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The Mechanism of the Hydrolysis of Polyphosphates. VI.[1] The Effect of Cations on the Hydrolysis of *cyclo*-Tri- and *cyclo*-Tetraphosphates

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The effect of cations on the rate of the hydrolysis of *cyclo*-tri- and *cyclo*-tetraphosphates was studied by adding metal chlorides to aqueous solutions of the ring phosphates. The concentrations of the phosphates and metal chlorides were 0.025 mol dm^{-3} and 0.1 mol dm^{-3} respectively. Alkali-metal cations retarded the hydrolysis of both the *cyclo*-phosphates in acidic media and accelerated it in basic media. The following sequence of efficiency resulted:

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

Magnesium, calcium, and nickel(II) cations retarded the hydrolysis of the *cyclo*-phosphates in the pH range of 1.0—2.0 or 1.0—2.7, while they accelerated it in the pH regions higher than 2.7 or 3.5. A copper(II) ion retarded the hydrolysis at pH 1.0, and accelerated it in the pH ranges higher than 2.0. An aluminium ion highly accelerated the hydrolysis of both the ring phosphates at pH 1.0 and 2.0.

Though many papers concerning the hydrolysis of polyphosphates have been reported, there have been few reports about the effect of metal cations on the hydrolysis. Thilo and Wieker studied the catalytic efficiencies of cations on the hydrolysis of high polyphosphates at pH 8 and obtained the following sequence of efficiency:

$$Al^{3+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > H^+ > Li^+ > Na^+ > K^+.^{2-4)}$$

Osterheld recently presented a review on the hydrolysis of condensed phosphates.[5] The present author has reported the reaction mechanism of the hydrolysis of chain and small-ring polyphosphates from the point of view of the interaction between a water molecule and a polyphosphate ion by using aqueous organic solvents.[6–9] In a previous paper,[1] the effect of metal cations on the hydrolysis of di- and triphosphates was reported. This paper describes the effect of metal cations on the hydrolysis of *cyclo*-tri- and *cyclo*-tetraphosphates.

Experimental

Materials and Procedure. All the materials other than sodium *cyclo*-tri- and *cyclo*-tetraphosphates were commercial grade. Sodium *cyclo*-tri- and *cyclo*-tetraphosphates were produced by the method described in Refs. 10 and 11. The initial concentration of sodium *cyclo*-tri- and *cyclo*-tetraphosphates was 0.025 mol dm^{-3}. This concentration is suitable for analysis. *cyclo*-Tri- and *cyclo*-tetraphosphate solutions free from sodium ions were prepared by passing the sodium *cyclo*-phosphate solutions mentioned above through cation-exchange resin in the H$^+$ form. The *cyclo*-phosphate solutions without sodium ions were used to study the effect of alkali-metal cations on the rate of the hydrolysis of the *cyclo*-phosphates in both acidic and basic media. These *cyclo*-phosphate solutions could not be used to investigate the effect of alkaline-earth, aluminium and some transition-metal cations over a wide pH range of the solution, because precipitates were formed. So the sodium *cyclo*-phosphate solutions were used to test the effect of these cations on the rate of the hydrolysis of the *cyclo*-phosphates. Metal chloride was added to the phosphate solutions to make it 0.1 mol dm^{-3}. The metal chlorides used were LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $AlCl_3$, $NiCl_2$, and $CuCl_2$. The pH's of the *cyclo*-phosphate solutions containing one of the cations mentioned above were controlled with hydrochloric acid and/or aqueous tetramethylammonium hydroxide by using a Hitachi-Horiba pH meter, F-7, at a given reaction temperature. The pH of the solution was periodically measured and if it was in need of adjustment, enough tetramethylammonium hydroxide or hydrochloric acid was added to bring it back to the proper pH. The pH adjustment was made within ±0.1 pH unit of the required value. At measured intervals of time, about a 1-cm^3 portion of the *cyclo*-phosphate solution was withdrawn. About 50 mg of disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA) was added to the phosphate solution containing a metal cation, and then the pH of the solution was adjusted to 7—9 with aqueous ammonia or hydrochloric acid and 8 mm^3 of the solution was spotted on Toyo No. 51A filter paper (2 by 50 cm) for the separation of the phosphates in the solution. When the *cyclo*-phosphate solution did not contain any metal ion, the pH of the withdrawn 1-cm^3 portion of the phosphate solution was adjusted to about 7 with aqueous ammonia or hydrochloric acid. The separation of the phosphate species in the solution was made by spotting 8 mm^3 of the solution on the filter paper mentioned above. The separation and determination of the phosphates in the sample solution were carried out by the method described in previous papers.[6,8,9] When some precipitate was formed during the hydrolytic processes of the *cyclo*-phosphates, no further treatment was made.

Results and Discussion

The Effect of Cations. The rate of the hydrolysis of *cyclo*-tri- and *cyclo*-tetraphosphates obeyed first-order kinetics with respect to the concentration of the respective *cyclo*-phosphates under all the conditions studied. The hydrolysis of sodium *cyclo*-tri- and *cyclo*-tetraphosphates is an acid- and base-catalyzed reaction.[8,9] As Tables 1 and 2 show, the hydrolysis of *cyclo*-tri- and *cyclo*-tetraphosphates in an aqueous solution containing alkali-metal cations or in a solution free from metal cations gave the result mentioned above. The rate of the hydrolysis of the *cyclo*-phosphates in a solution containing Mg^{2+}, Ca^{2+}, or Ni^{2+} decreased with an increase in the pH of the solution from 1.0 to 2.7 or 3.5, while the rate of the hydrolysis of *cyclo*-triphosphate containing Mg^{2+} and of *cyclo*-tetraphosphate containing

Table 1. Rate constants/min^{-1} of the hydrolysisof *cyclo*-triphosphate

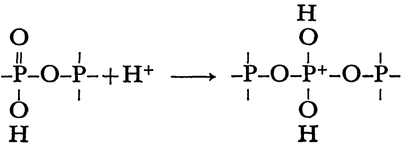
Phosphate	Added cation	pH	Reaction temp/°C		
			30	50	70
$(HPO_3)_3$	—	1.0	2.46×10^{-3}	1.59×10^{-2}	1.35×10^{-1}
		2.0	7.51×10^{-5}	6.91×10^{-4}	5.34×10^{-3}
		11.5	3.78×10^{-6}	5.03×10^{-5}	6.32×10^{-4}
	Li^+	1.0	1.61×10^{-3}	7.27×10^{-3}	1.10×10^{-1}
		2.0	5.09×10^{-5}	5.69×10^{-4}	3.80×10^{-3}
		11.5	1.68×10^{-5}	2.28×10^{-4}	4.39×10^{-3}
	Na^+	1.0	1.78×10^{-3}	8.96×10^{-3}	1.07×10^{-1}
		2.0	5.85×10^{-5}	5.87×10^{-4}	4.33×10^{-3}
		11.5	9.19×10^{-6}	1.48×10^{-4}	1.51×10^{-3}
	K^+	1.0	2.28×10^{-3}	1.12×10^{-2}	1.32×10^{-1}
		2.0	6.01×10^{-5}	6.47×10^{-4}	4.68×10^{-3}
		11.5	8.56×10^{-6}	1.22×10^{-4}	1.37×10^{-3}
$(NaPO_3)_3$	—	1.0	1.35×10^{-3}	1.13×10^{-2}	7.50×10^{-2}
		2.0	6.28×10^{-5}	5.89×10^{-4}	4.37×10^{-3}
		2.7	1.29×10^{-5}	1.21×10^{-4}	9.44×10^{-4}
		3.5	1.73×10^{-6}	2.46×10^{-5}	1.64×10^{-4}
		5.0	4.42×10^{-7}		
		11.5	7.86×10^{-6}	1.31×10^{-4}	1.60×10^{-3}
	$Mg^{2}{}_{+}$	1.0	6.86×10^{-4}	4.36×10^{-3}	1.83×10^{-2}
		2.0	3.81×10^{-5}	2.38×10^{-4}	1.21×10^{-3}
		2.7	1.15×10^{-5}	9.26×10^{-5}	8.22×10^{-4}
		3.5	3.31×10^{-6}	3.06×10^{-5}	2.50×10^{-4}
		5.0	4.14×10^{-6}		
	Ca^{2+}	1.0	6.98×10^{-4}	4.85×10^{-3}	2.02×10^{-2}
		2.0	3.99×10^{-5}	3.54×10^{-4}	1.30×10^{-3}
		2.7	1.91×10^{-5}	1.53×10^{-4}	
	Ni^{2+}	1.0	8.67×10^{-4}	5.09×10^{-3}	2.75×10^{-2}
		2.0	3.54×10^{-5}	3.07×10^{-4}	1.66×10^{-3}
		2.7	1.54×10^{-5}	1.28×10^{-4}	8.62×10^{-4}
		3.5	1.02×10^{-5}	1.04×10^{-4}	5.57×10^{-4}
	Cu^{2+}	1.0	1.38×10^{-3}	9.63×10^{-3}	5.05×10^{-2}
		2.0	1.95×10^{-4}	$2.08\times10_{-}{}^{3}$	1.31×10^{-2}
		2.7	4.27×10^{-4}	3.68×10^{-3}	2.81×10^{-2}
	Al^{3+}	1.0	8.29×10^{-3}	6.75×10^{-2}	4.23×10^{-1}
		2.0	8.98×10^{-3}	9.02×10^{-2}	

Table 2. Rate constants/min^{-1} of the hydrolysis of *cyclo*-tetraphosphate

Phosphate	Added cation	pH	Reaction temp/°C		
			30	50	70
$(HPO_3)_4$	—	1.0	2.75×10^{-4}	2.80×10^{-3}	2.46×10^{-2}
		2.0	1.80×10^{-5}	1.96×10^{-4}	1.79×10^{-3}
		11.5	7.40×10^{-8}	1.58×10^{-6}	1.76×10^{-5}
	Li^+	1.0	1.42×10^{-4}	1.68×10^{-3}	1.40×10^{-2}
		2.0	7.00×10^{-6}	7.98×10^{-5}	7.35×10^{-4}
		11.5	7.76×10^{-7}	1.79×10^{-5}	
	Na^+	1.0	1.89×10^{-4}	1.92×10^{-3}	1.78×10^{-2}
		2.0	8.82×10^{-6}	1.13×10^{-4}	8.80×10^{-4}
		11.5	2.64×10^{-7}	6.24×10^{-6}	8.77×10^{-5}
	K^+	1.0	2.03×10^{-4}	2.01×10^{-3}	1.90×10^{-2}
		2.0	9.00×10^{-6}	1.16×10^{-4}	9.30×10^{-4}
		11.5	2.31×10^{-7}	5.55×10^{-6}	8.12×10^{-5}
$(NaPO_3)_4$	—	1.0	1.42×10^{-4}	1.54×10^{-3}	1.28×10^{-2}
		2.0	1.00×10^{-5}	1.29×10^{-4}	1.21×10^{-3}
		2.7	1.37×10^{-6}	2.11×10^{-5}	1.83×10^{-4}
		3.5	2.56×10^{-7}	3.29×10^{-6}	3.74×10^{-5}
		5.0		3.00×10^{-7}	
	Mg^{2+}	1.0	2.75×10^{-5}	2.24×10^{-4}	1.72×10^{-3}
		2.0	1.35×10^{-6}	1.25×10^{-5}	8.61×10^{-5}
		2.7	2.04×10^{-7}	3.53×10^{-6}	
	Ni^{2+}	1.0	2.84×10^{-5}	3.14×10^{-4}	2.09×10^{-3}
		2.0	1.83×10^{-6}	1.78×10^{-5}	1.51×10^{-4}
		2.7	5.30×10^{-7}	6.86×10^{-6}	6.86×10^{-5}
		3.5	5.04×10^{-7}	6.21×10^{-6}	6.64×10^{-5}
		5.0	1.27×10^{-6}	1.05×10^{-5}	
	Cu^{2+}	1.0	5.80×10^{-5}	5.38×10^{-4}	3.95×10^{-3}
		2.0	2.43×10^{-5}	3.13×10^{-4}	2.18×10^{-3}
		2.7	2.46×10^{-5}	3.12×10^{-4}	2.63×10^{-3}
		3.5	1.11×10^{-4}	1.59×10^{-3}	
	Al^{3+}	1.0	1.24×10^{-3}	8.16×10^{-3}	5.50×10^{-2}
		2.0	1.38×10^{-3}	1.33×10^{-2}	1.04×10^{-1}

Ni^{2+} increased with an increase in the pH of the solution from 3.5 to 5.0. The rate of the hydrolysis of the *cyclo*-phosphates in a solution containing Cu^{2+} decreased as the pH of the solution changed from 1.0 to 2.0. On the other hand, the rate increased as the pH of the solution increased from 2.0 to 2.7 and 3.5. In the case of the hydrolysis of the ring phosphates in a solution containing Al^{3+}, the rate of the hydrolysis of the *cyclo*-phosphates increased with an increase in the pH of the solution from 1.0 to 2.0. For the hydrolysis of the short-chain polyphosphates, these cations used here all retarded the rate of the hydrolysis of the polyphosphates in acidic media and alkali-metal ions accelerated the rate in basic media. This tendency is the same as that of the hydrolysis of the ring phosphates in a solution containing alkali-metal ions. Magnesium, calcium, and nickel ions retarded the rate of the hydrolysis of the *cyclo*-phosphates in the pH region of 1.0—2.0 or 1.0—2.7, while they seemed to accelerate the rate in the pH regions higher than 2.7 or 3.5. The rate was retarded by Cu^{2+} at pH 1.0, while it was accelerated at a pH region higher than 2.0. An aluminium ion extremely accelerated the rate of the hydrolysis of the *cyclo*-phosphates at pH 1.0 and 2.0. The acceleration of the rate of the hydrolysis by metal cations was not observed for the hydrolysis of di- and triphosphates in acidic media.

Reaction Mechanism. The activation parameters for the hydrolysis of *cyclo*-tri- and *cyclo*-tetraphosphates were calculated by means of an Arrhenius plot and are listed in Tables 3 and 4 respectively. In the case of the hydrolysis of both the *cyclo*-phosphates in a solution containing an alkali-metal ion or in a solution free from a metal ion, the activation energy increased with an increase in the pH of the solution. The activation energy also seemed to increase by addition of an alkali-metal ion into the phosphate solution. In previous papers,[6–9] the author proposed the following hydrolysis mechanism for chain and small-ring phosphates and concluded that Reaction 2 is the rate-determining step:



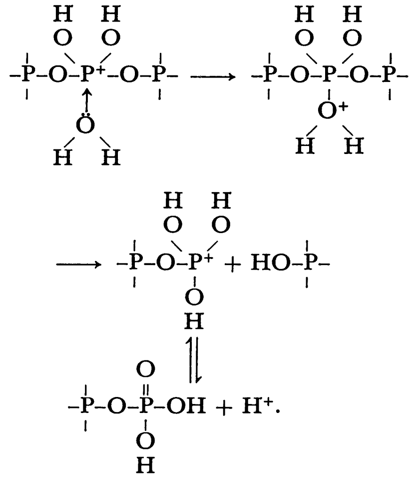
$$-\underset{|}{\overset{|}{P}}-O-\underset{\underset{H}{\overset{|}{O}}}{\overset{\overset{O}{\|}}{P}}-O-\underset{|}{\overset{|}{P}}-+H^+ \longrightarrow -\underset{|}{\overset{|}{P}}-O-\underset{\underset{H}{\overset{|}{O}}}{\overset{\overset{\overset{H}{O}}{|}}{P^+}}-O-\underset{|}{\overset{|}{P}}-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

TABLE 3. ACTIVATION PARAMETERS OF THE HYDROLYSIS OF *cyclo*-TRIPHOSPHATE

Phosphate	Added cation	pH	Activation energy/kJ mol^{-1}	log (frequency factor/min^{-1})
$(HPO_3)_3$	—	1.0	86.3	12.2
		2.0	92.0	11.7
		11.5	110.4	13.6
	Li^+	1.0	90.6	12.7
		2.0	93.2	11.8
		11.5	119.9	15.8
	Na^+	1.0	88.0	12.3
		2.0	93.0	11.3
		11.5	110.5	14.0
	K^+	1.0	87.2	12.3
		2.0	94.1	12.0
		11.5	109.9	13.9
$(NaPO_3)_3$	—	1.0	86.8	12.1
		2.0	91.6	11.6
		2.7	92.7	11.1
		3.5	102.5	12.6
		11.5	114.8	14.7
	Mg^{2+}	1.0	71.0	9.1
		2.0	74.7	8.5
		2.7	92.0	10.9
		3.5	93.6	10.6
	Ca^{2+}	1.0	72.8	9.4
		2.0	75.5	8.7
		2.7	84.8	9.9
	Ni^{2+}	1.0	74.6	9.8
		2.0	83.2	9.9
		2.7	86.9	10.2
		3.5	86.6	10.0
	Cu^{2+}	1.0	77.8	10.5
		2.0	91.0	12.0
		2.7	90.4	12.2
	Al^{3+}	1.0	84.9	12.6

TABLE 4. ACTIVATION PARAMETERS OF THE HYDROLYSIS OF *cyclo*-TETRAPHOSPHATE

Phosphate	Added cation	pH	Activation energy kJ/mol^{-1}	log (frequency factor/min^{-1})
$(HPO_3)_4$	—	1.0	97.0	13.1
		2.0	99.3	12.4
		11.5	118.3	13.3
	Li^+	1.0	99.2	13.3
		2.0	100.5	12.2
		11.5	127.9	15.9
	Na^+	1.0	98.1	13.2
		2.0	99.5	12.1
		11.5	125.4	15.1
	K^+	1.0	97.9	13.2
		2.0	100.2	12.2
		11.5	126.7	15.2
$(NaPO_3)_4$	—	1.0	97.2	12.9
		2.0	103.6	12.9
		2.7	105.9	12.4
		3.5	107.6	11.9
	Mg^{2+}	1.0	89.2	10.8
		2.0	89.8	9.6
	Ni^{2+}	1.0	93.2	11.5
		2.0	95.5	10.7
		2.7	105.0	11.8
		3.5	105.3	11.8
	Cu^{2+}	1.0	91.1	11.5
		2.0	97.3	12.2
		2.7	100.9	12.8
	Al^{3+}	1.0	82.0	11.2
		2.0	93.3	13.2

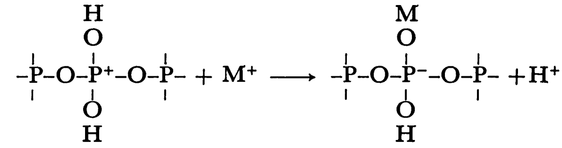


$$-\overset{|}{\underset{|}{P}}-O-\underset{\overset{\uparrow}{\underset{H\ \ H}{O}}}{\overset{HO\ \ OH}{P^{+}}}-O-\overset{|}{\underset{|}{P}}- \longrightarrow -\overset{|}{\underset{|}{P}}-O-\underset{\underset{H\ \ H}{O^{+}}}{\overset{HO\ \ OH}{P}}-O-\overset{|}{\underset{|}{P}}- \qquad (2)$$

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

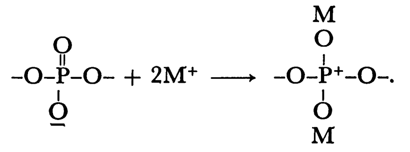
$$\rightleftarrows -\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{O}{\|}}{P}}-OH + H^{+}. \qquad (4)$$

As mentioned above, the effect of alkali-metal ions on the kinetics parameters and the order of the efficiency of alkali-metal ions for the hydrolysis of both the ring phosphates was the same as that of the hydrolysis of di- and triphosphates. So the same reaction mechanism described in a previous paper[1)] may be applicable for the hydrolysis of the *cyclo*-phosphates, and the retardation of the hydrolysis rate by alkali-metal ions in acidic media could be attributable to the exchange of a hydrogen ion with a catalytically less effective alkali-metal ion as follows:



$$-\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{H}{O}}{P^{+}}}-O-\overset{|}{\underset{|}{P}}- + M^{+} \longrightarrow -\overset{|}{\underset{|}{P}}-O-\underset{\underset{H}{O}}{\overset{\overset{M}{O}}{P^{-}}}-O-\overset{|}{\underset{|}{P}}- + H^{+}. \qquad (5)$$

The acceleration of the rate by alkali-metal ions in basic media could be explained by the formation of the complex as follows:



$$-O-\underset{\underset{O^{-}}{|}}{\overset{\overset{O}{\|}}{P}}-O- + 2M^{+} \longrightarrow -O-\underset{\underset{\underset{M}{O}}{|}}{\overset{\overset{\overset{M}{O}}{|}}{P^{+}}}-O-. \qquad (6)$$

As Tables 3 and 4 show, this acceleration is exclusively dependent on the entropy term. The retardaction of the rate of the hydrolysis of *cyclo*-tri- and *cyclo*-tetraphosphates by Mg^{2+}, Ca^{2+}, Ni^{2+}, and Cu^{2+} in highly acidic media depended exclusively upon the entropy term. So, when the exchange of a hydrogen ion with a catalytically less effective Mg^{2+} ion takes place according to Reaction 5, it could be concluded that there is a difference between the structures of the complexes of an alkali-metal ion and of an Mg^{2+}, Ca^{2+}, Ni^{2+}, or Cu^{2+} ion. The acceleration of the hydrolysis of the *cyclo*-phosphates by Cu^{2+} and Al^{3+} in acidic media depended upon the energy and/or the entropy term. Since Reaction 2 is the rate-determining step of the hydrolysis of polyphosphates, Cu^{2+} and Al^{3+} may affect Reactions 1 and 2. The exchange of a hydrogen ion with Cu^{2+} or Al^{3+} may occur according to Reaction 5 and the cations are considered to be catalytically more effective than a hydrogen ion for the hydrolysis of the small-ring phosphates.

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