SHORT COMMUNICATIONS

Hydration of 2-Cyanopyridine with Metal Chelates

Sigeo Komiya, Shinnichiro Suzuki, and Ken-ichi Watanabe
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received January 9, 1971)

It has been reported[1,2] that 2-cyanopyridine is hydrated with nickel(II) chloride or copper(II) chloride to afford the metal chelates of 2-pyridinecarboxamide. On the other hand, 2-cyanopyridine is hydrated into 2-pyridinecarboxamide by the catalytic action of metal chelates, *viz*. nickel(II) or copper(II) chealtes of picolinic acid and its amide.[1]

In this paper, we report that some other ordinary metal chelates are also effective for the hydration of 2-cyanopyridine to give only 2-pyridinecarboxamide. The metal chelates used as catalysts were $[Ni(en)_3]Cl_2\cdot 2H_2O$, $[Cu(en)_2]Cl_2\cdot 2H_2O$, $[Co(en)_3]Cl_2$, $Ni(piaH)_2Cl_2\cdot 2H_2O$, and $Co(piaH)_2Cl_2\cdot 2H_2O$ (en: ethylenediamine, piaH: 2-pyridinecarboxamide).

As a preliminary test, the hydration of 2-cyanopyridine was carried out without catalysts (60°C, 5 hr). It was found that no hydration took place in the pH range 5.5—8.5. Thus, the aqueous solution of 2-cyanopyridine (0.0471 M) containing each metal chelate (0.0058 M) was kept at 60°C in the pH range 5.5—8.5, and then a definite quantity of the reaction mixture was sampled every hour. The samples were charged into ion exchange column (Dowex 50 H-Type$\times$2) and developed with water. Thus, 2-cyanopyridine unreacted was separated completely from the reaction mixture. Then the decrease in amount of the starting material was followed spectrophotometrically at 272 mμ, and the yield of reaction product, 2-pyridnecarboxamide, was calculated.

It was confirmed that the reaction product was only the 2-pyridinecarboxamide and the chelates used for the reaction were recovered without any change. The results are given in Fig. 1. The chelates of copper(II), nickel(II), and cobalt(II) have a catalytic activity, but not cobalt(III) chelate.

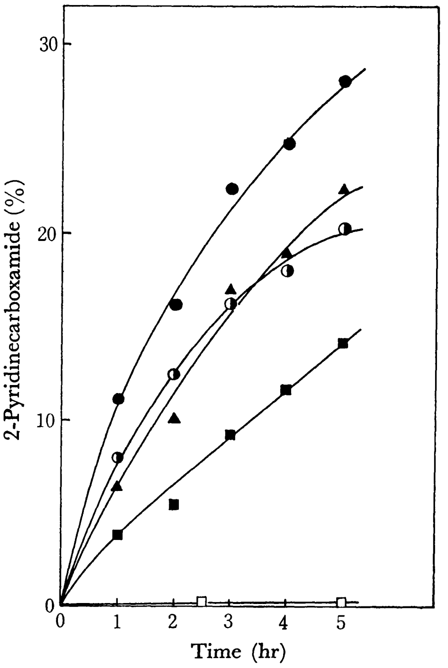

Fig. 1. Hydration of 2-cyanopyridine in the presence of metal chelates.
0.0471 M 2-cyanopyridine, 0.00578 M metal chelate, at 60°C.
■ $[Ni(en)_3]Cl_2\cdot 2H_2O$ (pH 8.0)
◑ $[Cu(en)_2Cl_2\cdot 2H_2O$ (pH 7.0—8.0)
● $Ni(piaH)_2Cl_2\cdot 2H_2O$ (pH 6.0)
▲ $Co(piaH)_2Cl_2\cdot 2H_2O$ (pH 6.9—6.8)
□ $[Co(en)_3]Cl_3$ (pH 6.9)
2-Pyridinecarboxamide (%)=
100−2-Cyanopyridine (%) (unreacted)

It is known that the former are labile complexes and the latter is an inert complex. Such characters of chelates were in accord with catalytic activity of the hydration. It is assumed that the hydration proceeds through the combination of the ligand exchange and the reaction of coordinated ligands.

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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.