

CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS

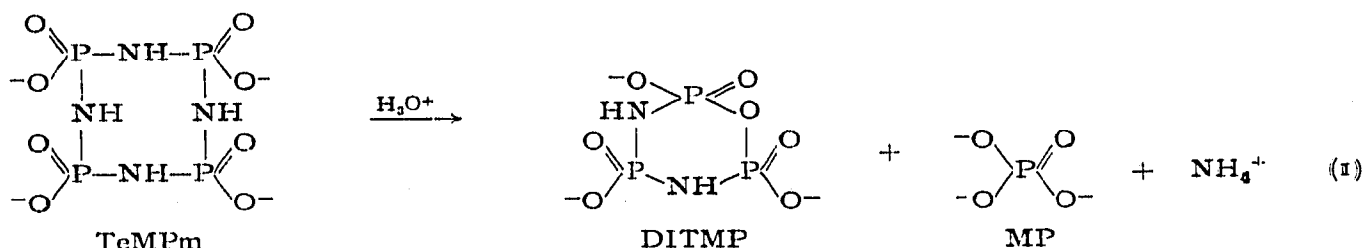
PART IX. A QUANTITATIVE STUDY OF THE HYDROLYSIS OF THE TETRAMETAPHOSPHIMATE ANION

F. H. POLLARD, G. NICKLESS AND A. M. BIGWOOD

Department of Chemistry, University of Bristol (Great Britain)

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Recent investigations¹, into the hydrolytic behaviour of the tetrametaphosphimate (TeMPm) anion, have indicated the unusual ring degradation upon acid hydrolysis, yielding the di-imidotrimetaphosphate (DITMP) anion, together with orthophosphate (MP).



The di-imidotrimetaphosphate undergoes further hydrolysis to mono-imidotrimetaphosphate (ITMP), and thence to trimetaphosphate (TMP), pyrophosphate (DP), and orthophosphate very slowly as described in earlier papers¹⁻⁵.

With improved methods of anion-exchange chromatography, it has been possible to study the hydrolysis of TeMPm quantitatively, and show that the eight-membered phosphimate ring is more stable to acid hydrolysis than its six-membered analogues.

EXPERIMENTAL

Preparation of ammonium tetrametaphosphimate

Investigations of the salts of TeMPm by STOKES⁶, showed that the tetra-sodium potassium and silver salts, as well as the acid itself, were all highly insoluble in water. However, the ammonium salt is fairly soluble, and hence is the only salt suitable for hydrolytic studies. The behaviour and stoichiometry of these salts have been investigated by STEGER AND LUNKWITZ^{7,8}.

10 g of pure tetraphosponitrilic chloride (PNCl₂)₄ (Albright & Wilson Ltd.), were dissolved in 200 ml of dioxan, and mixed with a solution of 40 g of ammonium acetate dissolved in 40 ml of water. The mixture was then stirred continuously for 90 h. The white precipitate was separated by filtration, and washed with methanol. Pure

ammonium tetrametaphosphimate was recovered from an aqueous solution by dissolution of this white product and precipitation with methanol. The yields were always of the order of 55 %; elemental analysis, together with infra-red, paper and anion-exchange chromatographic techniques, showed the product to be pure.

Analysis of hydrolytic products

To study quantitatively the hydrolytic breakdown of TeMPm to DITMP, ITMP, and MP, by anion-exchange chromatography, it is necessary to achieve good separations between the four anions concerned. However, it was found that using the standard 50×0.9 cm column packed with 100–200 mesh size Dowex-1 X 8 resin, and eluting with 0.075 M–0.75 M potassium chloride buffered to pH 5.0,⁵ that TeMPm and DITMP have almost identical retention volumes (Fig. 1a). Experimentation with different gradient chloride eluants proved of little value in separating the two anions,

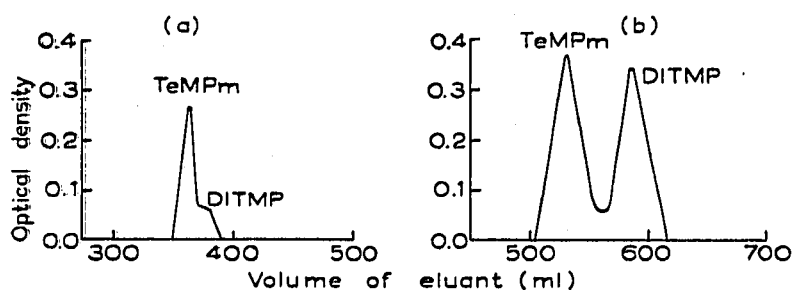


Fig. 1. Elution patterns of TeMPm and DITMP using differing columns and gradient elution conditions. (a) 0.075–0.75 M KCl solutions. (b) 0.050–0.80 M KCl solutions.

and thus this type of column geometry was abandoned. In order to overcome such difficulties, it was decided to use a column where the two anions might separate whilst exchanging slowly down a long column containing more bed volume of resin per unit column length than that previously described. With this in mind, a column 100 cm \times 1.2 cm diameter of Dowex-1 X 8, 100–200 mesh resin was used, with a chloride gradient eluant of 0.05 M–0.80 M potassium chloride solution. This gradient took a greater volume of eluant to reach the optimum value of desorption (see ref. 5), but

TABLE I

<i>Summary of column conditions</i>	
Column: 100 cm \times 1.2 cm diameter	
Resin: Dowex-1 X 8, 100–200 mesh size	
Eluants: 0.05 M KCl–0.80 M KCl buffered to pH 5.0	
Flow rate: 35–40 ml/h	
<i>Retention volumes</i>	<i>(ml)</i>
Orthophosphate	220
Trimetaphosphimate	420
Tetrametaphosphimate	520
Diimidotrimetaphosphate	580
Imidotrimetaphosphate	780
Trimetaphosphate	1100

caused sharper elution peaks, because the $d[Cl^-]/dt$ was greater. Such a gradient prevented broadening of peaks, and hence less error in evaluating absolute recoveries for kinetic measurements. The separation achieved is shown in Fig. 1b.

The separation achieved using the conditions mentioned above, was not improved upon markedly by experimentation using other differing gradients, and so was used for studying the hydrolysis of TeMPm (Table I).

Study of hydrolysis

Approximately 0.5 g of ammonium TeMPm were dissolved in 50 ml of acetate buffer pH 3.62 in a 100 ml graduated flask, which was placed in a thermostatically controlled water-bath at the required temperature. 5.0 ml samples were removed from the solution at noted time intervals, and the reaction stopped by pouring the samples

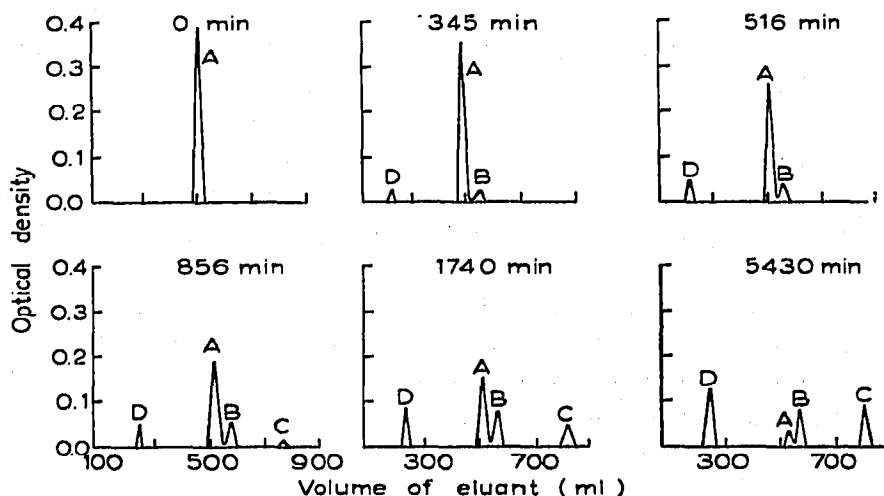


Fig. 2. Elution patterns for the hydrolysis of TeMPm at 65° and pH 3.62. A = TeMPm; B = DITMP; C = ITMP; D = MP.

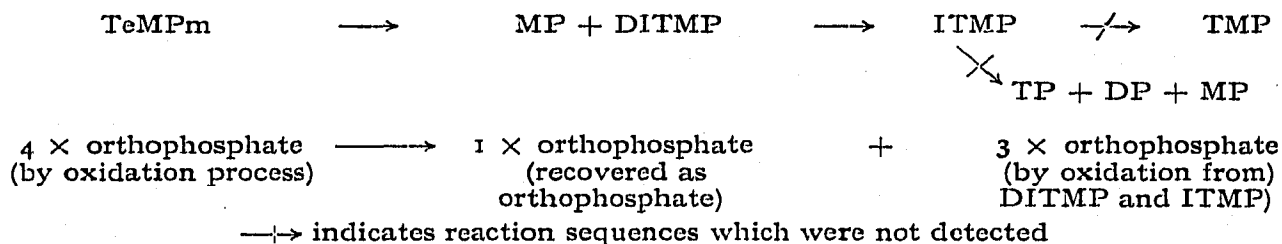
into 5 ml of ice-cold 0.2 *N* caustic soda solution. 1 ml of this solution was absorbed on to the anion-exchange column, eluted and the phosphorus-containing fractions estimated in the manner as previously described⁵. The results of analysis at the various time intervals are shown in Fig. 2, and typical results are given in Table II, where k_0

TABLE II

Temperature 65.0°		Temperature 80.0°	
Time of hydrolysis (min)	$k_0 \times 10^4$ (min ⁻¹)	Time of hydrolysis (min)	$k_0 \times 10^4$ (min ⁻¹)
345	3.63	355	1.35
516	3.75	634	1.31
856	3.78	879	1.32
1,268	3.65		
1,748	3.50		

is velocity constant of overall breakdown of TeMPm, which was calculated in the following manner.

Each phosphate species recovered by the anion-exchange separation is oxidatively hydrolysed to orthophosphate by heating with concentrated nitric acid, and then estimating the orthophosphate as the ammonium phosphovanadomolybdate complex. Thus we have the analytical recovery procedure:



It would be expected that the recovery of MP would be one-third that of the combined recoveries of DITMP and ITMP, provided that reaction (1) is followed. As reported previously¹, the recovery of MP always exceeds that of one-third of total recovery of DITMP + ITMP, which most probably indicates the partial breakdown of TeMPm to chain imido-phosphates which, in turn, immediately hydrolyses under the hot acid conditions, to MP. It has been proved⁵ that DITMP and ITMP decompose only very slowly to chain phosphates, hence the discrepancy in the analytical figures is directly attributable to the hydrolysis of TeMPm to chain species. Therefore k_0 does not express the true reaction constant for the breakdown of TeMPm to DITMP, since it incorporates the reaction constant for ring fission to chain phosphates. To evaluate k^1 , the rate constant for ring degradation, it is necessary to sum the total recovery of DITMP + ITMP, and take one-third of this value as the concentration of orthophosphate resultant from ring degradation. If one uses this factor as x in the equation:

$$k^1 = \frac{1}{t} \ln \frac{a}{a - x}$$

where a is the total recovery of phosphorus, which at time $t = 0$, is all TeMPm, then the variation of $\ln a/(a - x)$ versus time is shown in Fig. 3, and the values of k^1 are given in Table III.

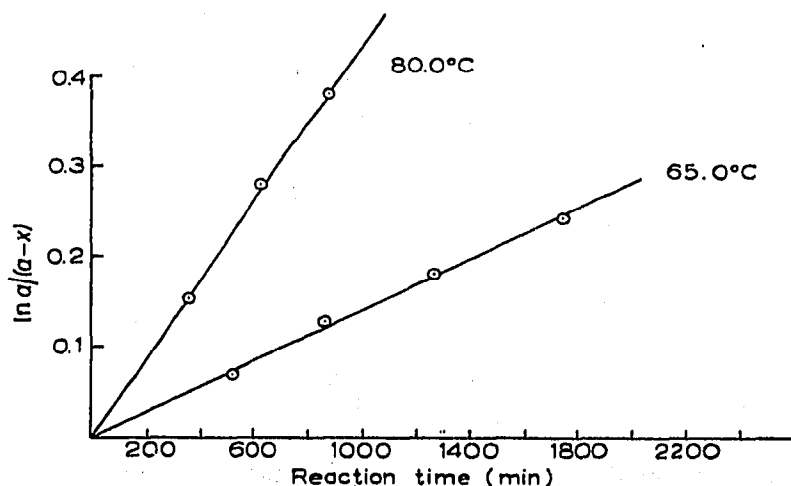


Fig. 3. Plot of $\ln a/(a - x)$ versus time (min) for the TeMPm degradation to DITMP and MP.

TABLE III

Temperature 65.0°		Temperature 80.0°	
Time (min)	$k^1 \times 10^4$ (min ⁻¹)	Time (min)	$k^1 \times 10^3$ (min ⁻¹)
345	—*	355	1.00
516	3.43	635	1.02
856	3.52	879	1.00**
1,268	3.28		
1,748	3.20		

* k^1 not calculated, only trace DITMP formed.

** This result may be in error due to further degradation of ITMP.

From the data of Table III, it is proposed that:

$$\left. \begin{aligned} k_{65.0^\circ}^1 &= 3.37 \cdot 10^{-4} \text{ min}^{-1} \\ k_{80.0^\circ}^1 &= 1.01 \cdot 10^{-3} \text{ min}^{-1} \end{aligned} \right\} \text{ at } 65.0^\circ$$

and from this:

$$E_{\text{TeMPm}}^* \longrightarrow \text{DITMP} = 17.3 \text{ kcal/mole}$$

DISCUSSION

From these quantitative studies on the breakdown of the TeMPm anion to DITMP, and further to ITMP; the validity of the ring degradation is shown by two factors:

(i) The results obtained for k^1 on assuming ring degradation are consistent within themselves, and give a straight line when $\ln a/(a-x)$ is plotted against time, which passes through the origin.

(ii) The rate of appearance of phosphate species, recovered after 740 ml of eluant had passed through the column, was calculated to be identical (within experimental error) to that of the rate breakdown of DITMP under similar conditions (see ref. 5).

$$\left. \begin{aligned} k_{\text{DITMP} \rightarrow \text{ITMP}} &= 1.02 \cdot 10^{-3} \text{ min}^{-1} \\ k_{\text{appearance}} &= 1.02 \cdot 10^{-3} \text{ min}^{-1} \end{aligned} \right\} \text{ at } 65.0^\circ$$

Thus indicating that it was in fact ITMP being recovered from anion-exchange separation, the ITMP being resultant from the hydrolysis of DITMP.

The overall acid hydrolysis of the tetrametaphosphimate was a factor of some twenty-five times slower than that of its six-membered ring homologue trimetaphosphimate ($k_{\text{TeMPm}}^{65^\circ} = 8.9 \cdot 10^{-3} \text{ min}^{-1}$). The stability of TeMPm lies between that of DITMP and ITMP.

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SUMMARY

A kinetic study of the hydrolysis of ammonium tetrametaphosphimate in acid solution at elevated temperatures is described. The degradation of an eight-membered ring to a six-membered ring appears to be a general type reaction in such phosphorus-nitrogen systems.

REFERENCES

- ¹ G. POLLARD, G. NICKLESS AND R. W. WARRENDER, *J. Chromatog.*, 9 (1962) 506.
- ² A. NARATH, F. H. LOHMAN AND O. T. QUIMBY, *J. Am. Chem. Soc.*, 78 (1956) 4493.
- ³ A. NARATH, F. H. LOHMAN AND O. T. QUIMBY, *J. Am. Chem. Soc.*, 82 (1960) 1099.
- ⁴ F. H. POLLARD, G. NICKLESS AND R. W. WARRENDER, *J. Chromatog.*, 9 (1962) 493.
- ⁵ F. H. POLLARD, G. NICKLESS AND A. M. BIGWOOD, *J. Chromatog.*, 11 (1963) 534.
- ⁶ H. N. STOKES, *J. Am. Chem. Soc.*, 18 (1896) 780.
- ⁷ E. STEGER AND K. LUNKWITZ, *Z. Anorg. Chem.*, 313 (1961) 262.
- ⁸ E. STEGER AND K. LUNKWITZ, *Z. Anorg. Chem.*, 313 (1961) 271.

J. Chromatog., 12 (1963) 527-532