The Mechanism of the Hydrolysis of Condensed Phosphates. I. The Solvent Effect on the Hydrolysis of Pyro- and Tripolyphosphates

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The hydrolysis of pyro- and tripolyphosphates was run in formic acid–water, acetic acid–water, dioxane–water, and water solvents with an initial concentration of 0.025 mol/l. The hydrolysis of both the phosphates followed first-order kinetics with respect to the concentration of the phosphate under all the conditions studied. The rate of the hydrolysis of both the phosphates in the formic acid–water and acetic acid–water solvents is slower, and that in dioxane–water solvent is faster, than in water. From the results, it has been concluded that, in the formic acid–water and acetic acid–water solvents, the nucleophilicity of the water molecule may decrease on account of the hydrogen bond of the water molecule with these acids, while, in the dioxane–water solvent, since the scission of the hydrogen bond between water molecules may occur by the interaction of the dioxane and the water molecules, the nucleophilicity of the water molecule may increase. The activation energy of the hydrolysis of the phosphates was 19—28 kcal/mol and increased with an increase in the pH value of a solution. The hydrolysis of pyro- and tripolyphosphates has been concluded to be a S_N2 reaction; the rate-determining step may be the nucleophilic attack of a water molecule on the phosphorus atom of the phosphates.

Many papers concerning the hydrolysis of condensed phosphates have been published during the last hundred years. The previous works on the hydrolysis of condensed phosphates have, however, been done chiefly for the purpose of determining the rate constant at a constant pH and of examing the effect of cations on the hydrolysis, rather than for studying the exact interaction of phosphates with the water molecule. It is well known that the hydrolysis of condensed phosphate in a several percent aqueous solution exhibits first-order kinetics with respect to the concentration of phosphate. The effect of the pyrophosphate concentration on the linearity of the rate plot was examined by Campbell and Kilpatrick.[1] In the present paper, the kinetics of the hydrolysis of pyro- and tripolyphosphates will be studied from the viewpoint of the nucleophilicity of a water molecule.

Experimental

Materials and Procedure. All the materials used other than the sodium tripolyphosphate were of a commercial grade. The sodium tripolyphosphate, I, was made by the method described in Reference[2] and was purified by recrystallization. The solvents employed in this experiment are listed in Table 1. When the solvent was water or aqueous dioxane, the pH of the solution was controlled with nitric acid and aqueous tetramethyl ammonium hydroxide by using a Hitachi-Horiba pH meter, F-5. The initial concentration of sodium pyro- and tripolyphosphate was 0.025 mol/l. About 25 ml of the solution was transferred to a test tube, and the tube was stoppered to prevent evaporation of the solvent. The test 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 the solution was withdrawn after the temperature of the solution in the test tube had reached the required temperature by using a microsyringe and spotted on to chromatograms. At measured intervals of time, further samples were similarly taken for quantitative chromatographic analysis. The pH of the solution was periodically measured. In the case of the formic acid–water and acetic acid–water solvents, the pH of the solution of the phosphates was not changed at any time, while in the case of the water and dioxane–water solvents, the pH of the solution was changed. Therefore, if they were in need of adjustment, enough tetramethyl ammonium hydroxide or nitric acid was added to bring them back to the proper pH. The pH adjustment was made within ±0.05 pH unit of the required value.

TABLE 1. SOLVENTS USED FOR THE HYDROLYSIS OF PYRO- AND TRIPOLYPHOSPHATES

Solvent	Symbol
35 vol% aqueous dioxane	S_1
25 vol% aqueous dioxane	S_2
15 vol% aqueous dioxane	S_3
Water	S_4
Formic acid–water	S_5
Acetic acid–water	S_6

Chromatography. One-dimensional paper-chromatographic separations were carried out by using filter paper of Toyo No. 51A of 2×50 cm. Samples of the phosphate solution (10 μl) were placed at the starting point of the filter paper and developed at 5 °C for 50 hr by using an acidic solvent; then the chromatograms were dried in an oven at 75 °C for more than 30 min. The acidic solvent was made by mixing 70 ml of isopropyl alcohol, 20 ml of 25% aqueous trichloroacetic acid, 10 ml of water, and 0.3 ml of 28% aqueous ammonia. The papers were then sprayed with a perchloric acid-molybdate solution, which had been 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. The paper was subsequently dried for about 10 min at 50 °C and exposed to ultraviolet rays until blue zones appeared.

Quantitative Analysis of Phosphates on Chromatograms. Every individual spot on the chromatogram was cut at the demarcation line and transferred to a 100-ml beaker. Ten milliliters of a 0.1 M-ammonium hydroxide solution were then added to the beaker. After one hr, the solution was transferred to a 25-ml volumetric flask together with 10 ml of wash water, and a 2-ml portion of Lucena-Conde and Prat's reagent[3] was added to the flask. The flask was heated in a boiling-water bath for one hr, subsequently cooled by placing it in a bath of cold water, and diluted to the mark with water. The absorbance of the blue solution was measured with a Hitachi 101 spectrophotometer at 830 nm. The absorbance of a reagent blank was deducted from each of the readings to give a net absorbance for each phosphate fraction. The phosphorus content of each spot was expressed as a portion of the total phosphorus present as follows:

$$P(\%) = \frac{\text{Net absorbance for each fraction}}{\text{Sum of the net absorbances for each fraction}} \times 100$$

Results and Discussion

Order of Reaction and the pH Dependence of the Reaction Rate. The rate of the hydrolysis of pyro- and tripolyphosphates followed first-order kinetics with respect to the concentration of the phosphate under all the conditions studied. The pH dependences of the rate constant of pyro- and tripolyphosphates are shown in Figs. 1 and 2 respectively. In any solvent, the rate constant of the hydrolysis of pyro- and tripolyphosphates increases with a decrease in the pH of the solution. Therefore, the hydrolysis of the phosphates is an acid-catalyzed reaction, as has already been reported by many investigators.[1,4-9] There is a difference between the rate constants of the hydrolysis of pyro- or tripolyphosphate in different solvents at the same pH value. In a dioxane–water solvent, as the content of dioxane increases the rate constant of pyro- and tripolyphosphates increases at any pH value. On the other hand, in the formic acid– and acetic acid–water solvents the reaction rate is slow in comparison with that in the other solvents at the same pH and the difference in the rate constant between the acid solvent and dioxane–water or water solvent is larger at larger pH values (the concentrations of the formic acid at the pH values of 1.1, 1.9, and 2.5 are about 30, 10, and 3.2% respectively, while those of acetic acid at the pH values of 1.3, 1.9, and 2.5 are about 76, 61, and 30% respectively). 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 or acetic acid combines with the water molecule by means of a hydrogen bond, the nucleophilicity of the water molecule for the phosphorus atom of phosphates may decrease, and since dioxane forms a hydrogen bond with 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 phosphates may increase in the dioxane–water solvent. When the nucleophilicity of the water molecule decreases through the hydrogen bond with the acids, the hydrolysis of phosphate may become energetically disadvantageous because of the hydrogen-bond energy, and the approach of the water molecule to the phosphorus atom of phosphate may also be prevented. Accordingly, the activation energy and log A (A; frequency factor) were calculated by means of the Arrhenius plot, and the relation between these values and the reaction process of the hydrolysis of pyro- and tripolyphosphates was considered.

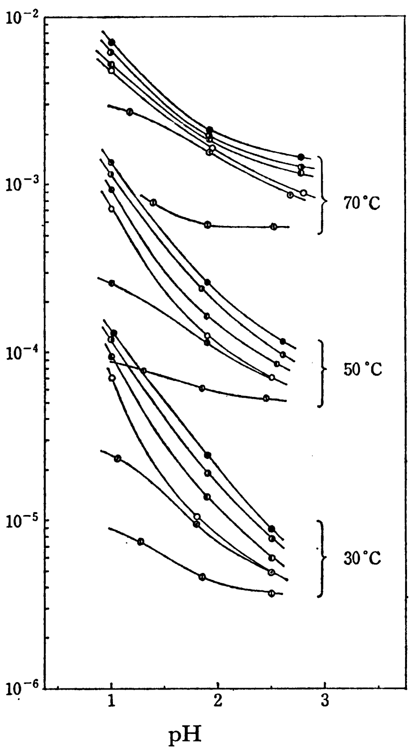


Fig. 1. pH dependence of rate constant of the hydrolysis of pyrophosphate.
●: S_1,[a) ◑: S_2, ◐: S_3, ○: S_4, ⊙: S_5, ⦶: S_6
a) The symbol refers to Table 1.

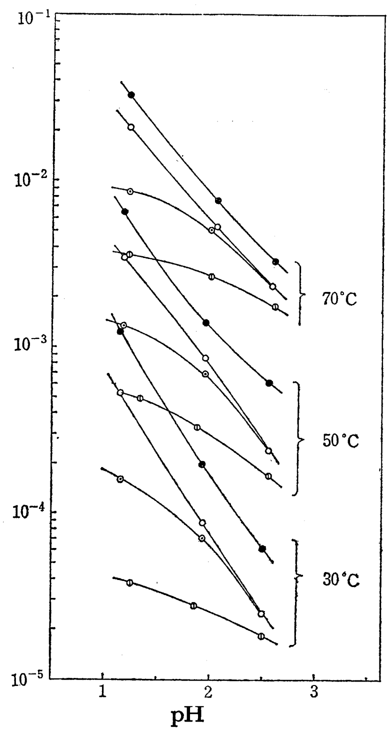


Fig. 2. pH dependence of rate constant of the hydrolysis of tripolyphosphate.
●: S_1,[a) ○: S_4, ⊙: S_5, ⦶: S_6
a) The symbol refers to Table 1.

Activation Energy and log *A*. The activation energy and log A of the hydrolysis of pyro- and tripolyphosphates are listed in Tables 2 and 3 respectively. In any solvent, the activation energy of both the phosphates increases with an increase in the pH value. This tendency is in accordance with the results obtained by Van Wazer and his co-workers,[6] and the values of activation energy are similar to their results. The activation energy of both the phosphates is smaller in the dioxane–water solvent and larger in the formic

TABLE 2. ACTIVATION ENERGY, ΔE_A(kcal·mol^{-1}) AND $\log A$(A: FREQUENCY FACTOR) OF THE HYDROLYSIS OF SODIUM PYROPHOSPHATE

Solvent[a)]	pH= 1.5		2.0		2.5	
	ΔE_A	$\log A$	ΔE_A	$\log A$	ΔE_A	$\log A$
S_1	21.2	11.0	23.8	12.5	26.8	14.3
S_2	22.0	11.5	24.6	12.9	26.8	14.2
S_3	23.9	12.7	26.0	13.8	27.6	14.7
S_4	26.2	14.1	27.3	14.6	28.4	15.1
S_5	26.6	14.3	27.5	14.7	28.4	15.1
S_6	24.6	12.5	24.8	12.5	25.8	13.2

a) Solvents refer to Table 1.

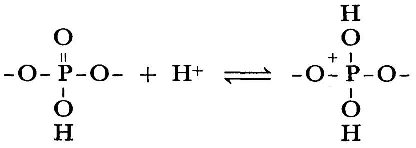
TABLE 3. ACTIVATION ENERGY, ΔE_A(kcal·mol^{-1}) AND $\log A$(A: FREQUENCY FACTOR) OF THE HYDROLYSIS OF SODIUM TRIPHOSPHATE

Solvent[a)]	pH= 1.5		2.0		2.5	
	ΔE_A	$\log A$	ΔE_A	$\log A$	ΔE_A	$\log A$
S_1	19.0	10.4	21.0	11.3	22.1	11.8
S_4	20.9	11.4	22.5	12.1	24.5	13.0
S_5	21.3	11.4	22.9	12.3	24.5	13.0
S_6	23.1	12.2	24.0	12.7	24.6	12.9

a) Solvents refer to Table 1.

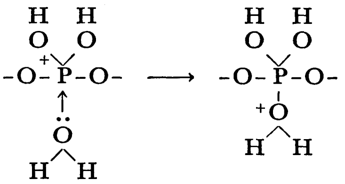
acid–water solvent than in water. In addition, the difference in the activation energy between water and the other solvents increases as the content of formic acid or dioxane increases. The results could be reduced to the formation or scission of the hydrogen bond of the water molecule with formic acid or dioxane respectively. In the acetic acid–water solvent, the hydrolysis of tripolyphosphate has the same solvent effect as that in the formic acid–water solvent, while the hydrolysis of pyrophosphate differs. The activation energy of the hydrolysis of pyrophosphate in the acetic acid–water solvent is smaller than that in water. Therefore, it can be concluded that the effect of entropy term is larger than that of the energy term for the rate of the hydrolysis of pyrophosphate in the acetic acid–water solvent. The compensation effect is valid between the activation energy and the entropy term under all the conditions studied.

Mechanism of Hydrolysis. According to the above results, the hydrolysis of pyro- and tripolyphosphates may be a dipole-dipole-type S_N2 reaction of the classification of Ingold and Hughes.[10)] Since the hydrolysis of pyro- and tripolyphosphates is an acid-catalyzed reaction, the following reaction mechanism can be considered. In an acidic solution, a rapid equilibrium may be set up between the phosphate and hydrogen ion;



$$-O-\overset{\overset{O}{\|}}{\underset{\underset{H}{\overset{|}{O}}}{P}}-O- + H^+ \rightleftharpoons -O-\overset{\overset{\overset{H}{O}}{+|}}{\underset{\underset{H}{\overset{|}{O}}}{P}}-O-$$

The phosphate ion on the right-hand side of the above equation may more readily accept the nucleophilic attack of the water molecule than the phosphate on the left-hand side. The rate-determining step of this reaction may be this next reaction;



$$-O-\overset{\overset{H\ H}{O\ O}}{\underset{\underset{\underset{H\ H}{\ddot{O}}}{\uparrow}}{\overset{+\vee}{P}}}-O- \longrightarrow -O-\overset{\overset{H\ H}{O\ O}}{\underset{\underset{H\ H}{{}^{+}O}}{\overset{\vee}{P}}}-O-$$

Thus, in an acidic solution, a rapider rate process of the hydrolysis of the phosphate may be given. The first-order kinetics of the hydrolysis of pyro- and tripolyphosphates with respect to the concentration of the phosphates can be reduced to the constancy of the activity of the water molecule because of the dilute nature of the concentration of the phosphates.

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