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A Chromatographic Study of the Acidic Hydrolysis of *cyclo*-Hexa- and *cyclo*-Octaphosphate

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The hydrolysis rate of inorganic *cyclo*-hexa- and *cyclo*-octaphosphate in 0.1 mol dm^{-3} HCl was determined by means of anion-exchange chromatography. The phosphorus content in the column effluent was determined automatically by the use of the Mo^{V}–Mo^{VI} reagent. The hydrolysis reactions were first-order. The rate constant decreases from *cyclo*- tri- to *cyclo*-hexaphosphate with the increased ring, however, that of *cyclo*-octaphosphate increases again. This increase is thought to be due to the stronger proton affinity of *cyclo*-octaphosphate. The Arrhenius activation energies for *cyclo*-hexa- and *cyclo*-octaphosphate hydrolysis were 91.5 and 96.9 kJ mol^{-1} respectively.

Of the condensed cyclic phosphates, six-membered *cyclo*-tri- and eight-membered *cyclo*-tetraphosphate have been known since the 19th century.[1] Investigations of the higher-membered cyclic phosphates have, however, progressed only slowly.[2–5] We have recently reported some chemical properties of these phosphates.[6–10] These phosphates are very important electrolytes because of their high negative charge on relatively compact structure. When using these anions in the aqueous state for various purposes, for example, as a complexing agent with various cations or a food additive in place of higher-membered linear phosphates, their hydrolysis properties, which have rarely been described, must be known clearly.

The hydrolysis reaction of *cyclo*-tri- and *cyclo*-tetraphosphate have been reported by several authors.[11,12] However, most investigators have used paper chromatography as an analytical tool. As has previously been pointed out by us, though, it is difficult to obtain reliable data on hydrolysis kinetics by this technique.

We ourselves have applied anion-exchange chromatography to the analysis of the hydrolysis products of *cyclo*-tri-[13] and *cyclo*-tetraphosphate.[14] The phosphorus content in the column effluents was determined automatically by the use of the Mo^{V}–Mo^{VI} reagent. From the chromatograms of the hydrolysis products, the kinetic data of *cyclo*-tri- and *cyclo*-tetraphosphate in a 0.1 mol dm^{-3} hydrochloric acid solution were obtained.

In both cases, the chromatographic run of each hydrolysis sample was finished within 50 min. Our analytical method is thought to be more fitting than the paper chromatographic method in terms of rapidity and reliability.

For *cyclo*-tetraphosphate hydrolysis studies, various experimental conditions were examined for the separation of parent compound and the hydrolysis products-linear tetra-, tri-, di- and monophosphates. Finally, suitable conditions for than purpose were found.

Similar analytical conditions for the *cyclo*-tetraphosphate hydrolysis products were also examined for studies of the hydrolysis of twelve-membered *cyclo*-hexaphosphate and sixteen-membered *cyclo*-octaphosphate.

Futhermore, the hydrolysis reaction of these cyclic phosphates might be utilized in the preparation of higher-membered linear phosphates which are their hydrolysis products.

In this paper, linear and cyclic phosphate are abbreviated as P_n and P_{nm} respectively, where n is the degree of polymerization.

Experimental

Materials. As an anion-exchanger, Hitachi Custom Ion-exchange Resin 2630 was used.

The sodium *cyclo*-hexa- and *cyclo*-octaphosphate was prepared by the methods of Griffith and Buxton[4] and Schülke[5] respectively.

Chromatographic System. The system is shown in Fig. 1. Pump A is a part of the Hitachi Model 635 liquid chromatograph. Pump B is a Model KHU-W-52 apparatus made by the Kyowa Seimitsu Co.

As eluents, a mixture of 0.4 mol dm^{-3} of potassium chloride and 0.005 mol dm^{-3} EDTA (2Na salt), the pH of which has been adjusted to 10.2 with a sodium hydroxide solution, was used. In this eluent, EDTA acts as the buffer reagent, while the masking reagent of the metal ions present as an impurity.

Hydrolysis. The initial concentration of the *cyclo*-hexa- and *cyclo*-octaphosphate solution to be hydrolysed was adjusted to 1.25×10^{-3} mol dm^{-3}.

Hydrochloric acid was added to each solution at a concentration of 0.1 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 of a few cubic centimeters were withdrawn and neutralized with the same volume of a 0.1 mol dm^{-3} sodium hydroxide solution at nearly 0 °C.

The present author ascertained that the hydrolysis reaction of *cyclo*-hexa- and *cyclo*-octaphosphate in a neutral solution does not occur at a low temperature. For example, the hydrolysis products of both phosphates were not observed when the phosphates were boiled for 1 h in a neutral solution.

The sample solution were stored in a refrigerator until taken out for analysis.

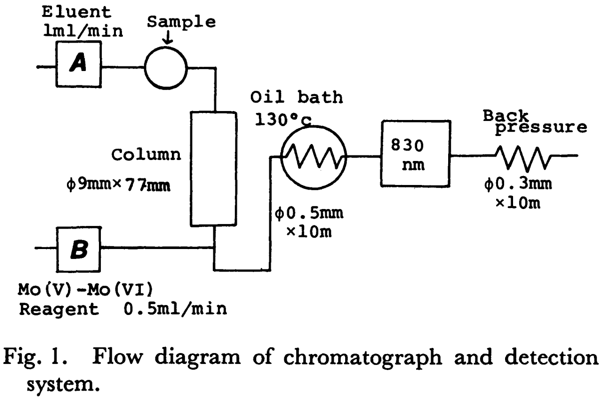
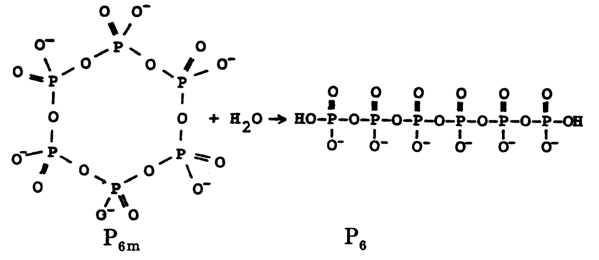


Fig. 1. Flow diagram of chromatograph and detection system.

Results and Discussion

When *cyclo*-hexaphosphate is hydrolysed as shown in Eq. 1, the initial hydrolysis product is linear hexaphosphate; it can also be hydrolysed to lower linear phosphates and probably to *cyclo*-triphosphate.



$$P_6O_{18}^{6-} + H_2O \rightarrow H_2P_6O_{19}^{6-} \rightarrow P_5 \rightarrow P_4 \rightarrow P_3 \rightarrow P_2 \rightarrow P_1 \quad (1)$$

It is necessary to separate the parent compound and the seven hydrolysis products for the determination of the hydrolysis rate. Anion-exchange chromatography was thought to be best fitted for this purpose. The present author has, with the use of Hitachi Custom Ion 2630 resin applied anion-exchange chromatography to the analysis. As reported in our previous paper[14] on the separation of *cyclo*-tetraphosphate and its hydrolysis products, the distribution ratio of cyclic phosphates on the anion-exchange resin is not affected by the variation in the pH when the chloride-ion concentration of an eluent is constant. In the case of linear di- and triphosphate, their distribution ratios decrease appreciably with the increase in the pH at a constant chloride concentration.[15] From the retention volume on the column presented in our previous paper,[14] it was found that the distribution ratio of linear tetraphosphate also decreases with the increase in pH. From this fact, it was expected that the increase in the pH in the eluent might result in the achievement of a separation between *cyclo*-hexaphosphate and its hydrolysis products, which is impossible in the lower-pH range. Therefore, a mixture of *cyclo*-hexaphosphate and polyphosphate glass ($\bar{n}=10$) was eluted on the column with the use of 0.4 mol dm^{-3} KCl at pH 10.2 as the eluent.

The resulting chromatogram is shown in Fig.2. At least, linear phosphates with the polymerization degree less than eight were eluted in stages earlier than *cyclo*-hexaphosphate. The peak volume of an elution curve of *cyclo*-triphosphate as a hydrolysis product was about 75 cm^3 under these conditions.

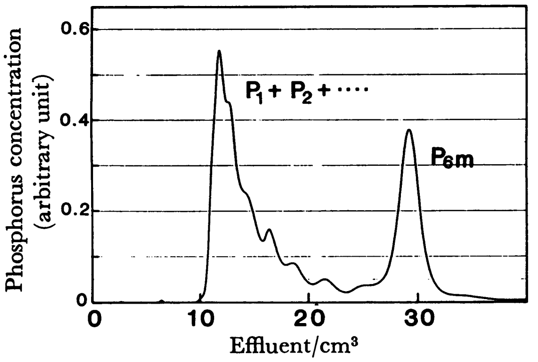


Fig. 2. Elution chromatogram of *cyclo*-hexaphosphate and linear oligophosphates mixture with 0.4 mol dm^{-3} potassium chloride solution (pH 10.2).

The hydrolysis products of *cyclo*-hexaphosphate were analyzed under these chromatographic conditions.

cyclo-Octaphosphate of the sixteen-membered ring was eluted 10 cm^3 later than *cyclo*-hexaphosphate. Consequently, *cyclo*-octaphosphate and its hydrolysis products were successfully separated under the same elution conditions.

As discussed in our earlier papers, first-order hydrolysis-rate constants of *cyclo*-tri- and *cyclo*-tetraphosphate in a 0.1 mol dm^{-3} HCl solution varied with their initial concentration up to the relatively lower-concentration region. The hydrolysis rates of *cyclo*-hexa- and *cyclo*-octaphosphate were measured by changing those initial concentrations. A constant rate constant was obtained when the initial concentrations of both phosphates were lower than 2.5×10^{-3} mol dm^{-3}.

In the following hydrolysis experiments, the initial concentration of the parent compound was fixed at 1.25×10^{-3} mol dm^{-3}. We have presumed that the variation in the rate constant with the initial concentrations is due to the change in the hydrogen concentration in a test solution as the hydrolysis reaction proceeds.

An example of chromatograms of the hydrolysis products of *cyclo*-hexaphosphate in 0.1 mol dm^{-3} HCl at 40 °C is shown in Fig. 3. It was confirmed by a separate experiment that the area of the chromatogram of the *cyclo*-hexaphosphate thus obtained *versus* the phosphate concentration known gave a straight line passing through the point of origin. From the chromatograms of the hydrolysis products, the hydrolysis rate was calculated. The area of the chromatograms of the hydrolysis sample was automatically estimated by connecting an output terminal from the spectrophotometer to a SORD Mark IIIB micro computer through an A-D converter.

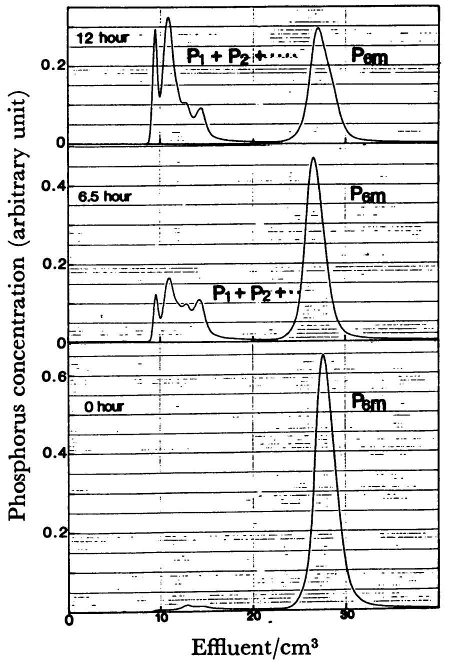


Fig. 3. Chromatograms of hydrolysis samples of *cyclo*-hexaphosphate in 0.1 mol dm^{-3} hydrochloric acid at 40 °C.

As was pointed out in the earlier papers,[13,14] the hydrolysis reactions of condensed phosphates have been known to be first-order. Let the total concentration of *cyclo*-hexaphosphate be c; the hydrolysis rate, $-\mathrm{d}c/\mathrm{d}t$, can thus be written as;

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = k_0[\mathrm{P_6O_{18}^{6-}}] + k_1[\mathrm{HP_6O_{18}^{5-}}] + k_2[\mathrm{H_2P_6O_{18}^{4-}}] + k_3[\mathrm{H_3P_6O_{18}^{3-}}] + k_4[\mathrm{H_4P_6O_{18}^{2-}}] + k_5[\mathrm{H_5P_6O_{18}^{-}}] + k_6[\mathrm{H_6P_6O_{18}}], \tag{2}$$

where $k_i(i=0\text{—}6)$ are rate constants for individual protonated species. If the molar fractions of the protonated species are written as X_6 for $\mathrm{H_6P_6O_{18}}$, X_5 for $\mathrm{H_5P_6O_{18}^-}$, and so on, the hydrolysis rate can be written as;

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = (k_0X_0+k_1X_1+k_2X_2+k_3X_3+k_4X_4 + k_5X_5+k_6X_6)c = k_{\mathrm{obsd}}c, \tag{3}$$

where;

$$k_{\mathrm{obsd}} = k_0X_0 + k_1X_1 + k_2X_2 + k_3X_3 + k_4X_4 + k_5X_5 + k_6X_6.$$

When the hydrogen-ion concentration is constant, k_{obsd} should be constant. Accordingly, from the first-order hydrolysis rate equation (3), if $[P]_0$ and $[P]_t$ are denoted as the concentrations of *cyclo*-hexaphosphate at time 0 and t respectively, $\log([P]_t/[P]_0)$ *versus* t plots should give a straight line.

Similar treatments are possible for the *cyclo*-octaphosphate hydrolysis reaction.

$\log([P]_t/[P]_0)$ *versus* t plots for *cyclo*-hexa- and *cyclo*-octaphosphate hydrolysis at various temperatures are shown in Figs. 4 and 5. Good straight lines were obtained, hence, the hydrolysis reactions of both phosphates are first-order. The apparent first-order rate constants, k_{obsd}, and half-lives, $t_{1/2}$, at various temperatures are shown in Table 1.

From the k_{obsd} at the various temperatures examined, the linear Arrhenius plots shown in Fig. 6 were obtained. The Arrhenius activation energies, Ea, were 91.5 and 96.9 kJ mol^{-1} for *cyclo*-hexa- and *cyclo*-octaphosphate respectively, nearly equivalent to those obtained for

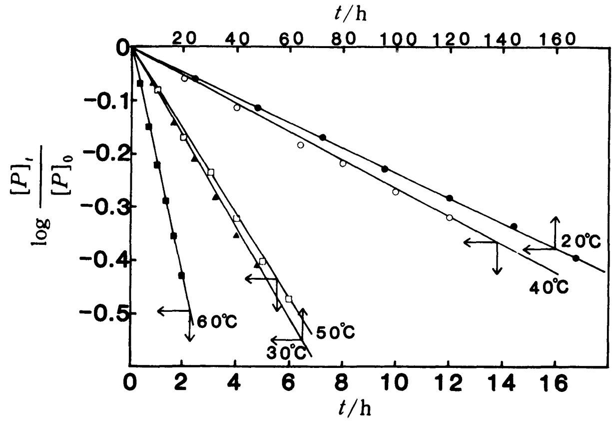


Fig. 4. Hydrolysis rate of *cyclo*-hexaphosphate in 0.1 mol dm^{-3} hydrochloric acid at various temperatures.

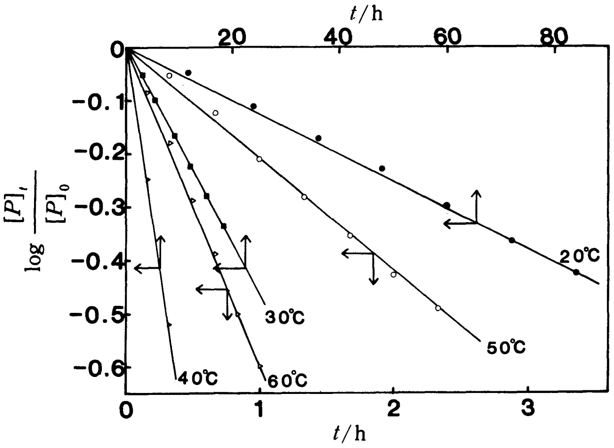


Fig. 5. Hydrolysis rate of *cyclo*-octaphosphate in 0.1 mol dm^{-3} hydrochloric acid at various temperatures.

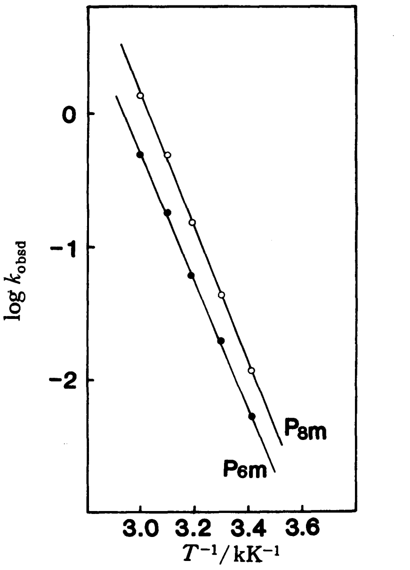


Fig. 6. Arrhenius plot for *cyclo*-hexa- and *cyclo*-octaphosphate in 0.1 mol dm^{-3} hydrochloric acid.

TABLE 1. KINETIC DATA ON *cyclo*-HEXA- AND *cyclo*-OCTAPHOSPHATE HYDROLYSIS IN 0.1 mol dm^{-3} HYDROCHLORIC ACID

		Temperature/°C				
		20	30	40	50	60
$\mathrm{P_{6m}}$	k_{obsd}/h^{-1}	5.40×10^{-3}	1.96×10^{-2}	6.07×10^{-2}	0.181	0.495
	$t_{1/2}$/h	128	35.4	11.4	3.82	1.40
$\mathrm{P_{8m}}$	k_{obsd}/h^{-1}	1.17×10^{-2}	4.31×10^{-2}	0.153	0.486	1.39
	$t_{1/2}$/h	59.3	16.1	4.53	1.43	0.500

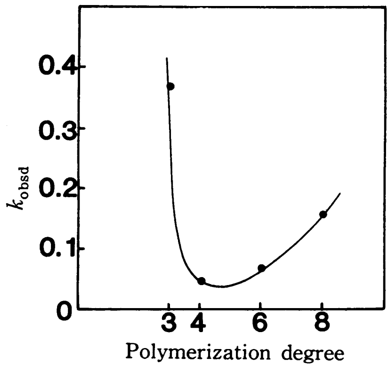


Fig. 7. First order rate constants as a function of polymerization degree in 0.1 mol dm^{-3} hydrochloric acid at 40 °C.

other condensed phosphates in acidic media.

The apparent rate constants, k_{obsd}, of *cyclo*-hexa- and *cyclo*-octaphosphate in 0.1 mol dm^{-3} HCl at 40 °C are plotted *versus* their polymerization degree in Fig. 7, along with the data for *cyclo*-tri- and *cyclo*-tetraphosphate reported in our previous papers.[13,14] This graph has a minimum at a polymerization degree near 5. This fact can be explained as follows. The present author has not obtained sufficient data on cyclic phosphate hydrolysis in alkaline media; however, from Ref. 3, it can be presumed that the stability of the ring structure of cyclic phosphate in an alkaline solution increases with an increase in the ring size. On the other hand, the hydrolysis rates of condensed phosphates are accelerated very much by the proton which binds to the phosphates. The bonding of the hydrogen ion to the oxygen atom involved in the phosphate tetrahedron renders the phosphorus atom more positive by reducing the electron density around that atom and more susceptible to nucleophilic attack by water molecules. As has been reported in our previous paper,[9] the degree of bonding with the hydrogen ion increase with an increase in the size of the ring. Accordingly, an increase in proton affinity would result in an increase in the k_{obsd}.

From the two opposite effects increasing and decreasing k_{obsd} presented above, k_{obsd} comes to have a minimum near the pentamer under acidic conditions.

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