Journal of Chromatography, 219 (1981) 385–391
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,202

STUDY OF THE ACIDIC HYDROLYSIS OF CYCLIC TRIMETAPHOSPHATE BY LIQUID CHROMATOGRAPHY

GENICHIRO KURA*, TAKAYUKI NAKASHIMA and FUMIO OSHIMA
Department of Chemistry, Fukuoka University of Education, Akama, Munakata, Fukuoka, 811-41 (Japan)
(Received July 17th, 1981)

SUMMARY

The hydrolysis of cyclic trimetaphosphate in acidic aqueous solution ($[H^+] = 0.1$) was investigated by liquid chromatography. The phosphate in the effluent from an anion-exchange column was detected automatically with the use of Mo(V)–Mo(VI) reagent.

From the rate constants at 10, 20, 30, 40 and 50°C, the Arrhenius activation energy in 0.1 *M* hydrochloric acid solution for scission of a P–O–P linkage was estimated as 21.3 kcal/mole.

INTRODUCTION

The chemical properties of condensed phosphates have been extensively investigated. Hydrolytic reactions of linear-chain phosphates of relatively short chain length have been also reported[1]. However, data on the hydrolysis of cyclic condensed phosphates are scarce. The most common members of cyclic condensed phosphates of the general formula $M_n^I(PO_3)_n$ are tri- and tetrametaphosphates, which have six- and eight-membered rings, respectively.

Several investigators have reported on the hydrolysis reactions of these two cyclic phosphates[2,3]. They used the precipitation method or paper chromatography for the separation of the parent compound and the hydrolysis products. However, it is difficult to obtain reliable data on the hydrolysis kinetics by the use of these techniques.

We have previously reported on the hydrolysis of cyclic octametaphosphate[4], with a 16-membered ring, in acidic media by using combined ion-exchange and gel chromatographic columns. In the study, the effluent from the combined columns was fractionated by a fraction collector and phosphate species in the effluent were analysed spectrophotometrically. The use of column chromatography improved the reliability of the kinetic data compared with the use of paper chromatography.

Nevertheless, the use of a fraction collector is time consuming. We therefore devised a method for the automatic determination of phosphorus concentrations in column effluents. This technique has been already reported by Hirai *et al.*[5], who employed the automatic spectrophotometric determination of phosphate species by

0021-9673/81/0000–0000/$02.50

forming heteropoly blue complexes of the phosphates through a flow cell. We modified their method.

In this study, trimetaphosphate was separated from the hydrolysis products by the use of an anion-exchange column. From the chromatograms obtained automatically, hydrolysis kinetics in 0.1 *M* hydrochloric acid at various temperatures were investigated. In this paper, cyclic phosphates and linear phosphates are abbreviated as P_{nm} and P_n; respectively, where n is the degree of polymerization and m denotes metaphosphate of cyclic structure.

EXPERIMENTAL

Materials

All the chemicals used were commercially available analytical-reagent grade materials and were used without further purification.

Sodium trimetaphosphate was prepared by the usual method[6].

Hitachi Custom Ion-Exchange Resin 2630 anion exchanger was purchased from Nissei Sangyo (Japan).

Apparatus

The chromatographic system is shown schematically in Fig. 1. Pump A and the column were part of a Hitachi Model 635 liquid chromatograph. The spectrophotometer was a Hitachi Model 100-50 with a flow cell unit. The length of the light path and the volume of the flow cell were 8 mm and 8 μl, respectively.

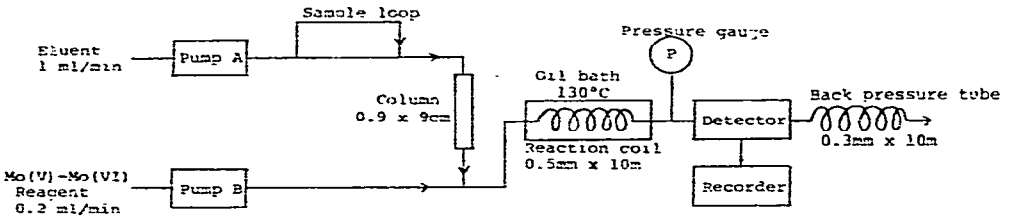


Fig. 1. Flow diagram of chromatograph and detection system.

Separation

The dimensions of the glass column used for packing the ion-exchange resin were 100 × 8 mm I.D. The eluent was 0.5 *M* potassium chloride solution with 0.1 % of EDTA (disodium salt) as a masking reagent, with a flow-rate of 1 ml/min. A 1-ml volume of sample solution was injected into the column through a sample loop.

Detection

The Mo(V)–Mo(VI) reagent was prepared by the method of Hosokawa and Oshima[7]. This reagent was diluted 4-fold with water and passed at a flow-rate of 0.2 ml/min to the stream of column effluent, which had a flow-rate of 1 ml/min. The mixed solution was heated at 130°C in an oil-bath by passage through 10 m of 1.5 × 0.5 mm I.D. PTFE tubing.

The heteropoly blue complex thus formed was detected at 830 nm in the flow

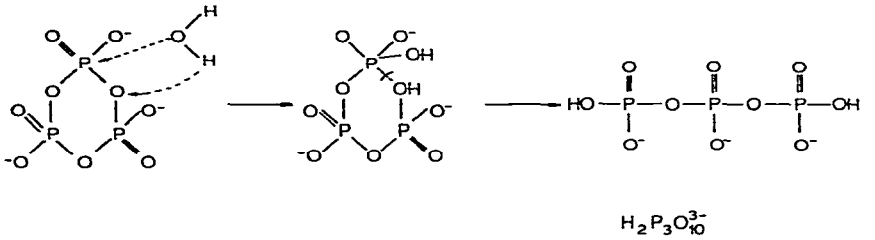
cell. A back-pressure PTFE coil (10 m × 2 mm O.D. × 0.3 mm I.D.) was connected to the end coil of flow cell outlet so as to prevent the formation of air bubbles on heating. The readings on the pressure gauge in the flow system were usually 6–7 kg/cm^2.

Hydrolysis

The initial concentration of the trimetaphosphate solution to be hydrolysed was varied from 0.05 to $6.25 \cdot 10^{-4}$ *M*. Hydrochloric acid was added at a concentration of 0.1 *M* to each solution 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 millilitres were withdrawn and neutralized with the same volume of 0.1 *M* sodium hydroxide solution at nearly 0°C. The sample solutions were stored in a refrigerator until taken for analysis.

RESULTS AND DISCUSSION

When trimetaphosphate is hydrolysed as showin in eqn. 1, first linear triphosphate is formed.



(1)

This triphosphate is also degraded to di- and monophosphate. To determine the hydrolysis rate of trimetaphosphate, this parent compound should be separated from the hydrolysis products. This separation was achieved by the use of a Hitachi

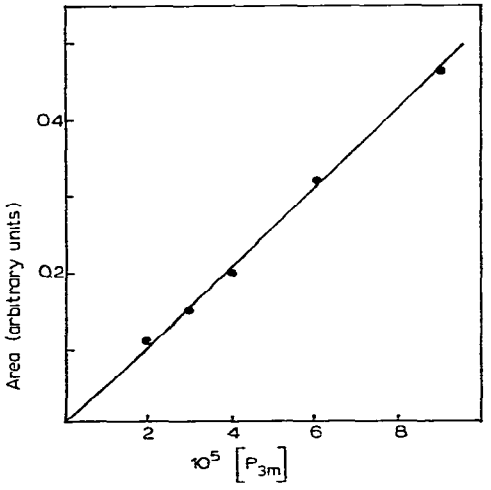


Fig. 2. Calibration graph for trimetaphosphate elution.

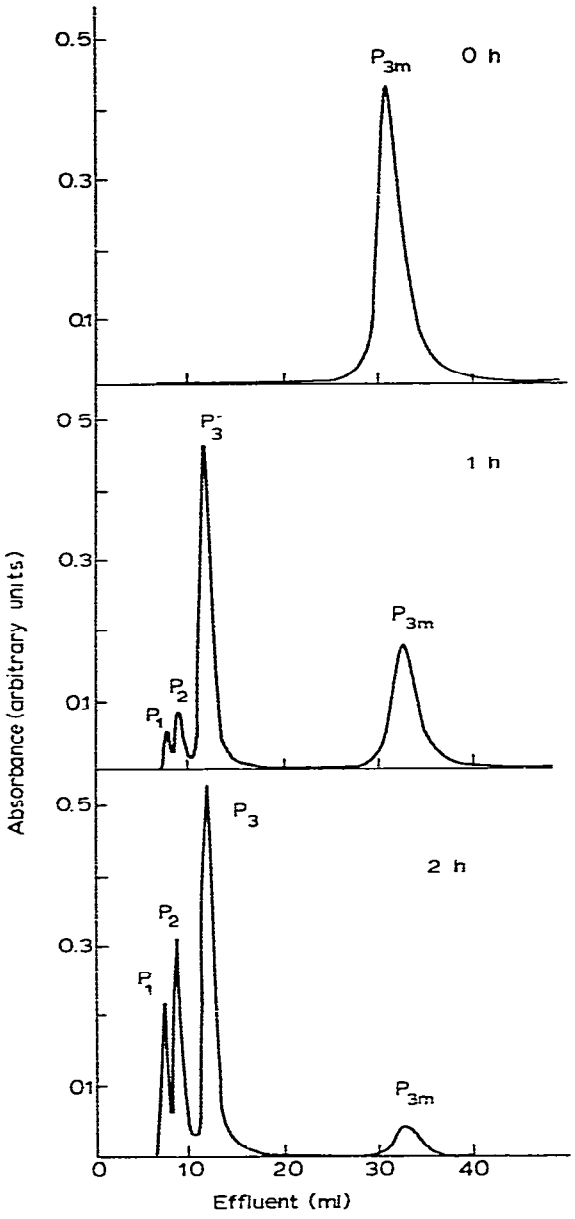


Fig. 3. Chromatograms of hydrolysis samples of trimetaphosphate in 0.1 *M* HCl at 50°C.

Custom Ion-Exchange Resin 2630 column with 0.5 *M* potassium chloride solution containing 0.1 % of EDTA (disodium salt) as the eluent. A good elution pattern of trimetaphosphate was obtained under the conditions described.

On eluting known amounts of trimetaphosphate, a graph of the area of the chromatograms obtained *versus* the phosphate concentration gave a straight line passing through the origin. The result is shown in Fig. 2.

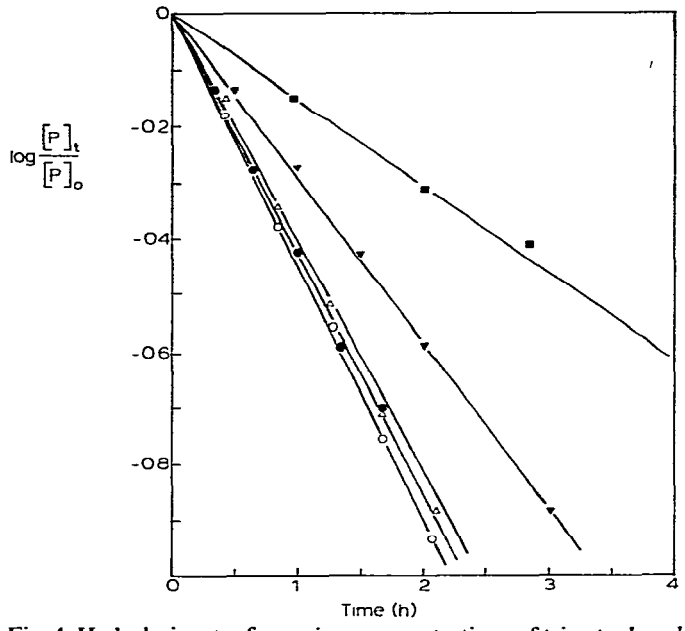


Fig. 4. Hydrolysis rates for various concentrations of trimetaphosphate in 0.1 *M* HCl at 50°C. ■, 0.05 *M*; ▼, 0.01 *M*; △, $2.50 \cdot 10^{-3}$ *M*; ○, $1.25 \cdot 10^{-3}$ *M*; ●, $6.25 \cdot 10^{-4}$ *M*.

As an example, chromatograms of hydrolysis samples in 0.1 *M* hydrochloric acid at 50°C are shown in Fig. 3. From the areas of these chromatograms of trimetaphosphate, the hydrolysis rate could be calculated.

The concentration of trimetaphosphate at times 0 and *t* were denoted by $[P]_0$ and $[P]_t$, respectively, and log $([P]_t/[P]_0)$ is plotted *versus* time in Fig. 4 for various initial concentrations of trimetaphosphate. As the plots are linear, the hydrolysis reaction of trimetaphosphate is first order and the slope of the straight line is the rate constant of the reaction. As shown in Fig. 4, a constant value was obtained when the

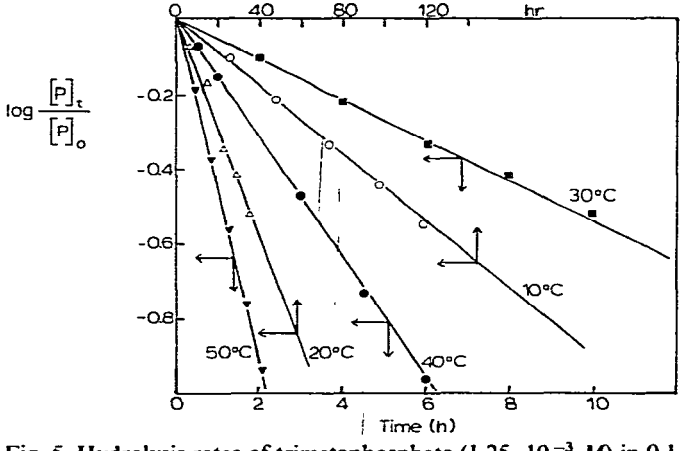


Fig. 5. Hydrolysis rates of trimetaphosphate ($1.25 \cdot 10^{-3}$ *M*) in 0.1 *M* HCl at various temperatures.

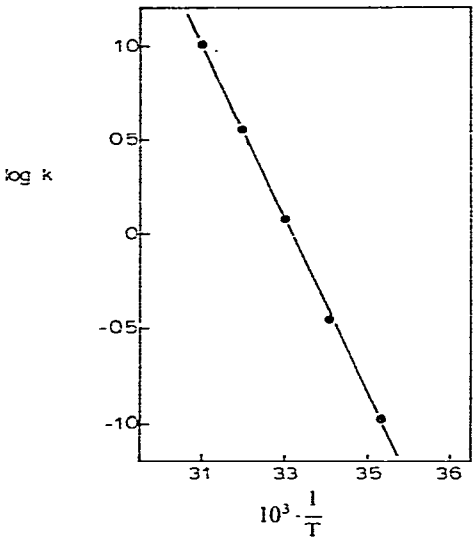


Fig. 6. Arrhenius plot for trimetaphosphate hydrolysis in 0.1 *M* HCl.

initial concentration of trimetaphosphate to be hydrolysed was lower than $2.5 \cdot 10^{-3}$ *M*. When initial concentration was higher than this, an increase in the pH of the test solution was observed. For example, after the hydrolysis reaction was almost completed, the pH of the test solution at an initial concentration of 0.05 *M* changed from 1.0 to 1.6. If the hydrolysis reaction of trimetaphosphate, $P_3O_9^{3-}$, proceeds as in eqn. 1 and only linear triphosphate, $H_2P_3O_{10}^{3-}$, is formed, the pH of the sample solution should be constant. However, as the pK_3 of $H_5P_3O_{10}$ acid is 2.30, $H_3P_3O_{10}^{2-}$ might be formed appreciably in 0.1 *M* hydrochloric acid solution. This effect results in a decrease in hydrogen ion concentration, *i.e.*, an increase in the pH of the test solution. When the initial concentration of trimetaphosphate is very low compared with the hydrogen ion concentration (0.1 *M*), the amount of hydrogen ion consumed by the hydrolysis products can be neglected. A "true" rate constant could then be obtained as the pH of the test solution was kept constant. Log $([P]_t/[P]_0)$ *versus* t plots at an initial concentration of $1.25 \cdot 10^{-3}$ *M* and at various temperatures is shown in Fig. 5. Good straight lines were obtained at the temperatures studied. Thus, the trimetaphosphate hydrolysis rate, $-d[P]/dt$, can be represented by

$$-\frac{d[P]}{dt} = k[H^-][P] \tag{2}$$

The first-order rate constants in eqn. 2 and the half-lives of trimetaphosphate at various temperatures are shown in Table I. From these data, linear Arrhenius plots as shown in Fig. 6 were obtained. The activation energy was 21.3 kcal/mole, which energy is nearly equivalent to that obtained for other condensed phosphates in acidic media.

The data on the trimetaphosphate hydrolysis rate under the conditions given in this paper have not previously been published. Nevertheless, the half-life of trimetaphosphate at 50°C and pH 1.0 was assumed to be 0.87 h by extrapolation of the data in

TABLE I

KINETIC DATA FOR TRIMETAPHOSPHATE HYDROLYSIS IN 0.1 *M* HYDROCHLORIC ACID SOLUTION

*Parameter**	*10°C*	*20°C*	*30°C*	*40°C*	*50°C*
$k(h^{-1})$	0.105	0.336	1.22	3.69	10.3
$t_{1/2}(h)$	65.0	20.6	5.67	1.88	0.67

* E_a = 21.3 kcal/mole.

Fig. 10 on p.169 of ref. 1. This value is slightly higher than our reliable value of 0.67 h.

Trimetaphosphate is the smallest six-membered ring in the cyclic phosphate series and is very readily hydrolysed in both acidic and basic media. This instability might be due to the strain in the six-membered ring.

We are now investigating the hydrolysis reactions of other cyclic phosphates in acidic aqueous solution by this automatic liquid chromatographic system.

ACKNOWLEDGEMENTS

The research was supported in part by Grant-in-Aid for Scientific Research No. 574233 from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1 R. K. Osterheld, in E. J. Griffith and M. Grayson (Editors), *Topics in Phosphorus Chemistry*, Wiley, New York, 1972.
2 R. M. Healy and M. L. Kilpatrick, *J. Amer. Chem. Soc.*, 77 (1955) 5258.
3 J. Crowther and A. E. R. Westman, *Can. J. Chem.*, 34 (1956) 969.
4 G. Kura, *J. Chromatogr.*, 211 (1981) 87.
5 Y. Hirai, N. Yoza and S. Ohashi, *Anal. Chim. Acta*, 115 (1980) 269.
6 J. R. Van Wazer, *Phosphorus and Its Compounds*, Vol. I, Interscience, New York, 1958.
7 I. Hosokawa and F. Oshima, *Water Res.*, 7 (1973) 283.