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Catalytic Function of Metal Chelates in the Hydration of 2-Pyridinecarbonitrile

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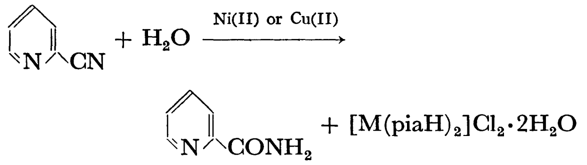
The catalytic effects of various transition metal complexes on the hydration of 2-pyridinecarbonitrile have been investigated. In these homogeneous catalytic reactions, free 2-pyridinecarboxamide was obtained as the sole reaction product. The transition metal species of the complexes used were Cu(II), Ni(II), Co(II), Co(III), and Pt(IV), while the ligands were ethylenediamine, bipyridine, glycine ion, and 2-pyridinecarboxamide. The complexes of Cu(II), Ni(II), and Co(II) were all catalytically active for the hydration, but those of Co(III) and Pt(IV) were inactive. No reaction occurred with 3- and 4-pyridinecarbonitriles under the same reaction conditions. The effect of the pH was remarkable. The active complex catalysts were classified into three types.

It has been reported[1,2] that 2-pyridinecarbonitrile is hydrated to afford the metal chelate of 2-pyridinecarboxamide by the catalytic action of transition metal ions such as Ni(II) or Cu(II). No hydration occurred with 2-pyridinecarbonitrile in a neutral solution without the metal ions. In this catalytic reaction, however, when an excess of 2-pyridinecarbonitrile was employed, free 2-pyridinecarboxamide was obtained together with its metal chelate, and the yield of the free amide increased with the reaction time.



M: Metal ion
piaH: 2-pyridinecarboxamide

It has been proved[1] that the Ni(II) or Cu(II) chelate of 2-pyridinecarboxamide also shows catalytic activity for the hydration of 2-pyridinecarbonitrile.

With this view, we have taken up an idea that metal chelates other than Ni(II) and Cu(II) chelates of 2-pyridinecarboxamide may also act as catalysts for this hydration; we have found that some chelates have enough catalytic activities. A brief note has been already reported.[3]

In this paper, we will report in detail on our studies of the catalytic hydration of 2-pyridinecarbonitrile with various kinds of metal chelates. The relation between the nature and the catalytic activity of the complex catalysts will be discussed.

The meal species of the complexes used were Cu(II), Ni(II), Co(II), Co(III), and Pt(IV), and the ligands were ethylenediamine(en), 2,2'-bipyridine(bipy), glycine ion(gly), and 2-pyridinecarboxamide(piaH). These metal complex catalysts are summarized in Table 1. To make a comparison, aquo metal ions were also used as catalysts. It is characteristic that no hydrolysis occurred; that is, no ammonia was generated in these chelate-catalyzed reactions. The only product was 2-pyridinecarboxamide, and the complex catalysts were recovered without any change in all except a few cases.

Table 1. Hydration of 2-pyridinecarbonitrile with metal chelates

2-pyridinecarbonitrile 0.0475 M, Reaction temp. 60 °C,
Metal chelate 0.0058 M, Reaction time 5 hr

Exp. No.	Metal chelate	pH[a)] *S*	*E*	Yield of amide (%)
1	$[Cu(en)_2]Cl_2 \cdot 2H_2O$	7.6	8.0	20
2	$Cu(gly)_2 \cdot H_2O$	6.7	7.2	46
3	$[Cu(bipy)(NO_3)_2]3H_2O$	6.1	5.6	32
4	$[Ni(en)(H_2O)_4]SO_4 \cdot H_2O$	6.3	6.7	20
		7.0	7.5	39
5	$[Ni(en)_3]Cl_2 \cdot 2H_2O$	8.0	8.0	14
6	$[Ni(bipy)(H_2O)_4]SO_4 \cdot 2H_2O$	6.3	6.2	16
7	$[Cu(piaH)_2]Cl_2 \cdot 2H_2O$	6.3	6.3	48
8	$[Ni(piaH)_2]Cl_2 \cdot 2H_2O$	6.5	6.6	29
9	$[Co(piaH)_2]Cl_2 \cdot 2H_2O$	6.9	6.8	22
10	*cis*-$[CoCl_2(en)_2]Cl$	6.4	7.9	16
11	$[Co(en)_3]Cl_3$	6.7	6.8	0
12	$[Pt(en)_3]Cl_4$	7.3	6.9	0
13	$CuCl_2 \cdot 2H_2O$	4.8	4.3	29
14	$NiCl_2 \cdot 6H_2O$	6.9	6.1	30

a) pH: S, starting point; E, end point (after 5 hr reaction).

Results and Discussion

Generally, an aqueous solution of 2-pyridinecarbonitrile containing a complex catalyst was kept at 60 °C, and a definite quantity of the reaction mixture was sampled every hour. The samples were submitted to an ion-exchange column (Dowex 50×2, H-form) and developed with water. The eluate was a solution of unreacted pure 2-pyridinecarbonitrile, which was separated completely from the reaction mixture. The decrease in the amount of the starting material was followed spectrophotometrically at 272 nm, and the yield of the reaction product, 2-pyridinecarboxamide, was calculated.

In other experiments, aqueous reaction mixture con-

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[1] K. Sakai, T. Ito, and K. Watanabe, This Bulletin, **40**, 1660 (1967).

[2] P. F. B. Barnard, *J. Chem. Soc., A*, **1969**, 2140.

[3] S. Komiya, S. Suzuki, and K. Watanabe, This Bulletin, **44**, 1140 (1971).

taining 2-pyridinecarbonitrile and catalyst were refluxed and then concentrated to small amounts in order to be extracted with ether. From the ethereal solution, only 2-pyridinecarboxamide was obtained in a high yield. The metal complex catalyst was recovered from the water layer.

The labile complexes of Cu(II), Ni(II), and Co(II) were catalytically active. On the other hand, the inert Co(III) and Pt(IV) complexes were inactive.

The Effect of pH on the Hydration of 2-Pyridinecarbonitrile. The effect of hydroxide ions on the hydration was preliminarily examined without catalysts. The reactions were caused to proceed at 60 °C for 5 hr in the pH range of 2—11, and the reactivity of 2-pyridinecarbonitrile was examined spectrophotometrically as has been described above. No reaction occurred in the 2.5—9 pH range, but it proceeded rapidly above pH 10.

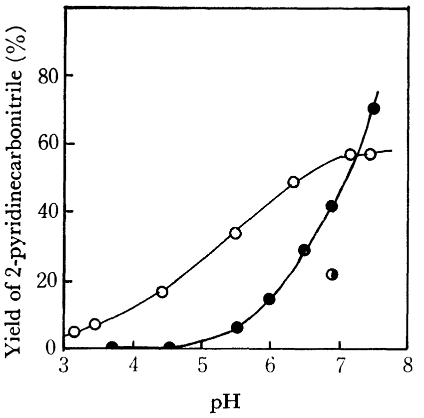

Fig. 1. Effect of pH on the hydration of 2-pyridinecarbonitrile with catalysts.
2-pyridinecarbonitrile: 0.0475 M, metal chelate: 0.00578 M, temp. 60 °C, time 5 hr.
○ $[Cu(piaH)_2]Cl_2 \cdot 2H_2O$, ● $[Ni(piaH)_2]Cl_2 \cdot 2H_2O$, ◑ $[Co(piaH)_2]Cl_2 \cdot 2H_2O$.
In our previous paper,[3] pH 6.0 of $[Ni(piaH)_2]Cl_2 \cdot 2H_2O$ (Fig. 1.) should be corrected to pH 6.5.

All the reactions with the complex catalysts proceeded in the 6—8 pH range. The pH dependence of these chelate-catalyzed reactions are remarkable; *e.g.*, the reactivity of 2-pyridinecarbonitrile was very low in the 9—10 pH range without catalysts, but the reaction with $[Ni(en)_3]Cl_2 \cdot 2H_2O$ was extremely fast in this pH range and the yield of 2-pyridinecarboxamide was about 75% after a 5 hr reaction. On the other hand, the yield decreased to 14% at pH 8 in the same reaction (Table 1). In order to investigate the effect of the pH in detail, solutions of 2-pyridinecarbonitrile and $[Ni(piaH)_2]Cl_2 \cdot 2H_2O$ or $[Cu(piaH)_2]Cl_2 \cdot 2H_2O$ were kept at 60 °C for 5 hr in the 3—7.5 pH range and the reactivities were examined. As is shown in Fig. 1, the reactivity becomes higher with a rise in the pH. Especially, for the nickel(II) complex, no reaction occurred below pH 4.5. The nickel(II) ion showed no catalytic activity at pH 3.9. 2-Pyridinecarbonitrile may not coordinate to the Ni(II) ion below pH 4.5. A solution of 2-pyridinecarbonitrile and nickel(II) chloride (1 : 1 mol) gave the same absorption spectrum as that of nickel(II) chloride at pH 3.8 and at room temperature.

Coordination of 2-Pyridinecarbonitrile. It is conceivable that the labile complexes exchange their ligands with the 2-pyridinecarbonitrile, and that, therefore, the hydration of the nitrile group occurs. The coordination of 2-pyridinecarbonitrile may be due to that of the nitrogen atom of the pyridine ring rather than that of the nitrile group. It is expected that 3- or 4-pyridinecarbonitrile also coordinates with the nitrogen atom of the pyridine ring. The catalytic hydration of the three kinds of pyridinecarbonitrile isomers was examined with $[Ni(en)(H_2O)_4]SO_4 \cdot H_2O$ and $Cu(gly)_2 \cdot H_2O$, but no reaction occurred with the 3- and 4-isomers. Thus, the effect of the coordination of 2-pyridinecarbonitrile is specific. It has been pointed out by Breslow[4] that the nitrile group of 1,10-phenanthroline-2-carbonitrile, although poorly placed for coordination, still has an interaction with the metal ion–Cu(II) or Ni(II)– and undergoes hydration.

Hydration of 2-Pyridinecarbonitrile. The results of the hydration of 2-pyridinecarbonitrile with various metal chelates are given in Table 1. The features of the reactions are not simple. In general, these homogeneous catalytic reactions proceed more rapidly at elevated temperatures. For example, the yield of amide was 22% in Exp. No. 9 (at 60 °C), but it became almost 100% when the reaction mixture was refluxed for three hours. However, no reaction occurred with the inert complex —Exp. Nos. 11—12— even when it was refluxed.

In the case of a metal ion-catalyzed reaction, 2-pyridinecarbonitrile first formed a complex with the metal ion, and then gradually underwent hydration along with a change in the color of the reaction mixture. However, when the initial pH value was about 7 or higher, metal ions afforded precipitates of thier hydroxides in the reaction systems. For this reason, the pH value of the reaction mixture was maintained in the acid region in Exp. No. 13. On the other hand, no hydroxides formed in the reaction with metal complexes, even in a basic solution. Further, metal complexes show different catalytic activities according to the kinds of thier ligands, as is shown in Table 1.

Function of Complex Catalysts. The catalytic functions of the complexes were classified into three types (Type I—III). Free 2-pyridinecarboxamide was obtained with the Type I and Type II complexes. The Type III complex afforded only the mixed complex.

Type I Complexes: The complexes used in Exp. Nos. 1, 2, 5, 7, 8, and 9 (Table 1) belong to Type I. They are recovered without any change after the reactions. Therefore, the complexes of Type I work as ideal catalysts.

Type II Complexes: The complexes used in Exp. Nos. 3, 4, and 6 belong to Type II. A part of their ligands is unidentate, NO_3 or H_2O. With these complexes, the hydration of 2-pyridinecarbonitrile proceeded, but the complexes were changed in composition after the reaction. For example, in the reaction with

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[4] R. Breslow, R. Fairwether, and J. Keana, *J. Amer. Chem. Soc.*, **89**, 2135 (1967).

$[Ni(en)(H_2O)_4]SO_4 \cdot H_2O$, the color of the reaction mixture changed from light blue to violet blue. The complex recovered was a mixture of tris(ethylenediamine)nickel(II) and bis(2-pyridinecarboxamide)nickel(II).

Type III Complex: In Exp. No. 10 (Table 1), the catalytic behavior of *cis*-$[CoCl_2(en)_2]Cl$ was different from that of the labile complexes. The amount of reacted 2-pyridinecarbonitrile was 16% after 5 hr, but it was 18% even after a 15 hr reaction. After the reaction, an orange complex was obtained as the main product, and it had almost no catalytic activity.

Experimental

Materials. The 2- and 4-pyridinecarbonitriles (Tokyo Kasei Co., Ltd, Tokyo) were recrystallized from ether (mp 28.5—29.5 °C and 78—79 °C respectively). The 3-pyridinecarbonitrile (Aldrich Chemical Co., Inc.) was used without further purification (mp 49—50 °C). The $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ were extra-pure chemicals (Wako Junyaku, Tokyo). $[Cu(piaH)_2]Cl_2 \cdot 2H_2O$,[5] $[Ni(piaH)_2]Cl_2 \cdot 2H_2O$,[5] $[Co(piaH)_2]Cl_2 \cdot 2H_2O$,[5] $Cu(gly)_2 \cdot H_2O$, $[Cu(en)_2]Cl_2 \cdot 2H_2O$, $[Ni(en)(H_2O)_4]SO_4 \cdot H_2O$, $[Ni(en)_3]Cl_2 \cdot 2H_2O$, $[Co(en)_3]Cl_3$, *cis*-$[CoCl_2(en)_2]Cl$, $[Pt(en)_3]Cl_4$, $[Cu(NO_3)_2(bipy)]3H_2O$, and $[Ni(bipy)(H_2O)_4]SO_4 \cdot 2H_2O$ were all prepared and recrystallized several times (piaH: 2-pyridinecarboxamide, en: ethylenediamine, bipy: 2,2′-bipyridine, gly: glycine ion).

Blank Test. In a 25 ml volumetric flask, were placed 10 ml of a 2-pyridinecarbonitrile solution (0.119 M) and 10 ml of a buffer (pH 1—4: 0.1 M gly—0.1 M NaCl—0.1 M HCl, pH 4—7: 0.2 N CH_3COOH—0.2 N CH_3COONa, pH 7—12: 0.1 M gly—0.1 M NaCl—0.1 M NaOH): the content was then made up to 25 ml with distilled water. Ten ml of the solution was placed in a sealed glass tube and kept at 60 °C for 5 hr. The content was charged on a column of ion-exchange resin (Dowex 50×2, H-form) and developed with water. By this elution, only the unreacted 2-pyridinecarbonitrile was obtained. This solution was then diluted to a definite quantity and analyzed spectrophotometrically ($\lambda_{max}=272$ nm).

The VIS–UV absorption spectra were obtained with a Hitachi Recording Spectrophotometer EPS-3T.

Hydration of 2-Pyridinecarbonitrile with Metal Chelates or Ions. In a sealed glass tube, were placed 10 ml of a solution containing 2-pyridinecarbonitrile (0.0475 M) and the metal chelate or ion (0.0058 M). The mixture was adjusted to the pH range of 6.0—8.0 with small amounts of 0.1 N HCl or 0.1 N KOH solution, and was then kept at 60 °C for 5hr. After the reaction, an aliquot quantity of the reaction mixture was charged on a column of the cation exchange resin (column: diameter 1 cm, length 3 cm) and developed with water. Thus, unreacted 2-pyridinecarbonitrile was separated completely from the reaction mixture. The decrease in the amount of the starting material was followed spectrophotometrically at 272 nm, and the yield of the reaction product, 2-pyridinecarboxamide, was calculated. The only reaction product was 2-pyridinecarboxamide. Yield (%)=100−unreacted 2-pyridinecarbonitrile (%).

Hydration of 2-Pyridinecarbonitrile with Chelates under Reflux. Thirty ml of a solution containing 2-pyridinecarbonitrile (0.160 M) and chelate (0.02 M) was refluxed for 5 hr. Then, the reaction mixture was concentrated and extracted with ether several times. From the ethereal solution, the reaction product, pure 2-pyridinecarboxamide (white crystals) were obtained in the free form (about a 100% yield; mp 105 °C). No other reaction products were found. From the mother liquor, only the chelate was obtained.

Hydration of 3- and 4-Pyridinecarbonitriles with Metal Chelates. The reaction conditions were the same as in the case with 2-pyridinecarbonitrile. After the reaction, the content was charged on a column of ion-exchange resin (Dowex 50×2, H-form) and developed with a 5.5% ammonia solution. Then, the eluate was analyzed spectrophotometrically; no change of absorbance was observed (3-isomer, 265 nm; 4-isomer, 276 nm). Therefore, it was concluded that no reaction occurred with the two isomers.

In the other reaction, 60 ml of a solution containing 4-pyridinecarbonitrile (0.158 M) and $[Cu(en)_2]Cl \cdot 2H_2O$ (or $Cu(gly)_2 \cdot H_2O$) (0.019 M) was kept at 65 °C for 6 hr. After the reaction mixture has been extracted with ether several times, only the starting material was obtained from the ethereal solution. No 4-pyridinecarboxamide was found at all.

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[5] M. Sekizaki and K. Yamasaki, *Nippon Kagaku Zasshi*, **87**, 1053 (1966).