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The Mechanism of the Hydrolysis of Condensed Phosphates. IV. The Hydrolysis of Pyro-, Tripoly-, Trimeta-, and Tetrametaphosphates in Aqueous Organic Solvents

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The hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates was run in water, aqueous ethanol, aqueous glycerol, aqueous acetonitrile, aqueous dimethyl sulfoxide, and aqueous tetrahydrofuran at various pH values and temperatures. The initial concentration of the phosphates was 0.025 mol/l. The hydrolysis of the poly- and metaphosphates followed first-order kinetics with respect to the concentration of the phosphate, under all conditions studied. The hydrolysis of sodium pyro- and tripolyphosphates was an acid-catalyzed reaction and that of sodium trimeta- and tetrametaphosphates was an acid- and base-catalyzed reaction. In acidic solutions, the rate of hydrolysis of the poly- and metaphosphates in water was slower than that in any aqueous organic solution. It is concluded that the nucleophilicity of the water molecule in the aqueous organic solutions may increase on account of the interaction of the water molecule with the organic molecules. The hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates in acidic solutions is considered to be of the S_N2 type, because the overall-reaction rate is highly dependent on the nucleophilicity of the water molecule. The solvent effect on the rate of hydrolysis of sodium tripolyphosphate in basic solutions was the same as that in acidic solutions and hence the mechanism of the hydrolysis of sodium tripolyphosphate in basic solutions may be the same as that in acidic solutions. The rate of hydrolysis of sodium trimeta- and tetrametaphosphates in a basic water solvent was much faster than that in basic aqueous ethanol and basic aqueous dimethyl sulfoxide and was largely slower than that in basic aqueous glycerol. Consequently, the mechanism of the hydrolysis of sodium trimeta- and tetrametaphosphates in basic solutions seems to differ from that in acidic solutions. The acceleration of the rate of hydrolysis of the metaphosphates by the organic molecules depends significantly upon the activation energy. The activation energy of the hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates was 17—34 kcal/mol in the pH range of 1.0—12.2 and increased with an increase in the pH value of the phosphate solution in water and aqueous ethyl alcohol solvents.

The tetrahedral phosphorus atom of organic compounds having a P=O bond is sensitive for nucleophilic attack.[1)] Wieker and Thilo proposed the same mechanism for the hydrolysis of long-chain polyphosphate by examining the catalytic effect of metal cations on the hydrolytic polyphosphate degradation.[2)] In previous papers by the authors,[3,4)] the solvent effect on the rate of hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates was examined by running the hydrolysis in water, aqueous dioxane, aqueous formic acid, and aqueous acetic acid. According to the results, the hydrolysis of sodium pyro- and tripolyphosphates at any pH value and that of sodium trimeta- and tetrametaphosphates in acidic solutions were considered to be S_N2 reactions. The types of solvents used in our previous experiments were not numerous. Therefore, in the present paper, the solvent effect on the rate of hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates is examined by using aqueous ethanol, aqueous glycerol, aqueous acetonitrile, aqueous dimethyl sulfoxide, and aqueous tetrahydrofuran as solvents. Ethanol and glycerol are protic solvents and acetonitrile, dimethyl sulfoxide, and tetrahydrofuran are dipolar aprotic solvents. The hydrogen atom of the OH-group contained in the first group can form a hydrogen bond with the oxygen atom of a water molecule and the oxygen or the nitrogen atom present in the second group can form a hydrogen bond with the hydrogen atom of a water molecule.

Experimental

Materials and Procedure. All the materials except sodium tripoly-, trimeta-, and tetrametaphosphates were of a commercial grade. Sodium tripoly-, trimeta-, and tetrametaphosphates were produced by the method described in Refs. 5 and 6. The solvents used in this experiment and their dielectric constants are listed in Table 1. The dielectric constants were measured by using an Ando Denki TR-1C VHF material characteristics test assembly. The initial concentration of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates was 0.025 mol/l. This concentration is suitable for analysis. pH control of the phosphate solutions was made by the same method as that described in previous papers by the authors by using nitric acid and aqueous tetramethyl ammonium hydroxide.[3,4)] The pH adjustment was made to within ±0.1 unit of the desired pH value. The pH change of

TABLE 1. SOLVENTS USED FOR THE HYDROLYSIS OF PYRO-, TRIPOLY-, TRIMETA-, AND TETRAMETAPHOSPHATES AND THEIR DIELECTRIC CONSTANTS

Solvent	Dielectric constant	Symbol
Water		S_1
25 vol% aqueous ethanol	63	S_2
20 vol% aqueous ethanol	65	S_3
35 vol% aqueous glycerol	64	S_4
30 vol% aqueous acetonitrile	69	S_5
25 vol% aqueous dimethyl sulfoxide	73	S_6
20 vol% aqueous dimethyl sulfoxide	73	S_7
25 vol% aqueous tetrahydrofuran	59	S_8
20 vol% aqueous tetrahydrofuran	65	S_9

the phosphate solution of the S_5 solvent in basic media with the elapse of reaction time was very large and it was difficult to maintain the pH of the solution to within ±0.1 unit of the desired pH value. Therefore, the hydrolysis of the phosphates in the S_5 solvent was not run in basic media. The reaction temperature was maintained at 30, 50, or 70±0.05 °C by using a thermostat. The separation and determination of the phosphate species in the sample solution were carried out by using the same method as described in previous papers.[3,4] However, the separation of the hydrolysis products of trimeta- and tetrametaphosphates for all alkaline solutions was not good, and hence, after the basic sample solutions were acidified with nitric acid, the acidified solutions were spotted on filter papers. For the hydrolysis of sodium trimeta- and tetrametaphosphates in the S_4 solvent, 1 ml of a saturated aqueous sodium chloride solution was added to 10 ml of the sample solution and then the separation of the phosphate species in the solution was carried out by using one-dimensional paper chromatography. Since the boiling point of tetrahydrofuran is 65 °C, the hydrolysis of the phosphates in the S_8 and S_9 solvents was not run at 70 °C.

Results and Discussion

Order of the Reactions and the pH Dependence of the Reaction Rates. The hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates obeyed first-order kinetics with respect to the concentration of the phosphate under the conditions studied. The rate constants of the hydrolysis of the phosphates are listed in Tables 2—5. In all the solvents used in this experiment, the rate of hydrolysis of the short-chain polyphosphates (pyro- and tripolyphosphates) decreases with an increase in the pH of the solution and this tendency is the same as that found in previous experiments.[3,7] Since the hydrolytic degradation of pyrophosphate is very slow in a basic solution and the measurement of the rate of hydrolysis of pyrophosphate in basic media is difficult, only the hydrolysis of tripolyphosphate was run in basic solutions. As Tables 2 and 3 show, the hydrolysis of the short-chain polyphosphates is an acid-catalyzed reaction in all solvents. In the case of the hydrolysis of the small-ring metaphosphates (trimeta- and tetrametaphosphates), the rate of hydrolysis of the small-ring metaphosphates decreases in acidic solutions and increases in basic solutions with an increase in the pH value for all solvents.[8] Therefore, the hydrolysis of

Table 2. Rate constants (min^{-1}) for the hydrolysis of pyrophosphate

pH	Solvent[a]	Reaction temp (°C)		
		30	50	70
1.0	S_1	8.50×10^{-5}	7.40×10^{-4}	4.70×10^{-3}
	S_2	1.42×10^{-4}	9.19×10^{-4}	5.27×10^{-3}
	S_4	1.03×10^{-4}	7.90×10^{-4}	4.79×10^{-3}
	S_5	1.02×10^{-4}	7.70×10^{-4}	4.70×10^{-3}
	S_6	2.68×10^{-4}	1.62×10^{-3}	7.82×10^{-3}
	S_8	1.61×10^{-4}	1.09×10^{-3}	
2.0	S_1	7.89×10^{-6}	1.30×10^{-4}	1.55×10^{-3}
	S_2	1.03×10^{-5}	1.54×10^{-4}	1.62×10^{-3}
	S_4	7.92×10^{-6}	1.33×10^{-4}	1.57×10^{-3}
	S_5	8.94×10^{-6}	1.38×10^{-4}	1.58×10^{-3}
	S_6	1.93×10^{-5}	2.47×10^{-4}	2.24×10^{-3}
	S_8	1.09×10^{-5}	1.60×10^{-4}	

a) For the solvents, refer to Table 1.

Table 3. Rate constants (min^{-1}) for the hydrolysis of tripolyphosphate

pH	Solvent[a]	Reaction temp (°C)		
		30	50	70
1.0	S_1	7.48×10^{-4}	5.38×10^{-3}	2.94×10^{-2}
	S_3	9.03×10^{-4}	6.30×10^{-3}	3.64×10^{-2}
	S_4	7.98×10^{-4}	5.48×10^{-3}	3.07×10^{-2}
	S_5	8.05×10^{-4}	5.60×10^{-3}	2.97×10^{-2}
	S_7	1.55×10^{-3}	9.89×10^{-3}	4.80×10^{-2}
	S_9	9.30×10^{-4}	6.60×10^{-3}	
2.0	S_1	8.70×10^{-5}	8.29×10^{-4}	6.10×10^{-3}
	S_3	1.05×10^{-4}	9.81×10^{-4}	7.04×10^{-3}
	S_4	8.99×10^{-5}	8.53×10^{-4}	6.30×10^{-3}
	S_5	9.41×10^{-5}	8.80×10^{-4}	6.34×10^{-3}
	S_7	1.84×10^{-4}	1.57×10^{-3}	1.02×10^{-2}
	S_9	1.18×10^{-4}	1.05×10^{-3}	
8.0	S_1		9.82×10^{-6}	
	S_3		1.19×10^{-5}	
	S_4		1.17×10^{-5}	
	S_5		1.09×10^{-5}	
	S_7		1.46×10^{-5}	
	S_9		1.23×10^{-5}	
10.0	S_1		3.31×10^{-6}	
	S_3		3.91×10^{-6}	
	S_4		3.61×10^{-6}	
	S_5		3.52×10^{-6}	
	S_7		5.73×10^{-6}	
	S_9		4.00×10^{-6}	

a) For the solvents, refer to Table 1.

Table 4. Rate constants (min^{-1}) for the hydrolysis of trimetaphosphate

pH	Solvent[a]	Reaction temp (°C)		
		30	50	70
1.0	S_1	1.35×10^{-3}	1.13×10^{-2}	7.50×10^{-2}
	S_2	1.62×10^{-3}	1.38×10^{-2}	8.95×10^{-2}
	S_4	1.49×10^{-3}	1.25×10^{-2}	8.11×10^{-2}
	S_5	1.40×10^{-3}	1.20×10^{-2}	7.80×10^{-2}
	S_6	2.58×10^{-3}	2.07×10^{-2}	1.30×10^{-1}
	S_8	1.82×10^{-3}	1.52×10^{-2}	
2.0	S_1	6.28×19^{-5}	5.89×10^{-4}	4.37×10^{-3}
	S_2	8.20×10^{-5}	7.71×10^{-4}	5.64×10^{-3}
	S_4	7.35×10^{-5}	6.92×10^{-4}	5.07×10^{-3}
	S_5	6.95×10^{-5}	6.52×10^{-4}	4.85×10^{-3}
	S_6	1.30×10^{-4}	1.16×10^{-3}	8.55×10^{-3}
	S_8	8.89×10^{-5}	8.13×10^{-4}	
11.5	S_1	7.86×10^{-6}	1.31×10^{-4}	1.60×10^{-3}
	S_2	2.16×10^{-6}	4.53×10^{-5}	6.69×10^{-4}
	S_4	4.86×10^{-5}	6.30×10^{-4}	6.17×10^{-3}
	S_6	8.12×10^{-7}	1.97×10^{-5}	3.28×10^{-4}
12.2	S_1	5.72×10^{-5}	9.61×10^{-4}	1.17×10^{-2}
	S_2	1.90×10^{-5}	4.07×10^{-4}	6.19×10^{-3}
	S_4	2.47×10^{-4}	2.62×10^{-3}	2.44×10^{-2}
	S_6	1.18×10^{-5}	2.64×10^{-4}	4.15×10^{-3}

a) For the solvents, refer to Table 1.

TABLE 5. RATE CONSTANTS (min^{-1}) FOR THE HYDROLYSIS OF TETRAMETAPHOSPHATE

pH	Solvent[a]	Reaction temp (°C) 30	50	70
1.0	S_1	1.42×10^{-4}	1.54×10^{-3}	1.28×10^{-2}
	S_2	1.86×10^{-4}	1.98×10^{-3}	1.58×10^{-2}
	S_4	1.58×10^{-4}	1.69×10^{-3}	1.40×10^{-2}
	S_5	1.61×10^{-4}	1.70×10^{-3}	1.44×10^{-2}
	S_6	3.20×10^{-4}	3.16×10^{-3}	2.46×10^{-2}
	S_8	2.61×10^{-4}	2.73×10^{-3}	
2.0	S_1	1.00×10^{-5}	1.29×10^{-4}	1.21×10^{-3}
	S_2	1.63×10^{-5}	1.81×10^{-4}	1.51×10^{-3}
	S_4	1.27×10^{-5}	1.49×10^{-4}	1.27×10^{-3}
	S_5	1.22×10^{-5}	1.43×10^{-4}	1.29×10^{-3}
	S_6	3.07×10^{-5}	3.22×10^{-4}	2.53×10^{-3}
	S_8	1.80×10^{-5}	1.91×10^{-4}	
12.2	S_1	1.17×10^{-6}	3.33×10^{-5}	6.51×10^{-4}
	S_2	6.00×10^{-7}	1.73×10^{-5}	3.35×10^{-4}
	S_4	3.17×10^{-6}	6.13×10^{-5}	8.30×10^{-4}
	S_6	4.01×10^{-7}	1.25×10^{-5}	2.62×10^{-4}

a) For the solvents, refer to Table 1.

small-ring metaphosphates is an acid- and base-catalyzed reaction in all solvents, and this is also in good agreement with the results obtained for previous experiments.[4,7] In the course of the hydrolysis of sodium tetrametaphosphate in the acidic S_1–S_8 solvents and the basic S_2 and S_5–S_8 solvents, trimetaphosphate was detected on a paper chromatogram and the quantity of the trimetaphosphate was too small for an accurate determination. Otani, Miura, and Doi have reported that trimetaphosphate was detected as the intermediate of the hydrolytic degradation of tetrapolyphosphate in an acidic aqueous solution.[9] Tetrametaphosphate is hydrolyzed to tetrapolyphosphate in the first step of hydrolytic degradation,[10] and hence, the trimetaphosphate detected in this experiment from the hydrolysis of sodium tetrametaphosphate may be produced by the hydrolysis of the tetrapolyphosphate which is produced by the hydrolysis of tetrametaphosphate. Accordingly, it can be said that there is little difference in the hydrolytic processes for tetrametaphosphate in either the S_1 and S_4 solvents or in the S_2, S_5, S_6, and S_8 solvents. In order to obtain information concerning the mechanism of the hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates, the activation energy and log A (A: frequency factor) of the hydrolysis of the phosphates were calculated by means of an Arrhenius plot and are listed in Tables 6—9. Since the activation energy and log A for the hydrolysis of sodium pyro- and tripolyphosphates in acidic solutions increase with an increase in the pH value, the decrease of the rate of hydrolysis for both the short-chain polyphosphates with increasing pH value depends highly upon the activation energy in all acidic solutions studied. The activation energy of the hydrolysis of sodium trimeta- and tetrametaphosphates increases with an increase in the pH value in all acidic solutions, while log A of the hydrolysis of both the small-ring metaphosphates decreases with an increase in the pH value. The decrease in the rate of hydrolysis with increasing pH value, therefore, depends upon both the activation energy and the frequency factor in all the acidic solutions studied. For basic solutions, the increase in the rate of hydrolysis of sodium trimetaphosphate with an increase in the pH value in

TABLE 6. ACTIVATION ENERGIES, ΔE_A (kcal/mol) AND log A (A: FREQUENCY FACTOR) FOR THE HYDROLYSIS OF SODIUM PYROPHOSPHATE

Solvent[a]	pH=1.0		pH=2.0	
	ΔE_A	log A	ΔE_A	log A
S_1	20.8	10.9	27.3	14.6
S_2	19.1	9.9	26.0	13.8
S_4	19.7	10.2	27.3	14.6
S_5	19.6	10.1	27.0	14.4
S_6	17.2	8.8	24.4	12.9
S_8	18.6	9.6	26.2	13.9

a) For the solvents, refer to Table 1.

TABLE 7. ACTIVATION ENERGIES, ΔE_A (kcal/mol) AND log A (A: FREQUENCY FACTOR) FOR THE HYDROLYSIS OF SODIUM TRIPOLYPHOSPHATE

Solvent[a]	pH=1.0		pH=2.0	
	ΔE_A	log A	ΔE_A	log A
S_1	19.1	10.7	22.5	12.1
S_3	18.9	10.5	21.8	11.7
S_4	19.0	10.6	21.9	11.7
S_5	18.8	10.5	21.7	11.6
S_7	17.4	9.8	20.7	11.2
S_9	19.1	10.7	21.3	11.4

a) For the solvents, refer to Table 1.

TABLE 8. ACTIVATION ENERGIES, ΔE_A (kcal/mol) AND log A (A: FREQUENCY FACTOR) FOR THE HYDROLYSIS OF SODIUM TRIMETAPHOSPHATE

Solvent[a]	pH=1.0		pH=2.0		pH=11.5		pH=12.2	
	ΔE_A	log A	ΔE_A	log A	ΔE_A	log A	ΔE_A	log A
S_1	20.7	12.1	21.8	11.6	27.4	14.7	27.5	15.6
S_2	20.8	12.2	21.8	11.7	29.6	15.7	29.9	16.8
S_4	20.7	12.1	21.8	11.6	25.0	13.7	23.4	13.2
S_5	20.8	12.2	21.8	11.6				
S_6	20.3	12.0	21.5	11.6	31.0	16.3	30.3	16.9
S_8	20.7	12.2	21.6	11.5				

a) For the solvents, refer to Table 1.

TABLE 9. ACTIVATION ENERGIES, ΔE_A (kcal/mol) AND log A(A: FREQUENCY FACTOR) FOR THE HYDROLYSIS OF SODIUM TETRAMETAPHOSPHATE

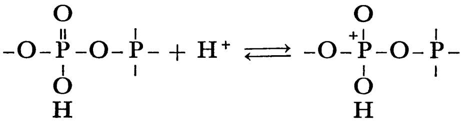
Solvent[a]	pH=1.0		pH=2.0		pH=12.2	
	ΔE_A	log A	ΔE_A	log A	ΔE_A	log A
S_1	23.2	12.9	24.8	12.9	32.6	17.6
S_2	23.0	12.8	23.4	12.1	32.7	17.4
S_4	23.1	12.9	23.9	12.3	28.8	15.3
S_5	23.1	12.8	24.0	12.4		
S_6	22.4	12.6	22.8	12.0	33.5	17.8
S_8	22.9	12.9	23.0	11.8		

a) For the solvents, refer to Table 1.

the S_1 and S_2 solvents is highly dependent upon an entropy term, while those in the S_4 and S_6 solvents depend on an energy term and on energy and entropy terms, respectively.

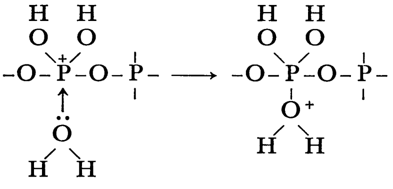
Difference in the Stability of the Hydrolysis of Phosphates. According to the results shown in Tables 2—5, sodium pyrophosphate is more stable against hydrolytic degradation than sodium tripolyphosphate and sodium trimetaphosphate much more subject to hydrolytic scission than is sodium tetrametaphosphate. It can be seen by comparing the results in Tables 6 and 8 with those in Tables 7 and 9, respectively, that the stability of sodium pyrophosphate against hydrolytic scission depends upon an energy term or upon both energy and entropy terms, while the stability of sodium tetrametaphosphate depends entirely on an energy term under the conditions studied. The stability of chain phosphate against hydrolytic degradation decreases, in general, with the chain length of the phosphate,[7] and it can reasonably be accepted that the longer the chain of the phosphate, the greater the probability of hydrolytic scission of a P–O–P linkage. This explanation can not be applied to the stability of small-ring metaphosphates because the chain length of tetrametaphosphate is longer than that of trimetaphosphate. The stability of tetrametaphosphate against hydrolysis is explained by Van Wazer as follows: a tetrametaphosphate ring exhibits a greater number of possible atomic configurations and modes of internal motion than does a trimetaphosphate ion, so that the latter is essentially more rigid and hence more subject to scission.[7] According to Griffith and Rutt,[11] a trimetaphosphate ion has D_{3h} symmetry (planar form) and a tetrametaphosphate ion has C_{2h} symmetry (chair form) in an aqueous solution. The former may be more rigid than the latter. By quantum-chemical consideration, the stability of a system generally proceeds with an increase in the number of obtainable states of the system. The discussion given above and the kinetic data obtained in this experiment seem to support Wazer's explanation of the stability of tetrametaphosphate against hydrolytic scission.

The Solvent Effect on the Rate of Hydrolysis. As is shown in Tables 2—5, in acidic media, the rate of hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates in pure water is slower than that in the ethanol–water, glycerol–water, acetonitrile–water, dimethyl sulfoxide–water, and tetrahydrofuran–water solvents at the same pH values and reaction temperatures. The solvent effect of ethanol, glycerol, and acetonitrile on the rate of hydrolysis of short-chain and small-ring phosphates in acidic media is a small, while that of dimethyl sulfoxide and tetrahydrofuran in acidic media is very marked. The rate of hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates in aqueous dimethyl sulfoxide and aqueous tetrahydrofuran is about 1.5—3.0 and 1.3—2.0 times faster, respectively, than that in pure water. In organic reactions, the effect of the dielectric constant of a solvent on a reactant has been discussed extensively.[12] The relation between the rate constant for the hydrolysis of the phosphates and the dielectric constant of the sample solutions is not parallel and is complex. The present authors have discussed the solvent effect on the rate of hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates by dioxane, formic acid, and acetic acid in previous papers.[3,4] Depending upon the same consideration of the previous papers, the solvent effect in this experiment can reasonably be explained in terms of the difference in the nucleophilicity of the water molecule in each solution as follows. (1) In the case of protic solvents, ethanol and glycerol can interact with a water molecule and hence the hydrogen bond between water molecules may be broken and a hydrogen bond may then be established between the hydrogen atom of the OH group of the protic organic molecules and the oxygen atom of a water molecule. The hydrogen bond between the protic organic molecules and a water molecule may be weaker than that between water molecules, because the polarity of a water molecule is larger than that of ethanol and glycerol molecules. Therefore, the nucleophilicity of the water molecule in aqueous ethanol and aqueous glycerol is larger than that in pure water. The nucleophilic attack by the water molecule of aqueous ethanol and aqueous glycerol on the phosphorus atom of the phosphates may be more favorable energetically than that in pure water. (2) The oxygen atom of dimethyl sulfoxide and tetrahydrofuran and the nitrogen atom of acetonitrile can form a hydrogen bond with the hydrogen atom of a water molecule, and hence the hydrogen bond between water molecules is broken. Accordingly, the nucleophilicity of the water molecule in the aqueous organic solvents may be larger than that in pure water and the nucleophilic attack of the water molecule in aqueous dimethyl sulfoxide, aqueous tetrahydrofuran, and aqueous acetonitrile may also be more favorable energetically than that in pure water. From the results listed in Tables 6—9, it can be said that the acceleration of the rate for short-chain and small-ring phosphates by the organic solvents in acidic media depends mainly upon the activation energy. This appears to support considerations (1) and (2) above. According to the above discussion, since the overall-reaction rates of the hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates in acidic media are highly dependent upon the nucleophilicity of the water molecule and the hydrolysis of the phosphates is an acid-catalyzed reaction, one can describe a series of elementary reactions for the hydrolysis of the poly- and metaphosphates as follows:



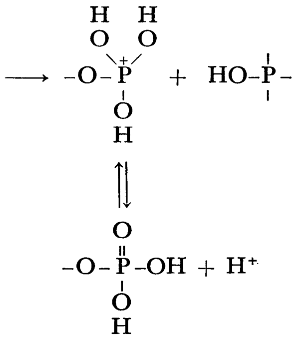
$$\text{-O-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\displaystyle O}}{\underset{|}{P}}}\text{-O-}\overset{|}{\underset{|}{P}}\text{-} + H^+ \rightleftarrows \text{-O-}\overset{\overset{\displaystyle H}{\overset{\displaystyle O}{+|}}}{\underset{\underset{\displaystyle H}{\displaystyle O}}{\underset{|}{P}}}\text{-O-}\overset{|}{\underset{|}{P}}\text{-} \quad (1)$$

(1)



$$\text{-O-}\overset{\overset{\displaystyle H\ \ H}{\displaystyle O\ \ O}}{\overset{\diagdown + \diagup}{P}}\text{-O-}\overset{|}{\underset{|}{P}}\text{-} \underset{\underset{\displaystyle H\ \ H}{\underset{\displaystyle O}{\ddot{}}}}{\uparrow} \longrightarrow \text{-O-}\overset{\overset{\displaystyle H\ \ H}{\displaystyle O\ \ O}}{\overset{\diagdown\ \diagup}{P}}\text{-O-}\overset{|}{\underset{|}{P}}\text{-} \quad \underset{\underset{\displaystyle H\ \ H}{\displaystyle O^+}}{|} \quad (2)$$

(2)



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

$$\Big\updownarrow$$

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

The phosphate ion on the right-hand side of reaction (1) may more readily accept the nucleophilic attack of a water molecule than the phosphate on the left-hand side of reaction (1). The rate-determining step for the hydrolysis of the poly- and metaphosphates in an acidic solution may be the second step because the overall-reaction rate is highly dependent upon the nucleophilicity of the water molecule, as mentioned above. Therefore, the hydrolysis of sodium pyro-, tripoly-, trimeta-, and tetrametaphosphates in acidic solutions may be of the S_N2 type. This conclusion is in good agreement with that of the reaction mechanism of organic phosphorus(V) compounds having P=O bonds[1] and that of the hydrolytic mechanism of long-chain polyphosphates proposed by Wieker and Thilo.[2]

In basic solutions, as is shown in Table 3, the solvent effect on the rate of hydrolysis of sodium tripolyphosphates is the same as that in acidic solutions, and the hydrolysis of the polyphosphate in basic solutions may also be of the S_N2 type. The kinetic data in Tables 4 and 5 show that the solvent effect on the rate of hydrolysis of sodium trimeta- and tetrametaphosphates in basic solutions is much different from that in acidic solutions. The rate of hydrolysis of both metaphosphates in pure water is much faster than that in the S_2 and S_6 solvents and is much slower than that in the S_4 solvent. From the results in Tables 8 and 9, the acceleration or the retardation of the rate of hydrolysis of both metaphosphates in the basic S_2, S_4, and S_6 solvents in comparison with the rate of hydrolysis in the basic S_1 solvent depends upon an energy term. This tendency is almost the same as that obtained in a previous paper by the authors.[4] The hydrolytic reaction mechanism for sodium trimeta- and tetrametaphosphates in basic solutions is not the same as that in acidic solutions. It can be concluded that there are other elementary reactions affecting the overall-reaction rate of the hydrolysis of sodium trimeta- and tetrametaphosphates in basic solutions, other than the nucleophilic attack of a water molecule on the phosphorus atom of the phosphates.

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