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The Catalytic Effect of Metal Ions on the Hydrolysis of Disodium Pyrophosphite

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It is well known that hydrolytic scissions of polyphosphate, the splitting of the $\overset{5}{\mathrm{P}}\text{–O–}\overset{5}{\mathrm{P}}$ linkage, and those of pyrophosphite, the splitting of the $\overset{3}{\mathrm{P}}\text{–O–}\overset{3}{\mathrm{P}}$ linkage, are strongly catalyzed by the hydrogen ion. Recently, Mesmer and Carroll[1] have studied in detail the kinetics and mechanism of the hydrolysis of pyrophosphite over an extensive pH range. The effect of metal ions on the acid hydrolysis of pyrophosphate has also been studied.[2] The present paper will deal with the effects of various metal ions on the rate of the hydrolysis of disodium pyrophosphite at pH 4.6.

The disodium pyrophosphite used in this work was prepared by heating purified monosodium orthophosphite under reduced pressure, and the product contained as much as 68% of disodium pyrophosphite when determined by iodine titration. This analysis is based upon the fact that the reaction of iodine with phosphite in a neutral solution occurs very rapidly, whereas the reaction with pyrophosphite is very slow under the same conditions.

The pH of a 0.03 M disodium pyrophosphite solution containing the metal ion added as the chloride was quickly adjusted to 4.6 with hydrochloric acid at 60°C. The flasks, each containing 20 m*l* of this solution, were transferred to a bath regulated at 60±0.1°C. After selected periods of time, these flasks were rapidly cooled to 0°C, and the solutions were neutralized with sodium hydrogen carbonate. An appropriate amount of the disodium salt of ethylenediaminetetraacetic acid to mask the metal ions was added to the solutions, and then 30 m*l* of a standardized iodine solution (0.1 N) were added. The flasks were subsequently allowed to stand for 15 min in the dark. These solutions were titrated with a standardized sodium thiosulfate solution (0.1 N) to the starch end point after being acidified with an acetic acid solution. The pH of the solutions could be maintained approximately at a constant value of 4.6 throughout each run, inasmuch as monosodium orthophosphite gives the pH value of 4.6.

Plots of the logarithm of the pyrophosphite concentration against the time are shown in Fig. 1, in which the linear relation indicates that the hydrolysis is to be regarded as of the first order. The addition of the copper (II) ion resulted especially in an increase in the rate constant, and the magnitude of this effect increased with an increase in the concentration.

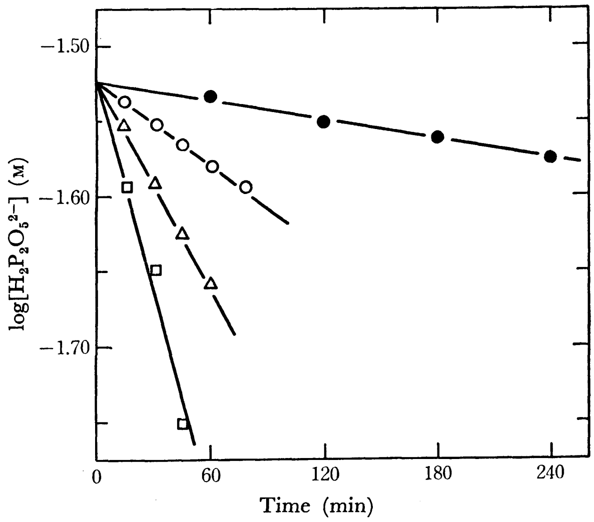

Fig. 1. Effect of concentration of copper(II) ion at pH 4.6 and 60°C. ● None added; ○ 0.5×10^{-3} M; △ 1.0×10^{-3} M; □ 2.0×10^{-3} M

The first-order rate constants, *K*, obtained with various metal ions are summarized in Table 1. The rates of hydrolysis in the presence of all the metal ions except the copper(II) ion were approximately equal to that in the absence of any metal ion, and were nearly independent of the metal-ion concentration.

Since the cleavage of the P–O–P linkage has generally been considered to be accelerated by the attack of hydrogen ion on the bridging oxygen atom, metal ions are also presumed to behave similarly. In this work, metal ions seem to act on the $\overset{3}{\mathrm{P}}\text{–O–}\overset{3}{\mathrm{P}}$ linkage in competition with the hydrogen ion and the sodium ion of disodium pyrophosphite. The behavior of the $\overset{3}{\mathrm{P}}\text{–O–}\overset{3}{\mathrm{P}}$ linkage towards the metal ion differs distinctly

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[1] R. E. Mesmer and R. L. Carroll, *J. Amer. Chem. Soc.*, **88**, 1381 (1966).

[2] J. M. Rainey, M. M. Jones, and W. L. Lockhart, *J. Inorg. Nucl. Chem.*, **26**, 1415 (1964).

Table 1. First-order rate constants of hydrolysis in the presence of metal ions at pH of 4.6

Metal ions	Concn. (10^{-3}M)	$K\times 10^4$ (min^{-1})	Metal ions	Concn. (10^{-3}M)	$K\times 10^4$ (min^{-1})
Li^+	2	7.8	Cd^{2+}	2	7.3
K^+	2	6.5	Cd^{2+}	4	9.2
Ba^{2+}	2	7.6	Co^{2+}	2	6.8
Sr^{2+}	2	7.2	Co^{2+}	4	6.8
Ca^{2+}	2	7.7	Ni^{2+}	2	8.6
Na^+	20	7.0	Ni^{2+}	4	8.5
Mg^{2+}	2	7.0	Cu^{2+}	0.5	22
Mg^{2+}	4	6.9	Cu^{2+}	1	55
Mn^{2+}	2	6.5	Cu^{2+}	2	110
Mn^{2+}	8	9.4	None added (pH 5.9)		2.2
Zn^{2+}	2	12	None added (pH 4.6)		7.4
Zn^{2+}	4	17	None added (pH 4.3)		11

Initial concentration of $Na_2H_2P_2O_5$: 3×10^{-2}M.

from that of the $\overset{5}{\text{P}}\text{–O–}\overset{5}{\text{P}}$ linkage because of the lower oxidation states of phosphorus. Unlike pyrophosphate, pyrophosphite has hardly ever been reported to form metal-ion complexes.[3] Complex-ion formation causes the half-wave potential of a metal to shift to a more negative value in a polarographic study. A polarographic experiment was attempted for these reaction systems under the following conditions: mole ratio of pyrophosphite/metal ion, 3.6; metal-ion concentration, 0.001 mol/*l*; tetramethylammonium-bromide concentration, 0.1 mol/*l*; pH, 4.6; temperature, 30°C. However, the shifts of the half-wave potentials were hardly observed in any case.

The strength of the affinity between the pyrophosphite ion and the metal ions is assumed to depend upon their electrode potentials. Since all the experiments with regard to the metal-ion effects were carried out at pH 4.6, the copper(II) ion, which is more noble than the hydrogen ion, appears to have promoted the hydrolysis. On the other hand, the other metal ions, less noble than the hydrogen ion, have negligibly affected the rate. Although a silver ion or mercury(II) ion, being more noble than copper(II) ion, seems to promote strongly the rate of hydrolysis, the rate constants cannot be obtained because of the oxidation reduction between these ions and pyrophosphite.

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[3] D. Grant and D.S. Payne, *J. Inorg. Nucl. Chem.*, **26**, 1985 (1964).