SHORT COMMUNICATIONS

The Selective Hydrolysis of Pentaphosphate by Copper Chelate Catalysts*

By Yoshiki MORIGUCHI and Masaji MIURA

(Received December 26, 1964)

Although several studies of the hydrolytic degradation of substances using chelates as the catalyst have recently been made,[1] these have dealt almost exclusively with kinetic problems; little attention has been paid to the selective action of the chelates. We have, therefore, attempted to study the selective hydrolysis of polyphosphates by chelate catalysts and have obtained some interesting results on the hydrolysis of pentaphosphate.

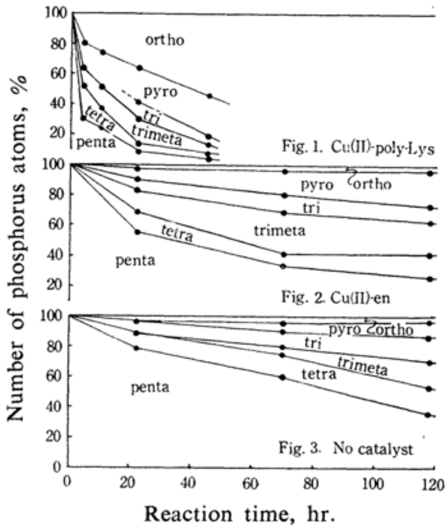


Fig. 1. Cu(II)-poly-Lys

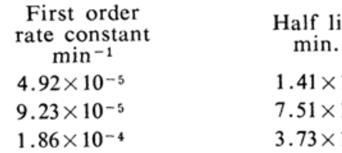
Fig. 2. Cu(II)-en

Fig. 3. No catalyst

Hydrolytic degradation of pentaphosphate in the presence of copper chelate catalysts at 45°C and pH 8.

Pentaphosphate was prepared by the method which has been reported previously.[2] The decomposition products were identified and determined quantitatively by ion-exchange chromatography, using ^{32}P as a tracer.[3]

As may be seen in Table I, the chelates used remarkably accelerate the decomposition rate of pentaphosphate. The main decomposition product is orthophosphate in the presence of copper(II)-polylysine (Fig. 1), while the product is trimetaphosphate in the presence of copper(II)-ethylenediamine (Fig.



$$HO-\overset{O}{\underset{O^-}{P}}-O-\overset{O}{\underset{O^-}{P}}-O-\overset{O}{\underset{O^-}{P}}-O-\overset{O}{\underset{O^-}{P}}-O-\overset{O}{\underset{O^-}{P}}-OH$$

Fig. 4

TABLE I. DATA ON THE HYDROLYTIC DEGRADATION OF PENTAPHOSPHATE BY COPPER CHELATE CATALYSTS AT 45°C AND pH 8

Metal (M)	Ligand (L)	M/P_5*1 mol. ratio	L/P_5 mol. ratio	First order rate constant min^{-1}	Half life min.
—	—	0	0	4.92×10^{-5}	1.41×10^{4}
Cu	—	1	0	9.23×10^{-5}	7.51×10^{3}
Cu	en*2	1	1	1.86×10^{-4}	3.73×10^{3}
—	Poly-Lys*3	0	5×10^{-3}	1.37×10^{-4}	5.06×10^{3}
Cu	Poly-Lys*4	1	5×10^{-3}	1.83×10^{-3}	3.79×10^{2}

*1 P_5: pentaphosphate
*2 Ethylenediamine
*3 Poly-L-lysine (M. W.: 85000)
*4 L/M ratio corresponds to two repeat units per copper.

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* Presented at the Annual Japanese Meeting on Coordination Chemistry, Fukuoka, November, 1964.

[1] E. g., R. Hofstetter and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 4461 (1959).

[2] M. Miura and Y. Moriguchi, This Bulletin, **37**, 1522 (1964).

[3] S. Otani, M. Miura and T. Doi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 593 (1963).

2). These results lead us to the conclusion that these two kinds of chelates act in different ways in the hydrolytic degradation of pentaphosphate; that is, the former accelerates the terminal chain attack (Fig. 4a), whereas the latter promotes the intermediate chain attack (Fig. 4b).

Similar studies of various polyphosphates and chelates are in progress.

Department of Chemistry
Faculty of Science
Hiroshima University
Higashisenda, Hiroshima