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STUDY OF THE ACID HYDROLYSIS OF CYCLIC TETRAMETAPHOSPHATE BY LIQUID CHROMATOGRAPHY

GENICHIRO KURA

Department of Chemistry, Fukuoka University of Education, Akama, Munakata, Fukuoka, 811-41 (Japan)

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SUMMARY

The hydrolysis of cyclic tetrametaphosphate in acidic aqueous solution ($[H^+] = 0.1 M$) was investigated by automatic liquid chromatography. Anion-exchange separation of tetrametaphosphate from the hydrolysis products was achieved with 0.4 *M* potassium chloride solution, the pH of which was adjusted to 10.2. From the rate constants at 20, 30, 40, 50 and 60°C, the Arrhenius activation energy in 0.1 *M* hydrochloric acid for scission of a P–O–P linkage was 24.0 kcal/mole.

INTRODUCTION

Cyclic phosphates having a ring of alternate phosphorus and oxygen atoms are members of the condensed phosphates prepared by the dehydration reaction of phosphorus(V) monooxo acid. The chemical properties of cyclic phosphates have been widely investigated and in particular their chromatographic behaviour¹ and their complex formation with various cations^{2,3} have been studied in detail.

Hydrolysis reactions in aqueous solutions of trimeta- and tetrametaphosphates have been studied by paper chromatography^{4,5}. However, paper chromatographic analysis is time consuming and the reliability of quantitative determinations by the technique is not good. Further, complete separation of the parent compound and the hydrolysis product is difficult. We have reported on the hydrolysis reaction of cyclic octametaphosphate with a combined anion-exchange and gel chromatographic column⁶. Trimetaphosphate hydrolysis was also investigated by automatic liquid chromatography⁷. The hydrolysis product was separated by anion-exchange chromatography and the phosphorus content in the column effluents passing through a micro flow cell was determined spectrophotometrically with Mo(V)–Mo(VI) reagent.

When trimetaphosphate is hydrolysed, linear triphosphate is formed, which will be hydrolysed to lower linear phosphate. Separation of the parent compound, trimetaphosphate and its hydrolysis products could be achieved with 0.5 *M* potassium chloride solution as the eluent.

In this work, we have investigated tetrametaphosphate hydrolysis by a similar automatic liquid chromatographic method to that used for trimetaphosphate⁷. Tetrametaphosphate could not be separated from the hydrolysis products, tetra-, tri-, di-

and monophosphates, with the same eluent as that used in trimetaphosphate hydrolysis. Various experimental conditions and eluent compositions were examined in order to separate the parent compound. We established the optimum conditions for the analysis of the phosphate and investigated the its hydrolysis reaction in 0.1 *M* hydrochloric acid at various temperatures from 20 to 60°C.

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

EXPERIMENTAL

Materials

Copper(II) tetrametaphosphate was prepared by heating phosphoric acid and copper(II) oxide. The copper salt was converted into the sodium salt with sodium sulphide. Linear tetraphosphate was prepared by the method of Griffith⁸. All of the chemicals used other than the phosphates were commercially available analytical-reagent grade materials and were used without further purification.

Hitachi custom ion-exchange resin 2630 was used as the anion-exchange resin.

Hydrolysis

The initial concentration of tetrametaphosphate solution to be hydrolysed was varied from 0.05 to $1.25 \cdot 10^{-3}$ *M*. The other hydrolysis conditions were the same as those used earlier⁷.

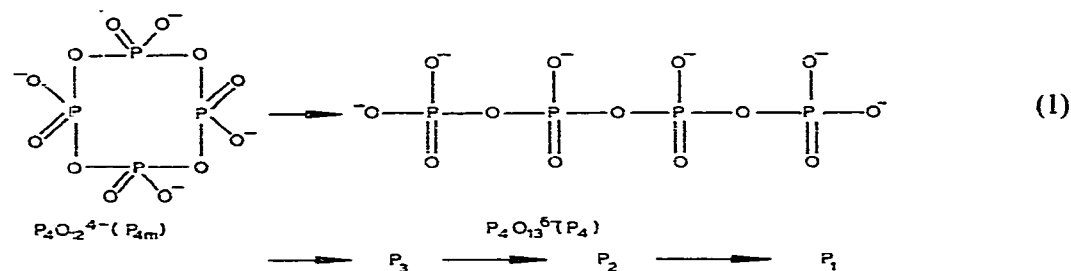
Analysis

The apparatus, the chromatography conditions and the detection system were as described earlier⁷.

Simple and gradient elution methods with potassium chloride of various concentrations were examined. The eluting agents were potassium chloride solution and 0.1% EDTA (disodium salt). To control the pH of the eluents at 10.2, the EDTA concentration was increased to $5 \cdot 10^{-3}$ *M* and sodium hydroxide was added.

RESULTS AND DISCUSSION

Separation of the hydrolysis products of trimetaphosphate was easily achieved with 0.5 *M* potassium chloride solution as the eluent⁷. When tetrametaphosphate is hydrolysed as shown in eqn. 1:



the initial hydrolysis product is linear tetraphosphate, which should be hydrolysed to lower linear phosphates, tri-, di- and monophosphate. Tetrametaphosphate must be separated from the four linear phosphates. An anion-exchange chromatographic method was devised for the separation and the phosphorus content in the column effluent was automatically detected by spectrophotometric measurement of heteropoly blue formed between phosphorus and Mo(V)–Mo(VI) through a flow cell.

At first, simple elutions using 0.5, 0.4, 0.35 and 0.3 *M* potassium chloride solution (no buffer added) as eluents were examined. With any of these eluents, tetrameta- and tetraphosphate could not be separated. As an example, results with 0.4 *M* potassium chloride solution as the eluent is shown in Fig. 1.

Next, we applied a gradient elution method to the separation. The initial potassium chloride concentration in a mixing bottle, the volume of which was 250 ml, and its concentration in a reservoir were varied widely in order to separate the phosphates. As shown in Fig. 2, when the initial concentration in the mixing bottle was 0.3

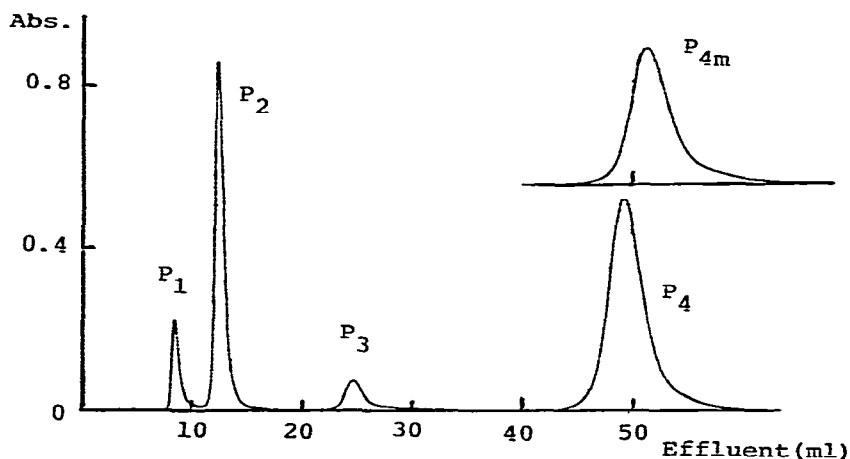


Fig. 1. Simple elution chromatogram of mono-, di-, tri- and tetraphosphate and tetrametaphosphate with 0.4 *M* potassium chloride solution (no buffer added).

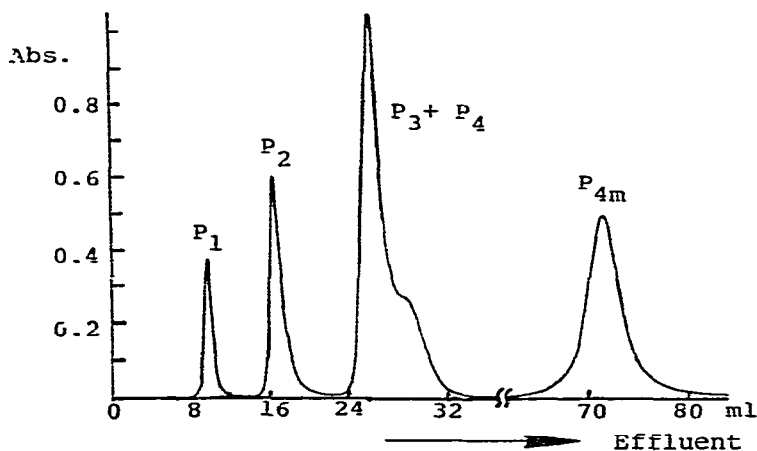


Fig. 2. Gradient elution chromatogram of mono-, di-, tri- and tetraphosphate and tetrametaphosphate.

M and that in the reservoir was $0.6 M$, and the pH of both eluents was adjusted to 10.2, tetrametaphosphate and other phosphates could be separated. However, it took 90 min for the elution of tetrametaphosphate and continuous operation with the same column is difficult. Accordingly, we devised a simpler elution system. The distribution ratio of tetrametaphosphate with respect to an anion-exchange resin should be constant because of its basic property³. However, from earlier data⁹, the distribution ratio of linear phosphates decrease with increase in the pH of the eluent. Thus, the difference in the distribution ratios of tetrametaphosphate and other linear phosphates was expected to increase as the pH of the eluent increased.

We examined the use of $0.4 M$ potassium chloride solution, the pH of which was adjusted to 10.2, as an eluent and the resulting chromatogram is shown in Fig. 3.

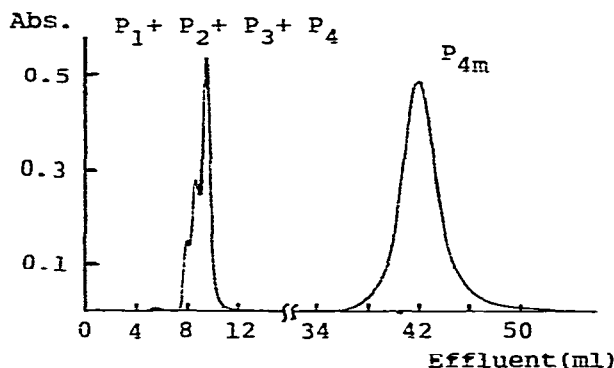


Fig. 3. Simple elution chromatogram of mono-, di-, tri- and tetraphosphate and tetrametaphosphate with $0.4 M$ potassium chloride solution (pH 10.2).

As expected the linear phosphates P_1 , P_2 , P_3 and P_4 were eluted in the early stages, and the separation of P_{4m} from the phosphates was satisfactory. We have used this elution system for the analysis of hydrolysis products. The area of the chromatogram of tetrametaphosphate obtained *versus* the phosphate concentration gave a straight line passing through the origin (Fig. 4).

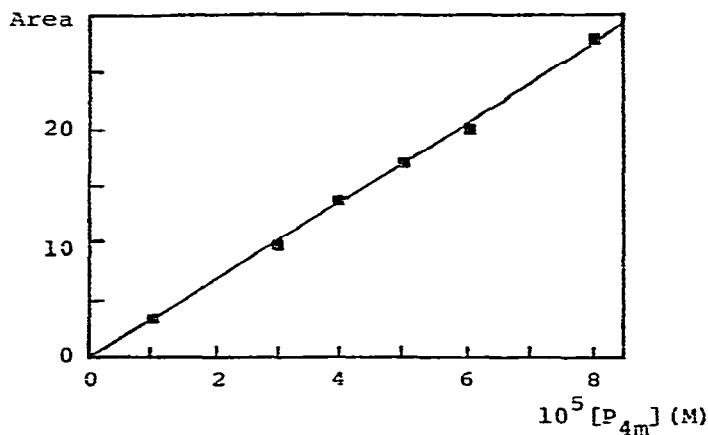


Fig. 4. Calibration graph for tetrametaphosphate elution.

From the chromatograms of the hydrolysis products, hydrolysis rate was calculated. Similar trends to those in trimetaphosphate hydrolysis namely that the rate constants change with the initial concentration of the phosphate to be hydrolysed, were expected. We therefore planned similar experiments to those for trimetaphosphate hydrolysis in order to determine the concentration region where constancy of the rate constant could be maintained. The results are shown in Fig. 5 and the initial concentration was fixed at $2.5 \cdot 10^{-3} M$.

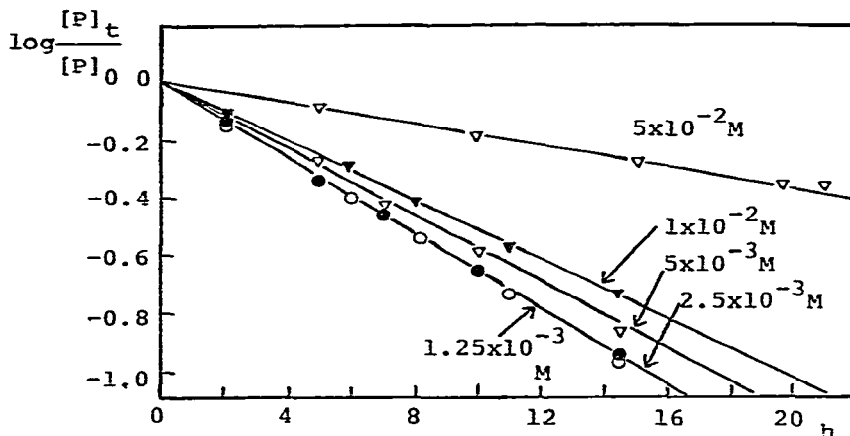


Fig. 5. Hydrolysis rates for various initial concentrations of tetrametaphosphate in 0.1 *M* hydrochloric acid at 50°C.

In acidic aqueous solution, if the tetrametaphosphate hydrolysis reaction is first order, the hydrolysis rate can be written as

$$-\frac{dc}{dt} = k_4[\text{H}_4\text{P}_4\text{O}_{12}] + k_3[\text{H}_3\text{P}_4\text{O}_{12}^-] + k_2[\text{H}_2\text{P}_4\text{O}_{12}^{2-}] + k_1[\text{HP}_4\text{O}_{12}^{3-}] + k_0[\text{P}_4\text{O}_{12}^{4-}] \quad (2)$$

where c denotes the total concentration of tetrametaphosphate and k_4 – k_0 are rate constants for individual protonated species. If the molar fractions of the protonated species are written as X_4 for $\text{H}_4\text{P}_4\text{O}_{12}$ and X_3 for $\text{H}_3\text{P}_4\text{O}_{12}^-$ and so on, the hydrolysis rate can be written as

$$-\frac{dc}{dt} = (k_4X_4 + k_3X_3 + k_2X_2 + k_1X_1 + k_0X_0)C = k_{\text{obs}}C \quad (3)$$

where

$$k_{\text{obs}} = k_4X_4 + k_3X_3 + k_2X_2 + k_1X_1 + k_0X_0$$

When the hydrogen ion concentration is kept constant, k_{obs} should be constant. From eqn. 3, the following equation can be derived:

$$\log\left(\frac{[P]_t}{[P]_0}\right) = -\frac{k_{\text{obs}}}{2.303} \cdot t \quad (4)$$

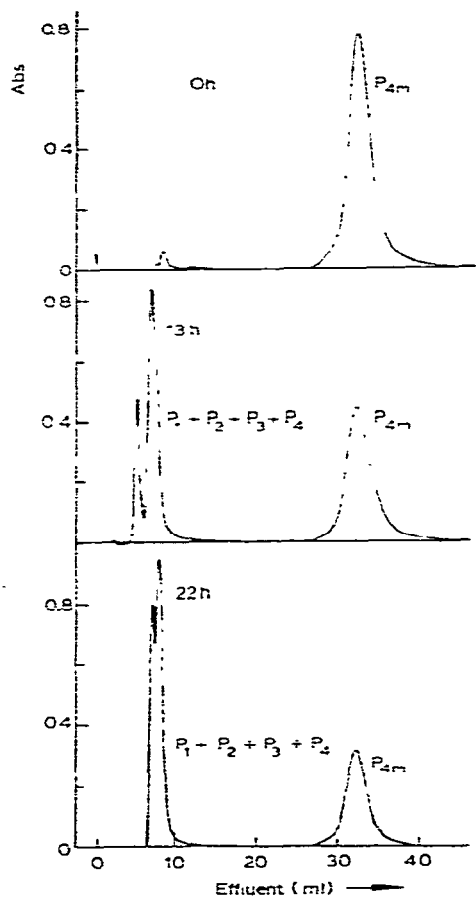


Fig. 6. Chromatograms of hydrolysis samples of tetrametaphosphate in 0.1 *M* hydrochloric acid at 40°C.

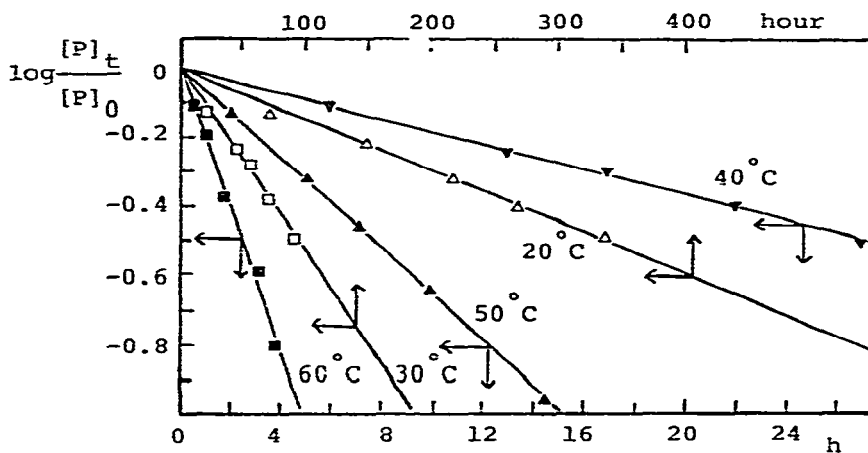


Fig. 7. Hydrolysis rates of tetrametaphosphate ($2.5 \cdot 10^{-3}$ *M*) in 0.1 *M* hydrochloric acid at various temperatures.

TABLE I

KINETIC DATA ON TETRAMETAPHOSPHATE HYDROLYSIS IN 0.1 M HYDROCHLORIC ACID

Parameter*	Temperature (°C)				
	20	30	40	50	60
k_{obs} (h^{-1})	$3.52 \cdot 10^{-3}$	$1.22 \cdot 10^{-2}$	$4.33 \cdot 10^{-2}$	0.146	0.456
$t_{1/2}$ (h)	197	56.5	16.0	4.75	1.52

* $E_a = 24.0$ kcal/mol.

where $[P]_0$ and $[P]_t$ are the concentration of tetrametaphosphate at time 0 and t , respectively.

An example of chromatograms of the hydrolysis product of tetrametaphosphate at 40°C in 0.1 M hydrochloric acid is shown in Fig. 6. The column length used in this example was 80% of that used in the experiment shown in Fig. 3. $\text{Log}([P]_t/[P]_0)$ versus t plots at various temperature are shown in Fig. 7. Good straight lines were obtained at the temperatures studied. Hence the hydrolysis reaction of tetrametaphosphate is first order. The apparent first-order rate constant, k_{obs} , and half-life of tetrametaphosphate at various temperatures are shown in Table I. From the temperature dependence of $\log k_{\text{obs}}$, linear Arrhenius plots as shown in Fig. 8 were obtained. The activation energy was 24 kcal/mole, which is nearly equivalent to that

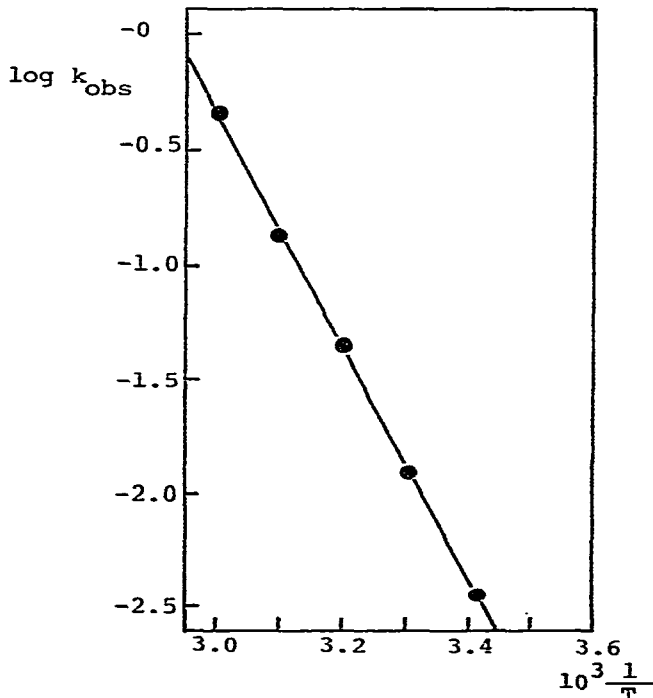


Fig. 8. Arrhenius plot for tetrametaphosphate hydrolysis in 0.1 M hydrochloric acid.

obtained for other condensed phosphates in acidic media and is somewhat larger than that for trimetaphosphate⁷.

The half-life of trimetaphosphate at 50°C in 0.1 *M* hydrochloric acid was 0.67 h (ref. 7) and that of tetrametaphosphate was 4.75 h under the same conditions. The increased stability of tetrametaphosphate ring agrees with the data on cyclic phosphates in basic media¹⁰. When the initial concentration of tetrametaphosphate was fixed at 0.1 *M* and paper chromatography was used, the half-life of tetrametaphosphate at pH 1 and 50°C was estimated to be 6.8 h from extrapolation of the data in ref. 11. This value is larger than our value. However, our analytical method seems to be superior to paper chromatography and perhaps more accurate.

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