of a basic character afford the corresponding amides in good yields, and that those of an acidic character afford no hydration products. On the other hand, the effects of pyridine and thiophene on the hydrogenation of nitriles with nickel catalysts both

---

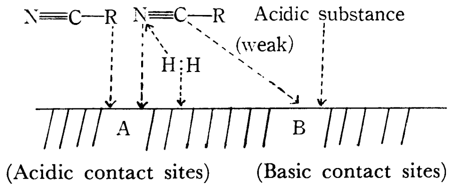
*[5] The experimental method with thiophene was that 0.5 g., 1 g. or 1.5 g. of thiophene was added respectively in each run, after the reactions were over, the benzonitrile which remained was analyzed by gas chromatography (Fig. 5).

*[6] The same reaction procedure with the hydration of benzonitrile.

in the liquid³⁾ and the vapor phases⁴⁾ have been studied in detail.⁵⁾ For instance, an organic base, ammonia or nitriles of a basic character effect an unfavorable hydrogenation. Thiophene does not. Consequently, it is significant that the effect of organic acids and bases on the hydration of nirtiles is in contrast to their effect on the hydrogenation of nitriles. It is of particular interest that *o*-aminobenzamide was obtained by the hydrogenation of *o*-nitrobenzonitrile with a nickel catalyst both in the liquid⁶⁾ and the vapor phase⁵,⁷⁾. It is presumed that the hydrogenating activity of the nickel catalyst is greatly depressed by the nitro group, and also by the amino group produced by the reduction of the nitro group, and that the nitrile group is hydrated with the water produced by the hydrogenolysis of the nitro group. From these facts, it may be inferred that the hydrogenation of nitriles is due to the catalytic action of a kind of active center which may be expressed as acidic contact sites of the nickel catalysts. In this case, the electronegative nitrogen atom of the nitrile group may be first adsorbed on the acidic contact sites and then be activated to cause hydrogenation. So long as other atoms of a more electronegative character cover the acidic contact sites of the catalysts, the nitrogen atom of the nitrile group will hardly ever be adsorbed firmly on the sites, consequently, the hydrogenation of the nitrile group will be depressed. On the other hand, the hydration of the nitrile group with water may occur by means of the activation of the carbon atom of the nitrile group on the other kind of free active-contact sites of the catalysts in spite of the existence of hydrogen. Therefore, the hydration of nitriles is apt to take place instead of hydrogenation when the acidic contact sites of the catalysts are covered with bases or basic substances. From many experimental facts, it may be concluded that the active-contact sites serving to introduce the hydration of nitriles are endowed with a more electronegative character (they are, that is, the basic contact sites of the catalysts). This may be expressed as in Fig. 7 (A). On the contrary, acidic substances may cover the basic contact sites of the catalysts, and interfere with the strong adsorption of nitriles on the same sites, so suppressing the hydration. This may be expressed as in Fig. 7 (B).



(A) Favorable hydration model



(B) Unfavorable hydration model

Fig. 7

The conception that the carbon atom of the nitrile group is adsorbed predominantly on the basic contact sites of the nickel catalysts has been proved by some other experiments. When benzonitrile was hydrogenated with a nickel catalyst in the vapor phase (250°C), toluene was obtained (87%) by the cleavage of the C–N bond. However, in the reaction at 350°C, about 35% of benzene was formed, and when amine was added to the benzonitrile, the yield of benzene increased to 47%.⁵⁾ The formation of benzene is apparently due to the cleavage of the C–CN bond, in this hydrogenolysis, the carbon atom of the nitrile group should be adsorbed on the other kind of active-contact sites of the catalysts (the basic contact sites). It was proved that the cleavage of the C–CN bond occurs before the hydrogenation of the nitrile group.⁸⁾ Amine worked on the acidic contact sites to accentuate the function of the basic contact sites of the catalysts. When *o*-nitrobenzonitrile was hydrogenated, 48 per cent of aniline was obtained at a reaction temprature of 300°C.⁷⁾ It was about the same with the reaction of *o*-aminobenzonitrile.⁵⁾ When benzonitrile mixed with about 35 per cent of water was hydrogenated at 250°C, the yield of toluene was decreased to 60 per cent and amines and unreacted nitrile were obtained.⁵⁾ On the other hand, *o*- and *p*-hydroxybenzonitrile afforded no phenols in reactions at 300°C, and only the *o*-compound afforded even 11 per cent of phenol at 350°C.⁹⁾ From these results, it can be concluded that the carbon atom of the nitrile group is likely to be adsorbed on the basic contact sites of the nickel catalysts and so cause the hydrogenolysis of the C–CN bond at elevated temperatures. Amine and water relate to the acidic contact sites of the catalysts. The hydroxyl group relates to the basic contact sites and suppreses the hydrogenolysis. As for the cleavage of the C–CN bond in water, it has obviously been shown that hydrogen cyanide, formic acid and propionic

---

3) T. Okazawa, M. Hayashi, K. Watanabe and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 254 (1961); *Chem. Abstr.*, **56** 1003 7h (1962).

4) K. Watanabe, ibid., **78**, 1478 (1957); *Chem. Abstr.*, **54**, 1370b (1960).

5) K. Hata and K. Watanabe, This Bulletin, **32**, 861 (1959); *Chem. Abstr.*, **54**, 1305 4h (1960).

6) H. Rupe, *Helv. Chim. Acta*, **8**, 832 (1925).

7) K. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **76**, 398 (1955); *Chem. Abstr.*, **51**, 17815 i (1957).

8) M. Tanaka, K. Watanabe and K. Hata, ibid., **76**, 1392 (1955); *Chem. Abstr.*, **51**, 17813 a (1957).

9) M. Tanaka, K. Watanabe and K. Hata, ibid., **77**, 980 (1956); *Chem. Abstr.*, **52** 9015 a (1958).

acid are formed in the hydrolysis of acetonitrile with a nickel catalyst. Thus, it may also be assumed that the cleavage of the C–CN bond takes place on the basic contact sites of the catalysts. As was shown in a previous paper,1) it is of interest that no hydration product was obtained in the reaction of *p*-hydroxybenzonitrile with a nickel catalyst in water. This fact suggests a strong interaction between the hydrogen atom of the hydroxy group and the basic contact sites of the catalysts.

When benzonitrile is hydrogenated with a nickel catalyst in ethanol, amines are obtained as the main products (ordinary hydrogenation). However, it has now been observed that no reaction takes place when water is used as the solvent instead of ethanol at room temperature (the carbylamine test is negative), while, the hydration of the nitrile to benzamide occurs predominantly when the reaction mixture is refluxed with enough hydrogen gas (amide yield; 75%). To examine the effect of thiophene on the reactions mentioned above, 1 g. (25% of the nickel catalyst) and 0.2 g. (5% of the nickel catalyst) of thiophene were added to the catalysts. In the reactions, both at room temperature and at the refluxing temperature (ca. 100°C), even very small quantities of amines were hardly ever obtained. No favorable effect of thiophene on the hydrogenation was observed. On the other hand, the unfavorable effect of thiophene on the hydration of the nitrile was just the same as that shown in Fig. 5 when it was refluxed. Thus, it is evident that water suppresses the hydrogenation of nitriles, causing the hydration in some way. Apparently, the fact that water is the most suitable solvent for this hydration is important. That is, water has two functions, one is to react with nitriles, affording amides, while the other is to suppress other side reactions, especially the hydrogenation of nitriles. It may be assumed, consequently, that the free electron pair of the oxygen atom of the water molecule interacts with the acidic contact sites of the nickel catalysts and interferes with the strong adsorption of the nitrogen atom of the nitrile group on the same sites of the catalysts. The fact that the addition of basic substances to the catalysts does not have an unfavorable effect may mean that the interaction of water and catalysts is fairly strong. From a different point of view, however, if this nickel-catalyzed hydration is essentially due to the ionization or half-ionization of water on the catalysts, the hydrolysis of nitriles to acids should be the main reaction, as is observed in the hydrolysis with acid or base catalysts.

According to the conception of the acidic and basic functions of the nickel catalysts, the nitrile-catalysts-water interaction may be represented as in Fig. 8, while the course of the hydrolysis of nitriles to acids may be represented as in Fig. 9. However, it has not been proved that there are two kinds of active contact sites, A and B, really fixed on the surface of the catalysts. This serves only to explain the phenomena and results of the nickel-catalyzed hydration and hydrogenation of nitriles. It is assumed that the hydrolysis of nitriles may arise also by the activation of the carbon atom of the amide group, and that it is less active than the hydration of nitriles. Attention should be focussed on the fact that the hydrolysis of benzamide and acetamide with a nickel catalyst is much more difficult than that of benzonitrile or acetonitrile. This is the reason why two courses, II–IV–VI and II–III–V–VI, have been postulated. The former is expected to be faster than the latter.

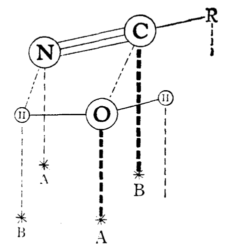


Fig. 8

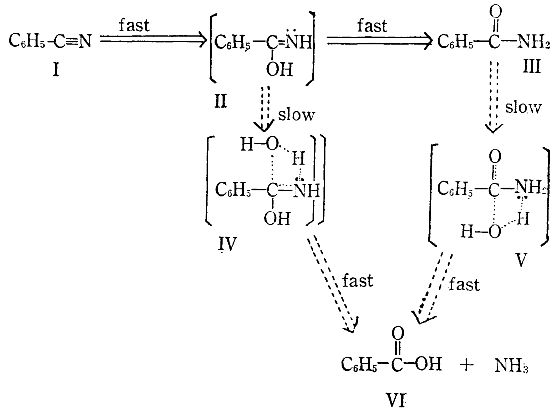


Fig. 9. The hydration of Benzonitrile

⇒ Main reaction

⇛ Hydrolysis

In the end, it is noteworthy that the nickel catalysts (U-Ni and Raney nickel) used in this hydration have been prepared somewhat differently from that used for hydrogenation. It does not matter if the catalyst is exposed to air and to common city water during the preparation.1) This may lead to an assumption that oxygen in the air or in undistilled water attacks the acidic contact sites of the catalysts, but does not have the unfavorable effect on the basic contact sites of causing the hydration of nitriles.

Experimental

According to the common reaction procedure reported previously1), were refluxed nitriles for eight hours in water with U-Ni-B. After the reactions, the catalysts were separated by filtration, the filtrates were analyzed by gas chromatography, and the reaction products were obtained by the careful evaporation of the filtrates on a water bath. In general, rather pure amides were thus obtained.

The Hydration of Benzyl Cyanide.—Ten grams of benzyl cyanide and 150 ml. of water were refluxed vigorously with U-Ni-B (containing 4 g. of nickel) for ten hours. During the reaction a small quantity of ammonia was generated as was detected with litmus. After the reaction was over, the catalyst was separated by filtration while hot and washed with hot water. The filtrate, combined with the washings, was extracted with ether. When the aqueous solution (filtrate) was then evaported carefully on a water bath, phenylacetamide was obtained in a 58% yield as the main product, m. p. 153.5—154.2°C. A small quantity of an oily by-product was obtained from the ether extract and was analyzed successfully by gas chromatography.[*7] The by-products seemed to be small quantities of phenylacetic acid, phenethylamine and benzaldehyde. However, the presence of benzaldehyde was somewhat doubtful, because the Tollens' test[10] for it varied between being positive and negative; moreover, the detection of benzaldehyde was not always successful by gas chromatography.

The Hydration of Acetonitrile.—Thirty-five grams of acetonitrile and the catalyst (containing 20 g. of nickel) in 500 ml. of water were placed in a 1000-ml., three-necked, round flask and stirred while being refluxed for eight hours. During the reaction, ammonia gas was detected; sometimes hydrogen cyanide was detected as well. The hydrogen cyanide was identified by the method used for picric acid.[11] After the reaction was over, the catalyst was separated by filtration. The filtrates were alkalized with sodium hydroxide and then evaporated to a solid mass on a water bath. When the dried mass was extracted with chloroform in a Soxhlet extractor, crude acetamide was obtained from the extract in rather pure form, m. p. 81.5—81.7°C. The yield was 30.05 g. (ca. 70%). The sodium salt which remained was put into a small quantity of water and acidified with concentrated hydrochloric acid. The free acids were extracted with ether. The total weight of the free acids thus obtained was 6 g. The mixture of the acids was analyzed by means of their NMR spectrum[*8] (Fig. 2). On the other hand, they were esterified with diazomethane and the esters were analyzed by gas chromatography[*9] (Fig. 1). The acids were propionic acid, acetic acid and a small amount of formic acid. They were identified by NMR and by gas chromatography with three pure acids. Amine was extracted by hydrochloric acid and was identified by carbylamine reaction.

The Hydration of 2-Cyanopyridine.—Seven grams of 2-cyanopyridine and 100 ml. of water were refluxed vigorously with U-Ni-B (containing 4 g. of nickel) for ten hours. During this reaction, the colorless contents turned violet and then blue and the pH value of the contents became 9.4—9.2 and then 8.4—8.2. A small quantity of ammonia gas was generated during the reaction, as could be detected with litmus. The product obtained by the same method as in the other cases was dissolved in ethanol and then separated by column chromatography with active alumina. Thus, pyridine-α-carboxylic acid amide was obtained in ca. 40% yield (m. p. 105°C), along with a blue nickel complex. The weight proportion of pyridine-α-carboxylic acid amide and the nickel complex was about 3 : 1. The nickel complex immediately absorbed moisture in air and had the property of a solid solution. The paramagnetic character was observed. When it was heated with hydrochloric acid, both pyridine-α-carboxylic acid and its amide were obtained. When it was treated with dimethylglyoxime, free pyridine-α-carboxylic acid amide was obtained. As a result of an infrared analysis, it seems that this complex might be formed by an interaction of the nickel and pyridine-α-carboxylic acid amide. By refluxing 2-cyanopyridine with Raney-Ni-W_7 in water, the contents (color and pH) were observed as well as when U–Ni–B was used. However, a small quantity of pyridine was obtained besides pyridine-α-carboxylic acid amide and the nickel complex.

The Hydration of Benzonitrile Accompanied with Hydrogen Gas.—1) Five grams of benzonitrile was refluxed in 80 ml. of water with U-Ni-B (4 g. of nickel) for eight hours. A constant flow of hydrogen gas was introduced into the reaction mixture throughout the refluxing. Benzamide was thus obtained in a 75% yield, along with a very small amount of amine (almost the same reaction and result as were obtained without hydrogen gas; cf. Exp. No 1, Table II).

2) Five grams of benzonitrile, together with U-Ni-B (4 g. of nickel) and 0.2 g. of thiophene (5% of nickel catalyst), was stirred for eight hours at room temperature. A constant flow of hydrogen gas was introduced into the reaction mixture throughout the reaction. Benzamide was thus obtained in a 7% yield, while 80% of the nitrile was recovered. Amine was extracted by hydrochloric acid and was analyzed by means of a study of its infrared spectrum. Benzylamine was obtained in a 2% yield.

3) Five grams of benzonitrile, together with U-Ni-B (4 g. of nickel) and 1 g. of thiophene (25% of nickel catalyst), was refluxed in 80 ml. of water for eight hours. A constant flow of hydrogen gas was introduced into the reaction mixture throughout the refluxing. Benzamide was thus obtained in a 36.5% yield as the main product, while 58% of the nitrile was recovered. A small quantity of amine was obtained as hydrogen chloride-salt, as was detected by carbylamine reaction (almost the same reaction as that with 1 g. of thiophene without hydrogen gas; cf. Fig. 5).

The authors wish to express their hearty thanks to Professor Kazuo Hata for his kind advice.

[*7] Column, 30% Carbo-wax 1500 on Celite ca. 30—40 mesh; length, 2 m.; temp., 68°C; flow rate, 20/24 ml./sec.; carrier gas, H_2. Gas chromatograph: Yanagimoto GCG 220 Type, Yanagimoto Mfg. Co., Ltd, Kyoto, Japan.

10) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Reprint, Maruzen, Tokyo (1956), p. 162.

11) H. Meyer, "Nachweiss und Bestimmung der organischen Verbindungen", Copyright by Julius Springer in Berlin (1933), p. 99.

[*8] Solvent; CCl_4; filter bandwidth, 4 c.p.s.; r.f. field, 0.015 mG; sweep time, 500 sec.; sweep width, 500 c. p. s.; sweep offset, 200 c.p.s.

[*9] Column; 30% Carbo-wax 1500 on Celite ca. 30—40 mesh; length, 2 m.; temp., 40°C; flow rate, 20/12 ml./sec.; carrier gas, H_2.