The Hydrolysis of Pyridylmethyl Phosphates and the Catalysis of Metal Ions*[1]

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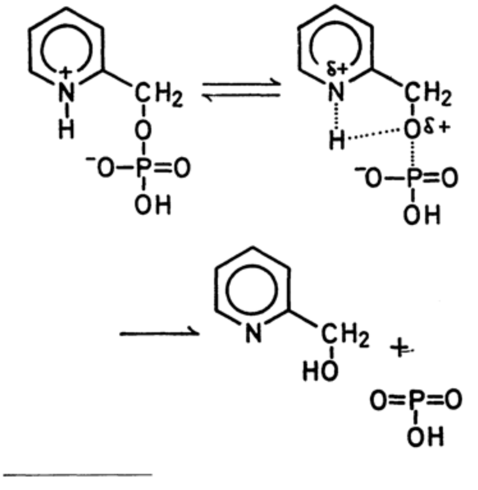
In this communication, the spontaneous hydrolysis of 2-, 3- and 4-pyridylmethyl phosphate (PMP, H_2A) and the effect of various metal ions on the hydrolysis reaction are described in brief.

The spontaneous hydrolysis of these phosphates follows the apparent first-order kinetics, and the pH-rate curves demonstrate rate maxima at pH 2.5 and shoulders around pH 6. Analysis of the kinetic data reveals that the reactive species are the neutral form (H_2A) and the monoanionic (HA^-) for each phosphate, where the former has a zwitter-ionic structure with a protonated pyridine ring. For all the three phosphates, the neutral species was found to be more reactive than the monoanionic as seen in Table 1. A large reactivity of the neutral species of 2-PMP may be attributed to the favorable intramolecular proton transfer process indicated by Eq. (1) which is not available for the 3- and 4-isomers.

TABLE 1. FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF PYRIDYLMETHYL PHOSPHATES
$90.0\pm0.1°C$, $\mu=0.10$

Phosphate	k_{H_2A} (hr^{-1})	k_{HA}(hr^{-1})
2-PMP	0.0840	0.0149
3-PMP	0.0349	0.0155
4-PMP	0.0355	0.0171



(1)

As to the effect of bivalent (alkaline earth and first transition) metal ions, there was practically no influence on the hydrolysis rate with the exception of the copper ion. Copper(II) accelerates the hydrolysis of 2-PMP much significantly as pH rises; *e. g.*, 15 times as fast as the spontaneous hydrolysis at pH 4.81 and 90°C with $\mu=0.10$, 2.85 times at pH 4.06, and 1.16 times at pH 3.43. Meanwhile, previous studies of the present authors provide the following facts: 1) copper(II) forms the most stable complexes with 2-pyridylmethanol among various bivalent metal ions with deprotonation of the hydroxyl group of the ligand(1); 2) copper(II) complexes with 2-PMP with highest stability among various metal ions, where both the pyridyl nitrogen and the phosphate group of the ligand participate in coordinate bond formation.(2) These experimental evidences seem to allow one to propose the reaction mechanism for the copper-promoted hydrolysis of 2-PMP, where the copper ion takes the place of intramolecularly transferable proton in spontaneous hydrolysis (Eq. (1)).

Polyvalent metal ions such as ferric(III) and aluminum(III) retarded the hydrolysis rate of all the pyridylmethyl phosphates, while thorium(IV) ion exceedingly promoted the hydrolysis rate at 90°C. The mechanism of the thorium catalysis seems not to resemble that of the copper. Detailed information of these studies will be given in the forthcoming paper.

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1) Y. Murakami and M. Takagi, This Bulletin, **38**, 828 (1965).

2) Y. Murakami and M. Takagi, *J. Phys. Chem.*, in press.