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Alkaline Hydrolysis of Inorganic *cyclo*-Polyphosphates

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The hydrolysis rates of inorganic *cyclo*-polyphosphates in alkaline solutions were determined. The rates in a NaOH solution were significantly faster than those in a $(CH_3)_4NOH$ solution. Ion-pair formation between PO^- and Na^+ renders the P atom more positive by reducing the electron density around the atom and more susceptible to the nucleophilic attack by OH^-. In a $(CH_3)_4NOH$ solution, higher-membered *cyclo*-polyphosphates with a larger ring structure became rather stable. Arrhenius' activation energy for each phosphate decreases in the order $HCl>NaOH>(CH_3)_4NOH$.

As the major compounds of the condensed phosphates produced by the dehydration of the oxoacid of phosphorus oxidation number 5, linear phosphates with linear chain structure and *cyclo*-polyphosphates with cyclic structure consisting of middle P-O-P bond have been well-known.[1] In these condensed phosphates, the chemical properties of linear phosphates with shorter chain length, especially those of di- and triphosphate have been extensively investigated in connection with ADP and ATP, both of which are biochemically important.

In the *cyclo*-polyphosphate series, *cyclo*-tri- and *cyclo*-tetraphosphates have been prepared since earlier time, and the chemical properties have extensively been studied.[1] As in the case of linear phosphates with a polymerization degree larger than four, the investigation about *cyclo*-polyphosphates above pentamer with a ten-membered ring structure has been hindered by the difficulty involved in their preparation or isolation. Since the preparation of *cyclo*-hexa- and *cyclo*-octaphosphate were reported by Griffith and Buxton,[2] and by Schülke,[3] respectively, we have investigated various properties of these higher-memberted *cyclo*-polyphosphates.[4-13]

cyclo-Polyphosphates of the general formula $M^I_n(PO_3)_n$ have a high negative charge on their relatively compact molecule and hence they can be utilized as important electrolytes in aqueous solutions since the anion is very weak as a Brønsted base. These *cyclo*-polyphosphates are very stable in a neutral aqueous solution even if they are boiled up to one hour.

However, in strong acidic or basic solutions, they are easily hydrolyzed and their hydrolysis rate is accelerated, especially by hydrogen ions.[13] Their hydrolysis rate in the alkaline solutions has not been elucidated as systematically as in acidic solutions. We predicted that *cyclo*-polyphosphates in alkaline solution would be hydrolyzed more slowly than in strong acidic conditions. Alkaline hydrolysis of *cyclo*-tetraphosphate was employed for the preparation of linear tetraphosphate.[14-17] In this regard, it is important to clarify the alkaline hydrolysis of *cyclo*-hexa- and *cyclo*-octaphosphate. Hydrolysis data on *cyclo*-penta- and *cyclo*-heptaphosphate could not be obtained since the isolation of both phosphates in sufficient quantity is difficult.[4,8]

Experimental

Materials. Sodium salts of *cyclo*-polyphosphates were prepared by the methods described in the literature.[2,3,18,19] Their purities were checked by an analytical system applied to the analysis of the hydrolysis products.[13]

A tetramethylammonium hydroxide solution was prepared by treating the chloride with an anion-exchange resin of the OH^- form.

All other chemicals used were reagent grade and commercially available.

Analytical System. The separation of *cyclo*-polyphosphates to be hydrolyzed from linear phosphates as hydrolysis products was achieved by an anion-exchange chromatography. As an anion exchanger, TSK Gel SAX 10 μm was used; column dimensions were 4 mm in diameter and 250 mm in height. As an eluting agent, 0.4 mol dm^{-3} KCl of pH 10.2 (plus 0.1% EDTA) was used. The phosphates in the effluent were automatically determined by spectrophotometry with the use of a Mo(V)-Mo(VI) reagent.[11]

Futher details on the analytical system are described in the references.[11-13]

Procedure. The initial concentration of each *cyclo*-polyphosphate to be hydrolyzed was adjusted to 1.25×10^{-3} mol dm^{-3} and the hydrolysis reaction was performed in a water bath, the temperature of which was maintained within ±0.1 °C. At measured time intervals, samples were withdrawn and neutralized with the same equivalents of hydrochloric acid, and stored in a refrigerator until taken out for analysis.

Results and Discussion

Hydrolysis rates of four *cyclo*-polyphosphates in 0.25, 0.5, 0.75, and 1 mol dm^{-3} NaOH solutions at 50 °C were determined by the liquid chromatography. If $[P]_0$ and $[P]_t$ denote the concentration of the phosphate at time zero and t, respectively, log ($[P]_t/[P]_0$) versus t plots for *cyclo*-octaphosphate hydrolysis are shown in Fig. 1 and in each case the rates are first order for the phosphate as

$$-\frac{dc}{dt}=k_{\mathrm{obsd}}c, \qquad (1)$$

where c is the total concentration of the phosphate. Since the hydrolysis rate is also a function of the OH^-

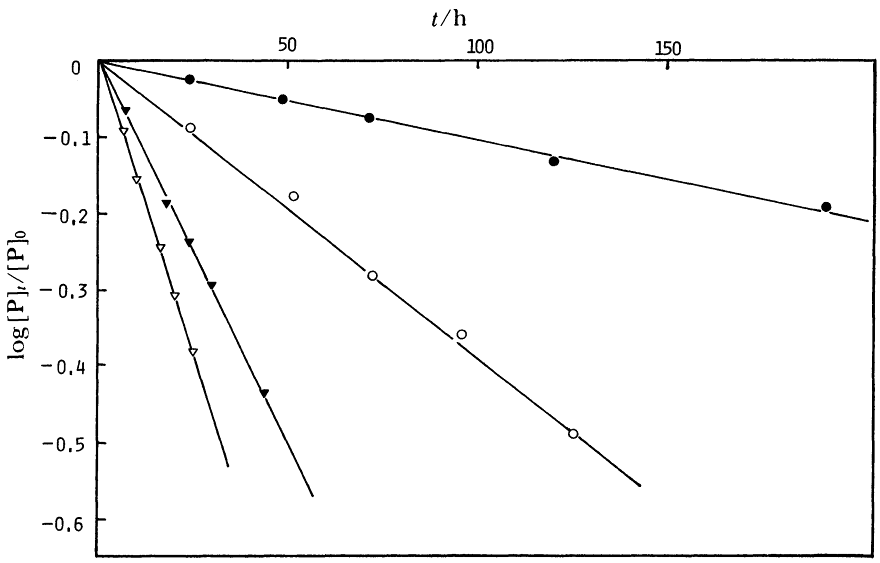


Fig. 1. Hydrolysis rates of *cyclo*-octaphosphate at different NaOH concentrations at 50 °C. ●; 0.25 mol dm^{-3}, ○; 0.5 mol dm^{-3}, ▼; 0.75 mol dm^{-3}, ▽; 1 mol dm^{-3}.

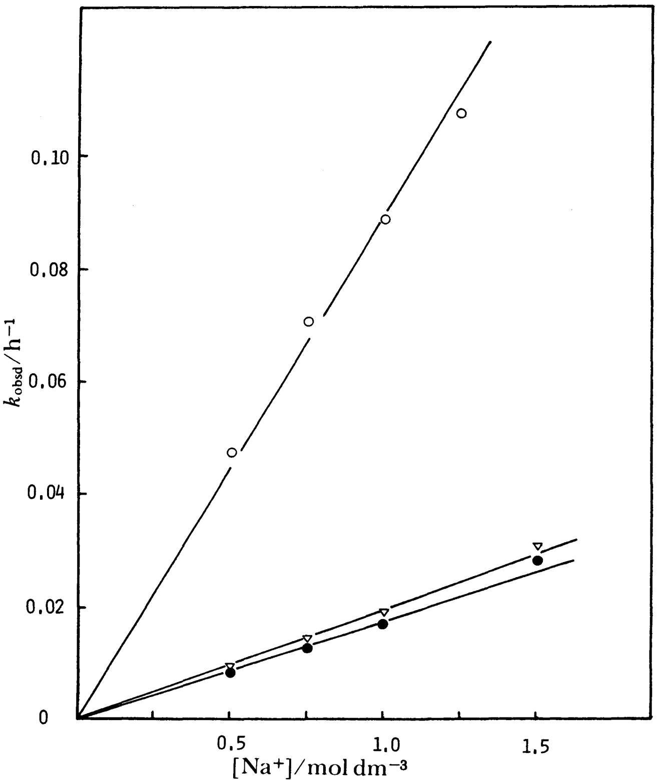


Fig. 2. Plots of the rate constants of *cyclo*-polyphosphates at 50 °C against sodium ion concentration ([OH$^-$]=0.5 mol dm^{-3}). ○; P_{4m}, ●; P_{6m}, ▽; P_{8m}.

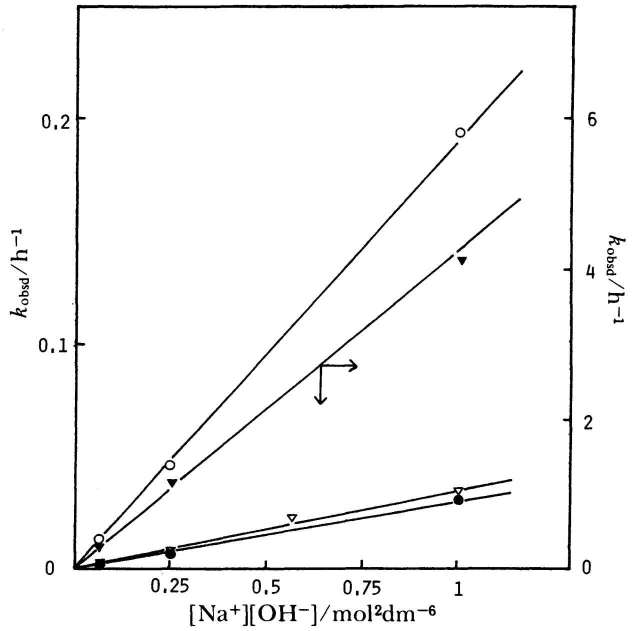


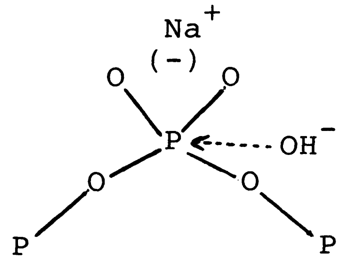
Fig. 3. Plots of the rate constants of *cyclo*-polyphosphates at 50 °C against the product of sodium ion and hydroxide ion concentration. ▼; P_{3m}, ○; P_{4m}, ●; P_{6m}, ▽; P_{8m}.

ion concentration, k_{obsd} can be written as $k[OH^-]^n$.

The hydrolysis rate was also measured at a constant hydroxide ion concentration ([OH$^-$]=0.5 mol dm^{-3}) by changing the sodium ion concentration by adding sodium chloride. As shown in Fig. 2, k_{obsd} changed in proportion to [Na$^+$]. From the above fact and the results of the hydrolysis rates at various sodium hydroxide concentration shown in Fig.3, the hydrolysis rate in NaOH solutions can be presented as Eq. 2. Sodium ions directly affect the hydrolysis rate in NaOH solutions.

$$-\frac{dc}{dt} = k[Na^+][OH^-]c \qquad (2)$$

It has been shown[3-5,8] that *cyclo*-polyphosphate anions having such high negative charge form complexes (or ion-pairs) with various cations. The ion-pair formation of PO$^-$ and Na$^+$ renders the phosphorus atom more positive by reducing the electron density around the P atom and more susceptible to the nucleophilic attack by OH^- in a similar manner at the acidic conditions.[13]



For a comparison with acidic conditions, the activation energy of *cyclo*-octaphosphate hydrolysis in a 0.5 mol dm^{-3} NaOH solution was determined. An Arrhenius' plot is shown in Fig. 4. The activation energy of 82.8±0.3 kJ mol^{-1} is slightly lower than the value of 96.7±0.3 kJ mol^{-1} in a 0.1 mol dm^{-3} HCl solution.[13]

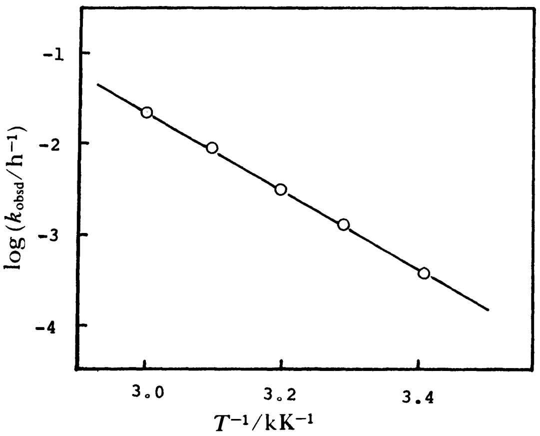


Fig. 4. Arrhenius' plots for *cyclo*-octaphosphate hydrolysis in 0.5 mol dm^{-3} NaOH solution.

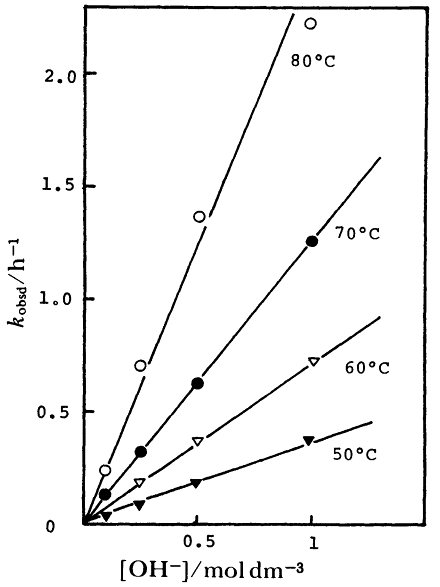


Fig. 5. Plots of the rate constant of *cyclo*-triphosphate at different temperatures and at different tetramethylammonium hydroxide concentrations.

The hydrolysis rates in tetramethylammonium hydroxide solutions were also determined. The hydroxide dose not contain a cation which interacts with *cyclo*-polyphosphate anions. Hydrolysis rates were also first-order for *cyclo*-polyphosphates. Reaction rates of *cyclo*-triphosphate at various hydroxide concentrations and various temperatures are shown in Fig. 5. At each temperature, k_{obsd} varied proportionally with $[OH^-]$. This suggests that the hydrolysis reaction in alkaline solutions in the absence of any cations which might interact with *cyclo*-polyphosphate anions is caused by the nucleophilic attack of OH^- on P atom in the phosphate tetrahedra. Similar results were obtained for *cyclo*-tetraphosphate hydrolysis. The rate constants in 0.5 and 1.0 mol dm^{-3} $(CH_3)_4NOH$ solutions at various temperatures are shown in Fig. 6. At each temperature, k_{obsd} in a 1.0 mol dm^{-3} $(CH_3)_4NOH$ solution was twice that in a 0.5 mol dm^{-3} $(CH_3)_4NOH$ solution. The activation energy of *cyclo*-tetraphosphate was 75.3±1.8 kJ mol^{-1} regardless of $(CH_3)_4NOH$ concentration. Analogously, that of *cyclo*-triphosphate was 62.8±0.8 kJ mol^{-1}. These values were lower than those in NaOH solutions and a 0.1 mol dm^{-3} HCl solution. However, a large discrepancy between them was not observed.

Since higher-membered *cyclo*-hexa- and *cyclo*-octaphosphates with a larger ring structure were not hydrolyzed very much, even if at higher $(CH_3)_4NOH$ concentrations and at higher temperatures, detailed data on their hydrolysis rate at various conditions were not obtained on the contrary to the case of *cyclo*-tri- and *cyclo*-tetraphosphate hydrolysis.

In Fig. 7, the rate constants of each *cyclo*-polyphosphate in 0.5 mol dm^{-3} $(CH_3)_4NOH$, 0.5 mol dm^{-3} NaOH and 0.1 mol dm^{-3} HCl solutions are shown for comparison. Each *cyclo*-polyphosphate is most rapid-

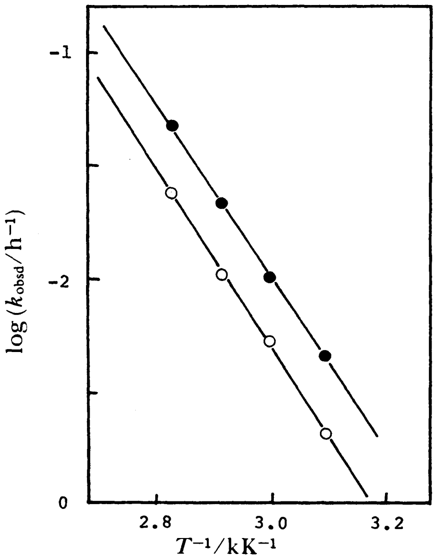


Fig. 6. Arrhenius' plots for *cyclo*-tetraphosphate hydrolysis in 0.5 and 1 mol dm^{-3} $(CH_3)_4NOH$ solution. ●; 1 mol dm^{-3}, ○; 0.5 mol dm^{-3}.

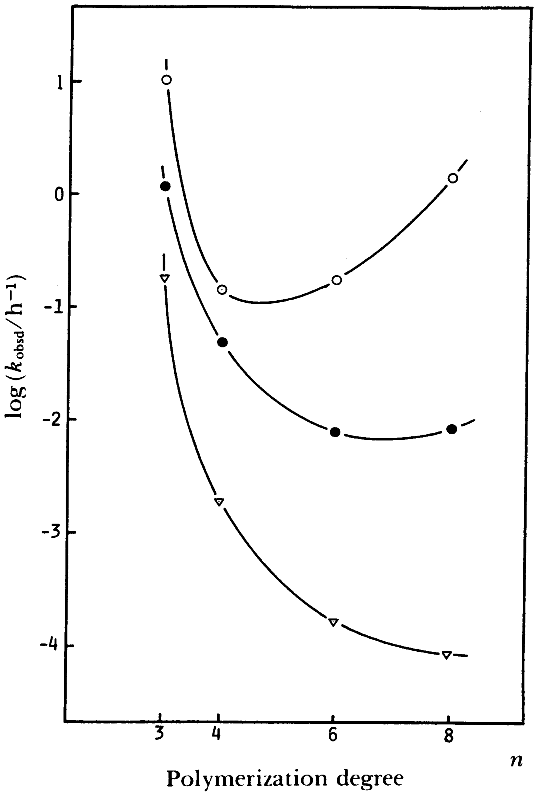


Fig. 7. Variation of the rate constants with the polymerization degree for the *cyclo*-polyphosphates hydrolysis at 50 °C. ○; 0.1 mol dm^{-3} HCl, ●; 0.5 mol dm^{-3} NaOH, ▽; 0.5 mol dm^{-3} $(CH_3)_4NOH$.

ly hydrolyzed in a 0.1 mol dm^{-3} HCl solution. In a $(CH_3)_4NOH$ solution where there are no cations which might interact with *cyclo*-polyphosphate anions, higher-membered *cyclo*-polyphosphates become extremely stable even at higher OH^- ion concentrations and temperatures.

In NaOH solutions, the interaction of sodium ions with the phosphate anions accelerates the hydrolysis rate. This tendency is more pronounced for *cyclo*-octaphosphate which has the highest flexibility.

The obtained results can be summarized as follows. The hydrolysis rate in alkaline solutions is affected not only by the hydroxide ion concentration but also, more strongly, by the presence of cations. The hydrolysis rates in NaOH solutions were significantly faster than those in $(CH_3)_4NOH$ solutions. This tendency is stronger in the case of higher-membered *cyclo*-polyphosphates. The acceleration of the rate is considered to be due to ion-pair formations between sodium ions and *cyclo*-polyphosphate anions. The activation energy decreases in the order of HCl (0.1 mol dm^{-3}) > NaOH > $(CH_3)_4NOH$, but great discrepancies were not observed.

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