The Mechanism of the Hydrolysis of Condensed Phosphates. III. The Mechanism of the Hydrolysis of Trimeta- and Tetrametaphosphates

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(Received March 3, 1975)

The hydrolysis of sodium trimeta- and tetrametaphosphates was run in water, dioxane-water, and formic acid-water solvents with an initial concentration of 0.025 mol/l at various pH values and temperatures. The hydrolysis of both the metaphosphates followed first-order kinetics with respect to the concentration of the phosphate under all the conditions studied and was an acid- and base-catalyzed reaction. In acidic solutions, the rate of hydrolysis of both the metaphosphates in water is faster than that in formic acid-water and slower than that in dioxane-water. Therefore, it is concluded that, in the formic acid-water solvent, the nucleophilicity of the water molecule may decrease on account of the solvation of the water molecule with the acid, while, in the dioxane-water solvent, since the scission of the hydrogen bond between water molecules may occur by the interaction of dioxane and water molecules, the nucleophilicity of the water molecule may increase. The hydrolysis of both metaphosphates in acidic solutions is considered to be an S_N2 reaction, because the overall-reaction rate is highly dependent upon the nucleophilicity of the water molecule. In basic solutions, the rate of hydrolysis of sodium trimeta- and tetrametaphosphates in water is faster than or almost the same as that in dioxane-water. Consequently, the mechanism of the hydrolysis of both the metaphosphates in basic solutions seems to differ from that in acidic solutions. The increase in the rate of hydrolysis of small-ring phosphates in acidic solutions depends upon the activation energy and frequency factor, while that in basic solutions depends significantly upon the frequency factor. This may cause the difference in the solvent effect on the rate of hydrolysis of small-ring phosphates between acidic and basic solutions. The activation energy of the hydrolysis of both ring phosphates was 20—40 kcal/mol in the pH range of 1.0—12.5. The rate of hydrolysis of the metaphosphates in an aqueous sodium hydroxide solution is faster than that in an aqueous tetramethyl ammonium hydroxide solution and this can be attributed to catalysis by a sodium ion. The hydrolysis of sodium tripolyphosphate was also carried out in basic water and dioxane-water solvents. The solvent effect on the rate of hydrolysis of tripolyphosphate in basic solutions was the same as that in acidic solutions.

The solvent effect on organic reactions has been studied by many investigators.[1,2] An S_N1 reaction is generally accelerated in an ionizing solvent, while the solvent effect on an S_N2 reaction is complex. The hydrolysis of condensed phosphates has never been considered from the viewpoint of the exact interaction between a phosphate and a water molecule. In previous works[3,4] by the present authors, the hydrolysis of sodium pyro-, tripoly-, and long-chain polyphosphates was carried out in water, formic acid–water, acetic acid–water, and dioxane–water solvents. Formic acid and acetic acid are so-called protic solvents and dioxane is a dipolar aprotic solvent.[5] It was concluded from the kinetic data that the nucleophilic attack of a water molecule on a phosphorus atom of pyro-, tripoly- (in acidic solution), and long-chain polyphosphates (in basic solution) plays an important role in the hydrolytic degradation of the phosphates. It is well known that the hydrolysis of short-chain phosphates is an acid-catalyzed reaction and that of small-ring phosphates is an acid- and base-catalyzed reaction.[6] The reason for the different hydrolytic reactivity between the short-chain and small-ring phosphates has never been discussed. In the present paper, the hydrolysis of sodium trimeta- and tetrametaphosphates will be accomplished in the same types of solvent mentioned above in order to obtain some information about the hydrolytic mechanism of the small-ring phosphates.

Experimental

Materials and Procedure. All the materials used other than the sodium trimeta-, tetrameta-, and tripolyphosphates were of commercial grade. Sodium trimetaphosphate hexahydrate, sodium tripolyphosphate hexahydrate, and sodium tetrametaphosphate tetrahydrate were prepared by the method described in Refs. 7 and 8. The solvents used in this experiment are listed in Table 1. The pH's of the phosphate solutions with water and dioxane-water solvents were controlled with nitric acid and/or aqueous tetramethyl ammonium hydroxide at reaction temperature by using a Hitachi-Horiba pH meter, F-5. The pH of the phosphate solution with formic acid-water did not change at any time, while those of the solutions with water and dioxane-water changed with the reaction time elapsed. Therefore, aqueous tetramethyl ammonium hydroxide or nitric acid was added to restore them to the proper pH. The pH adjustment was made to within ±0.1 unit of the desired pH value. For the hydrolysis of sodium trimeta- and tetrametaphosphates in basic water and dioxane-water solvents, aqueous sodium hydroxide was also used to obtain the required pH value in order to compare the hydrolysis of the phosphates with that in an aqueous tetramethyl ammonium hydroxide solution. Since a sodium ion is considered to act as a catalyzer for the hydrolysis of polyphosphates,[9–11] an equal volume of aqueous sodium hydroxide was added to each solvent in all conditions studied and the pH adjustment was made by using nitric acid; the concentration of the sodium ion was

TABLE 1. SOLVENTS USED FOR THE HYDROLYSIS OF TRIMETA- AND TETRAMETAPHOSPHATES

Solvent	Symbol
35 vol% aqueous dioxane	S_1
21 vol% aqueous dioxane	S_2
Water	S_3
Formic acid-water	S_4

TABLE 2. COMPOSITION OF THE SOLVENTS USED FOR PAPER-CHROMATOGRAPHY[12)]

Acidic solvent		Basic solvent	
isopropyl alcohol	70 ml	isopropyl alcohol	20 ml
25% aqueous trichroloacetic acid	20 ml	dimethylfolmamide	20 ml
water	10 ml	methyl ethyl ketone	20 ml
28% aqueous ammonia	0.3 ml	water	39.1 ml
		28% aqueous ammonia	0.9 ml

1.11 mol/l. The initial concentration of the phosphates was 0.025 mol/l. This concentration is suitable for analysis. The 0.025 mol/l concentration of the phosphates in the acidic S_1 solvent having pH values smaller than 2 and that in the basic S_2 solvent produced nearly saturated concentration. After the pH adjustment of a sample solution was completed at the reaction temperature, 10 μl of the sample solution was spotted on Toyo No. 51A filter paper (2×50 cm) for the paper-chromatographic separation of the phosphates. At measured time intervals, further samples were similarly taken for quantitative chromatographic analysis. When the pH of the sample solution was larger than 11, the separation of each phosphate on the chromatagram is not complete. Therefore, after the basic sample solution was acidified with nitric acid, the acidified solution was spotted on the filter paper. Development was made by using an acidic (for the separation of polyphosphates) and basic (for the separation of metaphosphates) solvents[12)] at 3 °C. The composition of the solvents is listed in Table 2. Each band of the phosphates on the filter paper was identified by the same treatment of a reference solution of known phosphates. The colorimetric determination of each band on the filter paper was carried out by using the method of a previous paper.[3)]

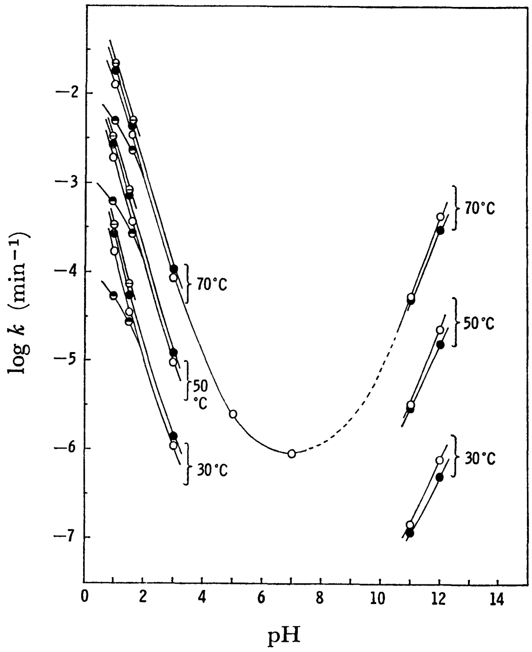

Fig. 2. pH dependence of rate constant of the hydrolysis of tetrametaphosphate.[a)]
⊖: S_1,[b)] ●: S_2, ○: S_3, ◓: S_4
a) pH adjustment was made by aqueous tetramethyl ammonium hydroxide and nitric acid.
b) The symbol refers to Table 1.

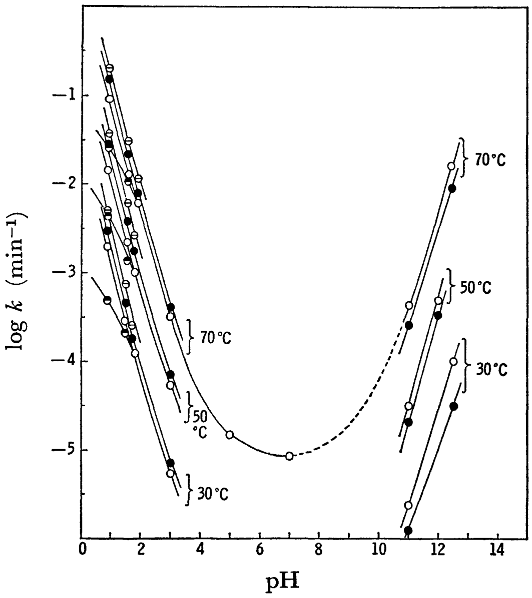

Fig. 1. pH dependence of rate constant of the hydrolysis of trimetaphosphate.[a)]
⊖: S_1,[b)] ●: S_2, ○: S_3, ◓: S_4
a) pH adjustment was made by aqueous tetramethyl ammonium hydroxide and nitric acid.
b) The symbol refers to Table 1.

Results and Discussion

Order of Reaction and the pH Dependence of the Reaction Rate. The rate of the hydrolysis of sodium trimeta-, tetrameta-, and tripolyphosphates follows first-order kinetics with respect to the concentration of the phosphates under all conditions studied. The pH dependences of the rate constant for trimeta- and tetrametaphosphates are shown in Figs. 1 and 2, respectively. In all solvents, the rates of hydrolysis of both the metaphosphates decreases in acidic solutions and increases in basic solutions with an increase in the pH value. The rate is slowest in a neutral solution. Therefore, the hydrolysis of both the metaphosphates is an acid- and base-catalyzed reaction. The results agree well with those reported in previous papers.[6)] To obtain information concerning the mechanism of the hydrolysis of trimeta- and tetrametaphosphates, the activation energy and log *A* (*A*: frequency factor) of the hydrolysis of both the phosphates were calculated by means of an Arrhenius plot and are listed in Table 3. In all acidic solutions, the activation energy of the hydrolysis of both the metaphosphates increases and the log *A* of the hydrolysis of both the metaphosphates decreases with an increase in the pH value. Accordingly, the increase in the rate of hydrolysis of both the metaphosphates in acidic solutions depends on the

Table 3. Activation energies, ΔE_A (kcal·mol^{-1}), and log A(A: frequency factor) of the hydrolysis of trimeta- and tetrametaphosphates

pH[a)]	Solvent[b)]	Phosphate[c)]	ΔE_A	log A
1.0	S_1	M_3	19.8	11.8
		M_4	22.8	12.9
	S_2	M_3	20.2	12.0
		M_4	23.1	12.9
	S_3	M_3	20.7	12.1
		M_4	23.6	12.9
	S_4	M_3	21.2	11.9
		M_4	23.9	12.9
2.0	S_1	M_3	20.1	11.1
		M_4	23.0	11.9
	S_2	M_3	20.3	10.8
		M_4	24.2	12.6
	S_3	M_3	21.8	11.6
		M_4	24.8	12.9
11.0	S_2	M_3	27.6	14.0
		M_4	30.6	13.2
	S_3	M_3	27.3	14.0
		M_4	30.6	13.6
12.0	S_2	M_3	29.3	16.2
		M_4	33.0	17.5
	S_3	M_3	27.5	15.3
		M_4	32.6	17.4

a) pH adjustment was made by using aqueous tetramethyl ammonium hydroxide and nitric acid. b) Solvents refer to Table 1. c) M_3 and M_4 stand for sodium trimeta- and tetrametaphosphates, respectively.

activation energy and frequency factor. In basic solutions, as the pH rises, the rate and activation energy of the hydrolysis of both the metaphosphates increase. Therefore, the increase in the rate of hydrolysis of both the metaphosphates in basic solutions is strongly dependent on the frequency factor.

The Stability of Tetrametaphosphate. The rate of hydrolysis of trimetaphosphate is about 4—30 times faster than that of tetrametaphosphate under all the conditions studied. The results agree well with those obtained by other investigators.[6)] In the case of the hydrolysis of short-chain polyphosphates, generally, the longer the chain of the phosphate, the faster is the reaction rate. 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.[6)] According to Griffith and Rutt,[13)] a trimetaphosphate ion has a D_{3h} symmetry (planer form) and a tetrametaphosphate ion has a 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. It can reasonably be concluded from the data in Table 3 that the stability of tetrametaphosphate against hydrolytic scission depends mainly on the activation energy.

The Solvent Effect on the Rate of Hydrolysis. As is shown in Figs. 1 and 2, in acidic solutions, the rate of hydrolysis of trimeta- and tetrametaphosphates in water is slower than that in dioxane–water and faster than that in formic acid–water at the same pH value. In an acidic dioxane–water solvent, as the content of dioxane increases, the rate constants of both the phosphates increase for all pH values. The rates of hydrolysis of both the metaphosphates in the acidic S_1 and S_2 solvents are about 2.1—2.6 and 1.6—2.0 times faster, respectively, than that in the acidic S_3 solvent for all pH values. While the rates of hydrolysis of both the metaphosphates in the S_4 solvent are about 3.3—3.6 and 1.3—1.6 times slower, respectively, than that in the S_3 solvent at respective pH values of 0.9 and 1.5 (the concentrations of formic acid at the pH values of 0.9 and 1.5 are about 30 and 10%, respectively), that is, the difference in the rate constants for the S_3 and S_4 solvents is larger at smaller pH values. This can reasonably be explained in terms of the difference in the nucleophilicity of the water molecule in each solution as follows; since formic acid (protic solvent) combines with a water molecule by means of a hydrogen bond (solvation), the nucleophilicity of the water molecule for the phosphorus atom of the phosphates may decrease, and since the oxygen atom of dioxane forms a hydrogen bond with the hydrogen atom of the water molecule and since, consequently, the hydrogen bond between water molecules may be broken, the nucleophilicity of the water molecule for the phosphorus atom of the phosphates may increase in the S_1 and S_2 solvents. When the nucleophilicity of the water molecule decreases through the hydrogen bond with the acid, the hydrolysis of the phosphate may become energetically disadvantageous and the approach of the water molecule to the phosphorus atom of the phosphates may also be prevented. The results given in Table 3 seem to support this contention, because the activation energy of hydrolysis of both the metaphosphates in the S_3 solvent is larger than those in the S_1 and S_2 solvents and is smaller than that in the S_4 solvent at pH 1 and 2. These results are in good agreement with those for the hydrolysis of pyro- and tripolyphosphates.[3)] Since the overall-reaction rate of the hydrolysis of both the metaphosphates is highly dependent upon the nucleophilicity of a water molecule in the acidic solution, the rate-determining step of the hydrolysis of both the metaphosphates in an acidic solution may be the nucleophilic attack of a water molecule on the phosphorus atom of the phosphates and the reaction may be of the S_N2 type.[3,4)]

In basic solutions, as is seen in Figs. 1 and 2, the rate of hydrolysis of both the metaphosphates in the S_3 solvent is faster than that in the S_2 solvent at all temperatures and pH values, and the activation energy of hydrolysis of both the metaphosphates in the S_3 solvent is smaller than or the same as that in the S_2 solvent at pH 11 and 12. This tendency is completely contrary to that in an acidic solution. The hydrolysis of sodium tripolyphosphate was also studied at 50 °C in the S_2 and S_3 solvents at pH 11.0, in order to compare the behavior of polyphosphate with that of trimeta- and tetrametaphosphates in basic solutions. The pH adjustment of the tripolyphosphate solutions was made by using nitric acid and aqueous tetramethyl ammonium hydroxide. The rate constants of the hydrolysis of tripolyphosphate in the S_2 and S_3 solvents at pH 11.0 are 3.27×10^{-6} and 1.54×10^{-6} min^{-1}, respectively. This tendency of the solvent effect on the rate of the hydrolysis of tripolyphosphate is the same as that in acidic solutions[3] and it can be concluded that the mechanism of the hydrolysis of short chain polyphosphates in basic solutions is analogous to that in acidic solutions. However, according to the above results, the mechanism of the hydrolysis of trimeta- and tetrametaphosphates in basic solutions differs from that in acidic solutions. The difference in the rates of hydrolysis of both the metaphosphates in the basic S_2 and S_3 solvents cannot be reduced to the difference in the nucleophilicities of the water molecule in each solvent. Therefore, it can hardly be considered that the nucleophilic attack of a water molecule on the phosphorus atom of the metaphosphates has the most important influence on the overall-reaction rate of the hydrolysis of trimeta- and tetrametaphosphates in basic solutions. As mentioned above, the acceleration of the rate of hydrolysis of both the metaphosphates in basic solutions depends very much upon the entropy term (as is clearly seen by comparing the results in Tables 3 and 4, the increase in the rate of hydrolysis of both the metaphosphates by a sodium ion is also highly dependent upon the frequency factor), while the increase in the rate of hydrolysis of both the metaphosphates in acidic solutions depends upon both the activation energy and frequency factor. This may be the reason for the difference in the solvent effects on the rate of hydrolysis of both the metaphosphates in acidic and basic solutions.

The Effect of the Sodium Ion. The hydrolysis of sodium trimeta- and tetrametaphosphates was also carried out in the S_2 and S_3 solvents at pH 12.5 and at 30, 40, 50, and 60 °C by adjusting the pH of the solutions with aqueous sodium hydroxide and nitric acid. The kinetic data are listed in Table 4. As is seen by comparing the data in Table 4 and those in Figs. 1 and 2, the rate of hydrolysis of both the metaphosphates in aqueous sodium hydroxide is very much faster than that in aqueous tetramethyl ammonium hydroxide in any solvent, and at all temperatures, and pH values. This can be attributed to catalysis by a sodium ion, because, excluding the concentration of sodium ions, the other conditions of the trimeta- and tetrametaphosphate solutions of aqueous sodium hydroxide are the same as those of aqueous tetramethyl ammonium hydroxide. The activation energies of the hydrolysis of both the metaphosphates in aqueous tetramethyl ammonium hydroxide at pH 12.5 were calculated by using an Arrhenius plot on the basis of the data obtained by extrapolating the lines in Figs. 1 and 2. The activation energy of the hydrolysis of trimetaphosphate was 34 kcal/mol in the S_2 solvent and 33 kcal/mol in the S_3 solvent, and that of tetrametaphosphate was 30 kcal/mol in the S_2 solvent and 27 kcal/mol in the S_3 solvent. The rate of hydrolysis of both the metaphosphates in all aqueous sodium hydroxide solutions is nevertheless very much faster than that in any aqueous tetramethyl ammonium hydroxide solution, the activation energy of the hydrolysis in the faster solutions being larger than in the latter solutions. Therefore, the increase in the rate of the hydrolysis of both trimeta- and tetrametaphosphates in basic solutions by a sodium ion depends entirely upon the frequency factor. As Table 4 shows, the rate of hydrolysis of trimetaphosphate in the S_3 solvent is about 1.5—1.7 times faster than that in the S_2 solvent, and the rate of hydrolysis of tetrametaphosphate in the S_3 solvent is the same as that in the S_2 solvent. The solvent effect on the rate of hydrolysis of both the metaphosphates in alkaline solutions differs from that in acidic solutions. Therefore, the nucleophilic attack of a water molecule on the phosphorus atom of the metaphosphates has little influence on the overall-reaction rate of the hydrolysis of both the phosphates in alkaline solutions. As stated above, the increase in the rate of hydrolysis of both the metaphosphates in alkaline solutions depends significantly upon the entropy term, and this may cause the solvent effect on the rate of hydrolysis of both the small-ring metaphosphates in alkaline solutions.

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Table 4. Rate constants (min^{-1}), activation energies, ΔE_A($\mathrm{kcal \cdot mol^{-1}}$), and log A(A: frequency factor) of the hydrolysis of trimeta- and tetrametaphosphates at pH 12.5[a]

Phosphate	Solvent[b]	Temp. (°C) 30	40	50	60	ΔE_A	log A
Trimeta	S_2	4.29×10^{-4}	3.40×10^{-3}	2.39×10^{-2}	1.53×10^{-1}	39.2	24.9
	S_3	7.30×10^{-4}	5.60×10^{-3}	3.78×10^{-2}	2.30×10^{-1}	38.5	24.6
Tetrameta	S_2	3.78×10^{-5}	2.45×10^{-4}	1.52×10^{-3}	8.58×10^{-3}	36.3	21.8
	S_3	3.92×10^{-5}	2.52×10^{-4}	1.43×10^{-3}	8.37×10^{-3}	36.3	21.7

a) pH adjustment was made by using aqueous sodium hydroxide and nitric acid. The concentration of sodium ion is 1.11 mol/l. b) Solvents refer to Table 1.

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