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The Mechanism of the Hydrolysis of Polyphosphates. V.[1)]
The Effect of Cations on the Hydrolysis of Pyro- and Triphosphates

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The effect of cations on the rate of hydrolysis of pyro- and triphosphates was studied by adding metal chloride to aqueous solutions of the phosphates. The concentrations of the phosphates and metal chlorides were 0.025 and 0.1 mol dm^{-3} respectively. Alkali metal, alkaline earth metal, aluminium, and some transition-metal (Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)) cations retarded the hydrolysis of the phosphates in acidic media. The following sequence of efficiency resulted:

trivalent > bivalent > univalent.

The efficiency of elements within one group of the periodic table decreased from top to bottom. On the other hand, in alkaline solutions, alkali metal cations accelerated the hydrolysis of the phosphates and the catalytic effectiveness decreased with an increase in the ionic radius.

Though many papers have been reported about the hydrolysis of polyphosphates, there have been few studies concerning the effect of cations except for hydrogen and oxonium ions. Many workers have discussed the rate order, the pH dependence, and the reaction process of the hydrolysis of polyphosphates, but no explanation of the reaction mechanism from the point of view of the interaction between a water molecule and a phosphate ion has ever been made. One of the present authors (M. W.) discussed the reaction mechanism of the hydrolysis of polyphosphates from this point of view by using aqueous organic solvents; he pointed out that the rate of the hydrolysis of chain and small-ring phosphates is seriously affected by the nucleophilicity of water molecules and that the hydrolysis is of an S_N2 type.[1–4)] Thilo and Wieker reported the catalytic efficiencies of cations on the hydrolysis of high polyphosphates at pH 8 and obtained the following sequence of efficiency:

$Al^{3+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > H^+ > Li^+ > Na^+ > K^+$.[5–7)]

In this paper, the effects of alkali metal, alkaline earth metal, aluminium, and some transition metal cations of the hydrolysis of pyro- and triphosphates will be discussed.

Experimental

Materials and Procedure. The materials used other than triphosphate were of a commercial grade. The sodium triphosphate was made by the method described in Ref. 8. The concentration of sodium pyro- or triphosphate was controlled to be 0.025 mol dm^{-3} because that concentration was suitable for analysis. Metal chloride was added to the phosphate solution to make it 0.1 mol dm^{-3}. The metal chlorides used were LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $AlCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$. The pH of the solution was controlled with hydrochloric acid and/or aqueous tetramethylammonium hydroxide, with the aid of a Hitachi-Horiba pH meter, F-7, at a given reaction temperature. The separation and determination of the phosphate species in the sample solution were carried out by the method described in our previous paper.[2)] The phosphates in the solution containing aluminium ions were not separated well by one-dimensional paper chromatography, so only the measurement of the hydrolysis of pyrophosphate to orthophosphate was done by means of the molybdenum-blue method. When any precipitate was formed during the experiment, no further treatment was made. Pyro- and triphosphate solutions free from sodium ions were prepared by passing the phosphate solutions mentioned above through cation-exchange resin in the H$^+$ form. The same treatment as in the case of sodium pyro- and triphosphate solutions was done for the phosphate solutions thus prepared in order to test the effect of coexisting sodium ions; the effect of alkali metal cations on the rate of the hydrolysis of triphosphate in basic media was also studied by using the triphosphate solution, but the effect of cations on the hydrolysis of pyrophosphate could not be studied because the rate of the hydrolysis of pyrophosphate was too slow to measure in basic media.

Results and Discussion

The Effect of Cations. The rate of the hydrolysis of pyro- and triphosphates obeyed first-order kinetics with respect to the concentration of the respective phosphates under all the conditions studied. As Tables 1 and 2 show, in every reaction system the rate of the hydrolysis of either phosphate decreased with an increase in the pH value of the solutions. These results agree well with those of previous studies.[1,2,9)] The hydrolysis of pyro- and triphosphates was retarded by the addition of the alkali metal ions in the pH ranges smaller than 7.0 and by the addition of other metal ions in the pH ranges smaller than 3.0. The rate of the hydrolysis of pyrophosphate in the system containing aluminium ions, measured at pH 0.9, was smaller than those of other systems measured at pH 1.0. As has been mentioned above, the hydrolysis of pyrophosphate is an acid-catalyzed reaction. Therefore, the retardation efficiency of aluminium ions is the largest among the cations tested here. According to the results, the following order of the retardation efficiency of metal ions on the rate of hydrolysis of short-chain polyphosphates resulted at pH 1.0:

$Mg^{2+} > Ca^{2+}$
typical element
$Al^{3+} > Mn^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Li^+ > Na^+ > K^+$.
transition element
(trivalent) (bivalent) (univalent)

Similar retardation effects were observed for alkali metal, alkaline earth metal, manganese(II), cobalt(II), and nickel(II) ions at pH 2.0 or at higher pH regions than that. However, the order of efficiency of man-

Table 1. Rate constants/min^{-1} of the hydrolysis of pyrophosphate

Phosphate	Added cation	pH	Reaction temp/°C 35	50	70
$Na_4P_2O_7$	—	1.0	1.44 10^{-4}	7.40 10^{-4}	4.73 10^{-3}
		2.0	1.52 10^{-5}	1.30 10^{-4}	1.55 10^{-3}
		3.0	6.40 10^{-6}	4.92 10^{-5}	6.95 10^{-4}
		5.0	5.32 10^{-6}	4.64 10^{-5}	6.03 10^{-4}
	Li^+	1.0	1.18 10^{-4}	6.78 10^{-4}	4.31 10^{-3}
		2.0	1.28 10^{-5}	1.02 10^{-4}	1.35 10^{-3}
		3.0	5.86 10^{-6}	4.43 10^{-5}	6.40 10^{-4}
		5.0	4.29 10^{-6}	3.52 10^{-5}	4.93 10^{-4}
	Na^+	1.0	1.25 10^{-4}	6.91 10^{-4}	4.53 10^{-3}
		2.0	1.40 10^{-5}	1.19 10^{-4}	1.49 10^{-3}
		3.0	6.38 10^{-6}	4.75 10^{-5}	7.03 10^{-4}
		5.0	4.93 10^{-6}	4.04 10^{-5}	5.49 10^{-4}
	K^+	1.0	1.40 10^{-4}	7.47 10^{-4}	4.58 10^{-3}
		2.0	1.48 10^{-5}	1.24 10^{-4}	1.51 10^{-3}
		3.0	6.86 10^{-6}	4.89 10^{-5}	7.18 10^{-4}
		5.0	5.04 10^{-6}	4.16 10^{-5}	5.86 10^{-4}
	Mg^{2+}	1.0	7.32 10^{-5}	3.48 10^{-4}	3.27 10^{-3}
		2.0	6.67 10^{-6}	5.31 10^{-5}	6.33 10^{-4}
	Ca^{2+}	1.0	7.46 10^{-5}	3.62 10^{-4}	3.54 10^{-3}
		2.0	9.70 10^{-6}	8.21 10^{-5}	1.12 10^{-3}
	Mn^{2+}	1.0	4.50 10^{-5}	2.41 10^{-4}	2.09 10^{-3}
	Co^{2+}	1.0	7.33 10^{-5}	3.53 10^{-4}	2.89 10^{-3}
	Ni^{2+}	1.0	7.73 10^{-5}	3.78 10^{-4}	3.31 10^{-3}
		2.0	8.34 10^{-6}	6.03 10^{-5}	8.30 10^{-4}
	Zn^{2+}	1.0	6.47 10^{-5}	3.06 10^{-4}	2.72 10^{-3}
	Al^{3+}	0.9	3.02 10^{-5}	1.92 10^{-4}	1.36 10^{-3}
$H_4P_2O_7$	—	1.0	1.61 10^{-4}	8.39 10^{-4}	5.01 10^{-3}
		2.0	1.91 10^{-5}	1.50 10^{-4}	1.61 10^{-3}
		3.0	7.79 10^{-6}	5.56 10^{-5}	7.88 10^{-4}
		5.0	5.83 10^{-6}	4.87 10^{-5}	6.44 10^{-4}
		7.0		8.22 10^{-6}	1.05 10^{-4}
	Li^+	3.0		4.95 10^{-5}	7.21 10^{-4}
		5.0		3.83 10^{-5}	4.96 10^{-4}
		7.0		5.97 10^{-6}	8.03 10^{-5}

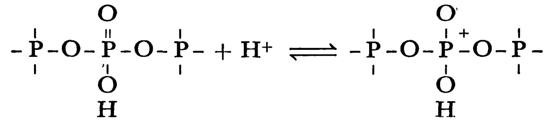
Table 2. Rate constants/min^{-1} of the hydrolysis of triphosphate

Phosphate	Added cation	pH	Reaction temp/°C 35	50	70
$Na_5P_3O_{10}$	—	1.0	1.06 10^{-3}	5.38 10^{-3}	2.94 10^{-2}
		2.0	1.36 10^{-4}	8.29 10^{-4}	6.10 10^{-3}
		3.0	2.51 10^{-5}	1.73 10^{-4}	1.87 10^{-3}
	Li^+	1.0	8.43 10^{-4}	3.02 10^{-3}	2.78 10^{-2}
		2.0	8.04 10^{-5}	6.91 10^{-4}	5.28 10^{-3}
		3.0	2.22 10^{-5}	1.48 10^{-4}	1.68 10^{-3}
	Na^+	1.0	9.76 10^{-4}	3.49 10^{-3}	2.80 10^{-2}
		2.0	8.90 10^{-5}	7.12 10^{-4}	5.61 10^{-3}
		3.0	2.30 10^{-5}	1.68 10^{-4}	1.85 10^{-3}
	K^+	1.0	1.05 10^{-3}	3.52 10^{-3}	2.93 10^{-2}
		2.0	9.59 10^{-5}	7.33 10^{-4}	5.79 10^{-3}
		3.0	2.44 10^{-5}	1.80 10^{-4}	1.96 10^{-3}
	Mg^{2+}	1.0	3.23 10^{-4}	1.32 10^{-3}	9.16 10^{-3}
		2.0	2.66 10^{-5}	1.70 10^{-4}	1.66 10^{-3}
		3.0	1.16 10^{-5}	8.01 10^{-5}	9.06 10^{-4}
	Ca^{2+}	1.0	3.49 10^{-4}	1.54 10^{-3}	1.04 10^{-2}
		2.0	5.11 10^{-5}	4.07 10^{-4}	3.91 10^{-3}
	Mn^{2+}	1.0	1.64 10^{-4}	6.28 10^{-4}	5.95 10^{-3}
		2.0	2.36 10^{-5}	1.72 10^{-4}	1.82 10^{-3}
	Co^{2+}	1.0	2.70 10^{-4}	9.80 10^{-4}	7.65 10^{-3}
		2.0	2.35 10^{-5}	1.59 10^{-4}	1.56 10^{-3}
	Ni^{2+}	1.0	3.04 10^{-4}	1.36 10^{-3}	9.05 10^{-3}
		2.0	2.86 10^{-5}	1.75 10^{-4}	1.63 10^{-3}
		3.0	1.27 10^{-5}	9.88 10^{-5}	1.10 10^{-3}
	Cu^{2+}	1.0	2.40 10^{-4}	9.25 10^{-4}	7.38 10^{-3}
	Zn^{2+}	1.0	2.46 10^{-4}	9.72 10^{-4}	7.40 10^{-3}
$H_5P_3O_{10}$	—	1.0	1.29 10^{-3}	6.34 10^{-3}	3.57 10^{-2}
		2.0	1.95 10^{-4}	9.47 10^{-4}	8.03 10^{-3}
		3.0	2.80 10^{-5}	1.93 10^{-4}	2.08 10^{-3}
		5.0		9.53 10^{-5}	1.03 10^{-3}
		7.0		1.39 10^{-5}	2.30 10^{-4}
		10.0		6.33 10^{-7}	
		11.5		5.42 10^{-7}	
	Li^+	3.0		1.51 10^{-4}	1.74 10^{-3}
		5.0		8.20 10^{-5}	9.15 10^{-4}
		7.0		1.13 10^{-5}	1.72 10^{-4}
		10.0		5.17 10^{-6}	
		11.5		4.69 10^{-6}	
	Na^+	3.0		1.87 10^{-4}	1.54 10^{-3}
		5.0		1.02 10^{-4}	1.21 10^{-3}
		7.0		1.57 10^{-5}	2.31 10^{-4}
		10.0		1.71 10^{-6}	
		11.5		1.61 10^{-6}	
	K^+	3.0		2.06 10^{-4}	1.83 10^{-3}
		5.0		1.07 10^{-4}	1.25 10^{-3}
		7.0		1.82 10^{-5}	2.32 10^{-4}
		10.0		1.19 10^{-6}	
		11.5		1.13 10^{-6}	

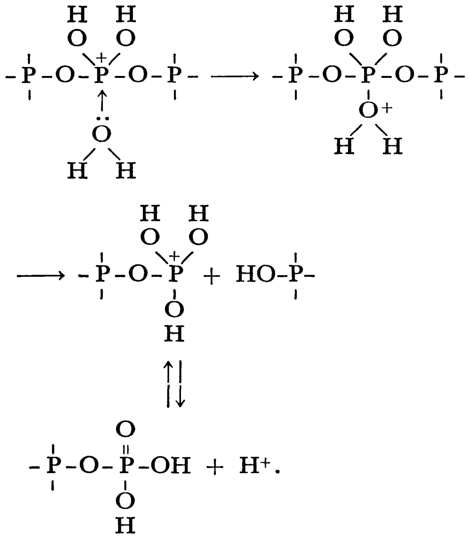
ganese(II) ions for the hydrolysis of triphosphate at pH 2.0 is not the same as that at pH 1.0. As is also shown in Tables 1 and 2, the rate of the hydrolysis of pyro- and triphosphates is larger than that of the respective sodium phosphates, and a similar retardation effect of lithium ions is observed in the pH regions smaller than 7.0. On the other hand, the rate of the hydrolysis of triphosphate was remarkably accelerated by the addition of alkali metal ions at pH 10.0 and 11.5. The order of the acceleration efficiency of alkali metal ions is as follows:

$$Li^+ > Na^+ > K^+.$$

Reaction Mechanism. The activation parameters for the hydrolysis of pyro- and triphosphates were calculated by means of the Arrhenius plot; they are listed in Tables 3 and 4 respectively. In any reaction system, the activation energy and the frequency factor increase with an increase in the pH value. This indicates that the catalytic action of H+ affects exclusively the energy term of the hydrolysis of short-chain polyphosphates. In our previous papers,[2,4] we proposed the following hydrolysis mechanism for pyro- and triphosphates and concluded that Reaction (2) is the rate-determining step:



$$-\overset{|}{\underset{|}{\mathrm{P}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{H}}{\overset{|}{\mathrm{O}}}}{\mathrm{P}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{P}}}- + \mathrm{H}^+ \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{P}}}-\mathrm{O}-\overset{\overset{\mathrm{H}}{\overset{\mathrm{O}}{|}}}{\underset{\underset{\mathrm{H}}{\overset{|}{\mathrm{O}}}}{\mathrm{P}^+}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{P}}}- \qquad (1)$$



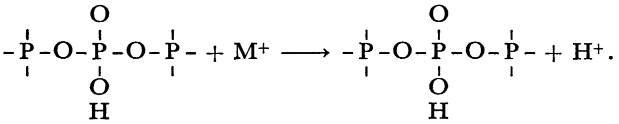
$$-\overset{|}{\underset{|}{P}}-O-\underset{\underset{\overset{\cdot\cdot}{\underset{H\ \ H}{O}}}{\uparrow}}{\overset{\overset{H\ \ H}{O\ \ O}}{\overset{\backslash+/}{P}}}-O-\overset{|}{\underset{|}{P}}- \longrightarrow -\overset{|}{\underset{|}{P}}-O-\underset{\underset{\underset{H\ \ H}{O^{+}}}{|}}{\overset{\overset{H\ \ H}{O\ \ O}}{\overset{\backslash\ /}{P}}}-O-\overset{|}{\underset{|}{P}}- \qquad (2)$$

$$\longrightarrow -\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{H\ \ H}{O\ \ O}}{\overset{\backslash+/}{P}}} + HO-\overset{|}{\underset{|}{P}}- \qquad (3)$$

$$\uparrow\downarrow$$

$$-\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{O}{\|}}{P}}-OH + H^{+}. \qquad (4)$$

The present kinetic measurements have shown that the retardation efficiency within one group of the periodic table decreases from top to bottom, that is, with an increase in the ionic radius, and increases with an increase in the charge of the cation. Since the reaction rate is retarded and the activation energy increases upon the addition of a metal cation in any reaction system, it could be considered that the elementary reactions (1) and (2) are affected by metal ions. Therefore, the retardation of the degradation reaction by metal ions in acidic solutions may be explained by the exchange of protons by the catalytically less effective metal ions. The ion-exchange efficiency of a cation increases with an increase in the charge. This fact well explains the order of the retardation efficiency of metal cations for the hydrolysis of pyro- and triphosphates. In one group of the periodic system, the ion-exchange efficiency of a cation decreases with a decrease in the ionic radius because of strong hydration. This tendency does not agree with the results obtained in this work. However, Strauss and Ross indicated that the binding constant of alkali metal and alkaline earth metal cations with phosphate ions decreases in the order of an increase in the ionic radius of the cations.[10] This result well explains the order of the retardation efficiency of alkali metal and alkaline earth metal cations obtained here. Accordingly, the retardation of the degradation may be caused by the following exchange reaction:



$$-\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{H}{O}}{P}}-O-\overset{|}{\underset{|}{P}}- + M^{+} \longrightarrow -\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{M}{O}}{P}}-O-\overset{|}{\underset{|}{P}}- + H^{+}.$$

TABLE 3. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF PYROPHOSPHATE

Phosphate	Added cation	pH=1.0		pH=2.0		pH=3.0	
		I a)	II b)	I	II	I	II
$H_4P_2O_7$	—	86.0	10.8	111.0	14.1	115.8	14.5
$Na_4P_2O_7$	—	87.4	11.0	115.8	14.8	117.5	14.7
	Li^+	89.9	11.3	116.7	14.9	117.7	14.7
	Na^+	89.8	11.3	116.9	15.0	118.0	14.8
	K^+	87.2	10.9	115.8	14.8	116.7	14.6
	Mg^{2+}	95.4	12.0	114.0	14.2		
	Ca^{2+}	96.9	12.3	119.0	15.2		
	Mn^{2+}	96.2	12.0				
	Co^{2+}	92.2	11.5				
	Ni^{2+}	94.3	11.9				
	Zn^{2+}	93.8	11.7				
	(Al^{3+}) c)	95.2	11.6				

a) I stands for the activation energy/kJ mol^{-1}. b) II stands for the log(frequency factor/min^{-1}). c) The values obtained at pH 0.9.

TABLE 4. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF TRIPHOSPHATE

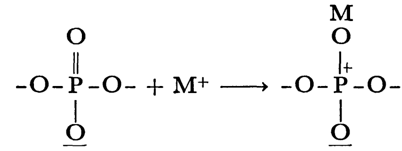
Phosphate	Added cation	pH=1.0		pH=2.0		pH=3.0	
		I a)	II b)	I	II	I	II
$H_5P_3O_{10}$	—	83.0	11.2	93.3	12.1	107.9	13.7
$Na_5P_3O_{10}$	—	83.0	11.1	95.1	12.3	108.0	13.7
	Li^+	88.0	11.8	104.4	13.7	108.5	13.7
	Na^+	84.4	11.3	103.5	13.5	110.0	14.0
	K^+	83.8	11.2	102.4	13.4	109.8	14.0
	Mg^{2+}	83.9	10.7	103.6	13.0	109.2	13.6
	Ca^{2+}	85.1	11.0	108.5	14.1		
	Mn^{2+}	90.4	11.5	108.8	13.8		
	Co^{2+}	84.1	10.7	105.1	13.2		
	Ni^{2+}	85.1	10.9	101.3	12.6	111.7	14.0
	Cu^{2+}	86.1	10.9				
	Zn^{2+}	85.5	10.9				

a) I stands for the activation energy/kJ mol^{-1}. b) II stands for log(frequency factor/min^{-1}).

In the case of transition metal-ions, the order of ionic radius is as follows:

$$Mn^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+},$$

and the order of the retardation efficiency at pH 1.0 is the same as that of the ionic radius. Therefore, the binding force of these transition metal ions with the phosphate ions may increase with an increase in the ionic radius in strongly acidic media. The catalytic effect of alkali metal ions for the degradation of triphosphate ions in alkaline solutions may be explained by the formation of the complex as follows:



$$-O-\underset{\underset{\underline{O}}{|}}{\overset{\overset{O}{\|}}{P}}-O- + M^{+} \longrightarrow -O-\underset{\underset{\underline{O}}{|}}{\overset{\overset{\overset{M}{O}}{|^{+}}}{P}}-O-,$$

because the phosphate ion on the right-hand side is considered to be more susceptible to the nucleophilic attack of a water molecule than that on the left-hand side.

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