The Mechanism of the Hydrolysis of Condensed Phosphates. II. The Mechanism of the Degradation of Long-chain Polyphosphates

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The hydrolysis of long-chain polyphosphates (Graham's salt) was carried out in water and dioxane–water solvents at various pHs in the range from 3.0 to 11.0 and at 30, 50, and 70 °C. The rates of the hydrolytic degradation of the polyphosphates into shorter chains and into trimetaphosphate obeyed the first-order kinetics with respect to the concentration of the polyphosphates. In acidic media, a small solvent effect was perceived on the rates of both the processes. On the other hand, in basic media the effect was very remarkable; that is, the rates of both the processes in the dioxane–water solvent were more rapid than in water. The results show that the rate of the hydrolysis of both the processes in basic media may be very dependent on the step of the nucleophilic attack of a water molecule on the phosphorus atom of phosphates, while in acidic media other factor, for example, the folding of the chains to a helix, may affect the overall rate. The activation energies for the two processes have been found to be 22—26 kcal/mol in the pH range from 3.0 to 7.0.

The hydrolysis of long-chain polyphosphates has been studied by several investigators.[1–4] According to them, there are two processes for the hydrolytic degradation of the polyphosphates. One is the hydrolysis into shorter chains, and the other is the degradation into trimetaphosphate. Both the processes have been found to be pH-dependent and to be catalytically accelerated by metal ions. The catalytic effect increases in this order; $K<Na<Li<Ba<Sr<Ca<Mg<Al$. Their kinetic studies also prove that the processes follow a first-order law with respect to the concentration of polyphosphates. In our own previous paper,[5] the solvent effect on the hydrolysis of pyro- and tripolyphosphates was examined from the viewpoint of the nucleophilicity of a water molecule. In the present paper, the solvent effect on the hydrolysis of the polyphosphates will be examined by using dioxane–water and water as solvents at various pH values and temperatures. Since the hydrolysis of the polyphosphates at a low temperature is very slow, only the hydrolysis at 70 °C was achieved for all the pH values.

Experimental

Materials and Procedure. All the materials used other than the glassy, high-molecular-weight polyphosphates (Graham's salt) were of a commercial grade. The polyphosphates were prepared by heating monosodium orthophosphate in a platinum crucible at 1000 °C for 3 hr and by then rapidly quenching the resulting melt by placing the crucible in ice water. Since the polyphosphates invariably contained 2—3% (as phosphorus %) of trimetaphosphate, the corresponding adjustment was made to the analytical results of the contents of the hydrolysis products. Water and 15 vol% aqueous dioxane were employed as solvents. The initial concentration of the polyphosphates was 0.025 mol/l. About 25 ml of the solution was transferred into a test tube, and the pH of the solution was controlled at a reaction temperature by adding nitric acid and aqueous tetramethylammonium hydroxide or sodium hydroxide by means of a Hitachi-Horiba pH meter, F-5. The test tube was stoppered to prevent evaporation of the solvent. The tube was then placed in water in a thermostat, and the temperature was maintained at 30, 50, or 70±0.05 °C. A measured sample of this solution was withdrawn by using a microsyringe as soon as the treatment mentioned above was finished; this sample was spotted on to chromatograms. At measured intervals of time, further samples were similarly taken out for quantitative chromatographic analysis. The pH of the solutions was periodically measured and maintained at the required pH by adding nitric acid, aqueous tetramethylammonium hydroxide, or aqueous sodium hydroxide. The pH adjustment of the solution by adding sodium hydroxide was made only at pH 11.0. Since the sodium ion affects the rate of the hydrolysis of the polyphosphates, the quantity of the sodium ion in water and dioxane–water solvents was made identical. The pH adjustment was done within ±0.2 pH unit of the required value.

Chromatography. One-dimensional paper-chromatographic separation were carried out by using filter paper of Toyo No. 51A of 2×50 cm. Sample solutions (8 μl) were placed at the starting point of the filter paper and developed at 3 °C for 50 hr by using an acidic or basic solvent. After the development, the chromatograms were dried in an oven at 75 °C for more than 30 min and then sprayed with a perchloric acid molybdate solution.[6] The papers were subsequently dried for about 10 min at 50 °C and exposed to ultraviolet rays until blue zones appeared. The compositions of the acidic and basic solvents are tabulated in Table 1. The former was used for the separation of ortho-, pyro-, tripoly-, and long-chain polyphosphates, while the latter was used for the separation of trimeta- and tetrametaphosphates.

Quantitative Analysis of Phosphates on Chromatograms. The contents (P%) of phosphates on the chromatograms were determined by means of the same colorimetric method used in our previous paper,[5] using a Hitachi 101 spectrophotometer.

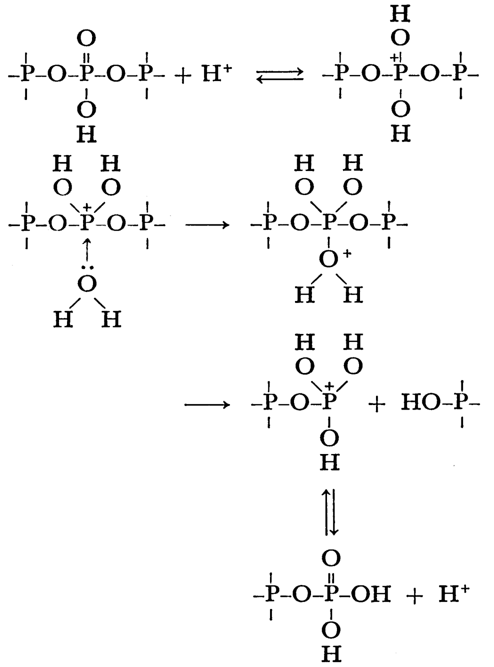
TABLE 1. COMPOSITION OF THE SOLVENTS USED FOR PAPER CHROMATOGRAPHY

Acidic solvent	Isopropyl alcohol	70 ml
	25% aqueous trichloroacetic acid	20 ml
	Water	10 ml
	28% aqueous ammonia	0.3 ml
Basic solvent	Isopropyl alcohol	20 ml
	Dimethylformamide	20 ml
	Methyl ethyl ketone	20 ml
	Water	39.1 ml
	28% aqueous ammonia	0.9 ml

Results and Discussion

All attempts to obtain high-molecular-weight polyphosphates free from a trimeta-ring were unsuccessful. The average chain length of the polyphosphates was measured by the pH titration method[7,8] and found to be about 100. The straightforward hydrolytic degradation of the polyphosphate chains into shorter chains and their degradation to trimetaphosphate occurred according to a first-order law with respect to the concentration of polyphosphates under all the conditions studied. The values of the specific rate constants, k_H for the hydrolysis of polyphosphates, and k_D for the splitting out of trimetaphosphate, are listed in Table 2 for the various temperatures and pH values. Since the rates of the hydrolysis of trimetaphosphate at pH 3.0 and 11.0 can not be ignored in comparison with that of the formation of trimetaphosphate from the polyphosphates, k_D was not measured at those pH values. In the case of the hydrolysis of the polyphosphates in a water solvent, both the rate constants decrease with an increase in the pH value at any reaction temperature. This tendency has been well substantiated.[1-4] However, the decrease at 50 and 70 °C in the pH range from 7.0 to 9.0 seems to be less than that obtained by Gill and Riaz.[4] This may be attributed to the difference in cations added to the polyphosphate solutions for the adjustment of the background pH. As for the hydrolysis of the polyphosphates in the dioxane–water solvent, the pH-dependency of both the reaction constants is not the same as that in a water solvent. In an acidic medium, both the rate constants of the reactions in the dioxane–water solvent are the same as, or a little smaller than, those of the reactions in a water solvent at the same pH value. On the other hand, in the polyphosphate solutions with pH values larger than 7.0, the reaction rates of both the processes in the aqueous dioxane are faster than those in a water solvent; the larger the pH value of the solution, the more remarkable is this tendency.

In our previous paper,[5] the solvent effects on the hydrolysis of pyro- and tripolyphosphates have been studied, and it has been concluded that a water molecule in aqueous dioxane has a larger nucleophilicity than in water throughout the pH range from 1.0 to 2.5. From the results of the examination of the catalytic effect of metal cations on the polyphosphate degradation, Wieker and Thilo proposed a mechanism for the degradation.[3] According to them, a positivation of the phosphorus atoms of the polyphosphates may be supposed to be the reason for the catalytic effect of the metal cations. In our previous work,[5] taking into account the findings that the hydrolyses of pyro- and tripolyphosphates are acid-catalyzed reactions, the same positivation of the phosphorus atoms of the phosphates was also proposed for the hydrolysis of the phosphates. On the basis of these results, and considering that the hydrolysis of the polyphosphates is also an acid-catalyzed reaction, one can describe a series of elementary reactions for the hydrolysis of the polyphosphates as follows:



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

$$-\mathrm{P}-\mathrm{O}-\underset{\uparrow\,\ddot{\mathrm{O}}\mathrm{H}_2}{\overset{\mathrm{HO}\;\mathrm{OH}}{\mathrm{P}^+}}-\mathrm{O}-\mathrm{P}- \longrightarrow -\mathrm{P}-\mathrm{O}-\underset{\mathrm{O}^+\mathrm{H}_2}{\overset{\mathrm{HO}\;\mathrm{OH}}{\mathrm{P}}}-\mathrm{O}-\mathrm{P}- \qquad (2)$$

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

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

Table 2. Rate constants (min^{-1}) of the degradation of polyphosphates

		Reaction temp. (°C)					
		30		50		70	
pH	Solvent[a]	k_H	k_D	k_H	k_D	k_H	k_D
3.0	S_1	2.90×10^{-5}		4.29×10^{-4}		4.74×10^{-3}	
	S_2	2.73×10^{-5}		4.07×10^{-4}		4.39×10^{-3}	
5.0	S_1			1.10×10^{-5}	4.52×10^{-6}	1.97×10^{-4}	5.51×10^{-5}
	S_2			1.14×10^{-5}	3.56×10^{-6}	1.74×10^{-4}	4.40×10^{-5}
7.0	S_1	6.80×10^{-7}	4.04×10^{-7}	6.99×10^{-6}	4.40×10^{-6}	5.50×10^{-5}	3.62×10^{-5}
	S_2	7.80×10^{-7}	5.48×10^{-7}	7.84×10^{-6}	5.31×10^{-6}	6.40×10^{-5}	4.02×10^{-5}
9.0	S_1			6.55×10^{-6}	3.02×10^{-6}	5.40×10^{-5}	3.55×10^{-5}
	S_2			9.79×10^{-6}	5.45×10^{-6}	8.38×10^{-5}	5.41×10^{-5}
11.0	S_1			5.79×10^{-6}		5.31×10^{-5}	
	S_2			1.00×10^{-5}		9.57×10^{-5}	
11.0	S_1Na					1.09×10^{-4}	
	S_2Na					1.95×10^{-4}	

a) S_1 and S_2 stand for water and 15 vol % aqueous dioxane respectively, and Na represents that the pH of the solution is controlled by aqueous sodium hydroxide.

For the hydrolysis of the polyphosphates in a basic solution, the second step can be considered to be the rate-determining step, because the rate of the hydrolysis of both the processes is very dependent on the nucleophilicity of a water molecule.

Because of the formation of ring phosphates larger than trimetaphosphate as hydrolysis products of polyphosphates, it has been concluded that, when polyphosphates are dissolved into water, the folding of the chain into a helix occurs with a random number of PO_4 tetrahedra in the repeating units, and that in the repeating unit of three PO_4 tetrahedra is statistically the most likely. In an acidic medium, it can hardly be considered that the first, second, and fourth steps influence the rate of the overall-hydrolytic reaction of polyphosphates, because the steps may be very rapid reactions. Since no solvent effect as in a basic medium is recognized in acidic systems, the rate of the overall reaction may be little dependent on the third step. Therefore, the overall-reaction rate seems to reflect the effects of other factors—for example, the folding of the chain into a helix. In order to examine the idea, the activation energies and log A (A; frequency factor) at pH 3.0 (for k_H) and 7.0 (for k_H and k_D) were calculated by the use of an Arrhenius plot; they are listed in Table 3. For the overall-hydrolytic degradation of the polyphosphates, in spite of the increase in the reaction rate, the activation energy increases with a decrease in the pH value. This result suggests that the contribution of an entropy term to the rate of the degradation is more important than that of an energy term in an acidic solution, and seems to support the consideration concerning the hydrolytic mechanism of polyphosphates presented above. The activation energies, listed in Table 3, of the degradation of the polyphosphates into trimetaphosphate at pH 7.0 are very similar to that obtained by Gill and Riaz.[4]

TABLE 3. ACTIVATION ENERGY, ΔE_A (kcal/mol) AND log A (A; FREQUENCY FACTOR) OF THE HYDROLYSIS OF POLYPHOSPHATES

pH	Solvent[a]	Process[b]			
		P_1		P_2	
		ΔE_A	log A	ΔE_A	log A
3.0	S_1	26.2	14.4		
	S_2	26.2	14.3		
7.0	S_1	22.7	10.2	23.3	10.4
	S_2	22.4	10.0	22.1	9.7

a) S_1 and S_2 represent water and 15 vol% aqueous dioxane respectively. b) P_1 and P_2 stand for the hydrolysis of polyphosphates and the hydrolytic splitting out of trimetaphosphate respectively.

The results of the hydrolytic degradation of the polyphosphates in an aqueous sodium hydroxide solution are also listed on the lowest two lines in Table 2. It can clearly be seen that sodium ions have a catalytical effect on the hydrolysis of polyphosphates and that the solvent effect is also very remarkable.

References

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2) W. Wieker and E. Thilo, *ibid.*, **306**, 48 (1960).

3) W. Wieker and E. Thilo, *ibid.*, **313**, 296 (1961).

4) J. B. Gill and S. A. Riaz, *J. Chem. Soc.*, *A*, **1969**, 183.

5) M. Watanabe, This Bulletin, **47**, 2048 (1974).

6) The perchloric acid molybdate solution was made by mixing 200 ml of 5% aqueous ammonium molybdate, 10 ml of conc. hydrochloric acid, and 50 ml of 70% aqueous perchloric acid and by then diluting the solution to 1000 ml with water.

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