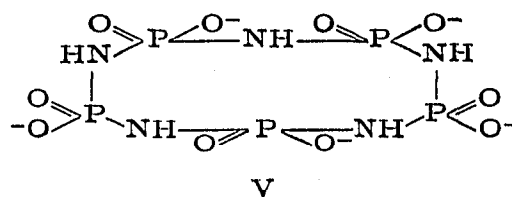
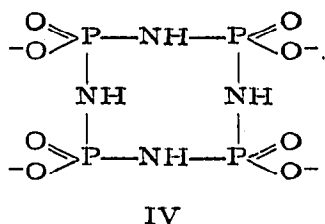
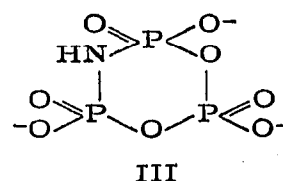
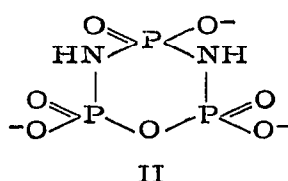
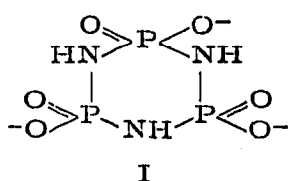


CHROMATOGRAPHIC STUDIES
ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS
PART X. INVESTIGATIONS INTO THE
HYDROLYSIS OF AMIDO- AND IMIDO-PHOSPHATES

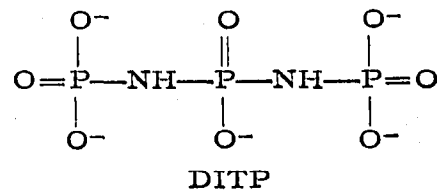
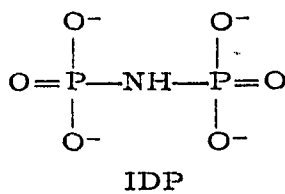
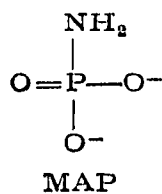
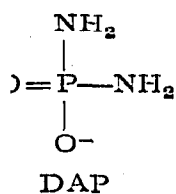
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During the course of investigations into the chemistry of imidometaphosphates¹⁻⁴, such as trimetaphosphimate (I), diimidotrimetaphosphate (II), monoimidotrimetaphosphate (III), tetrametaphosphimate (IV) and pentametaphosphimate (V) anions,



A study of the linear phosphorus-nitrogen acids was carried out. The investigation was thought necessary in an attempt to interpret the behaviour of the higher complexing acids in solution, in terms of the characteristics shown by the simpler acids, namely, diamidophosphate (DAP), monoamidophosphate (MAP), monoimidoliphosphate (IDP), and diimidotriphosphate (DITP).



All linear imidophosphates ultimately degrade in acid solution to monoamidoliphosphate MAP and orthophosphate^{5,6}. Therefore, it was necessary to develop a

suitable means of separating and identifying DAP, MAP, and orthophosphate (MP). Anion-exchange chromatography using a gradient elution technique with chloride solutions has been developed to separate the ring imidophosphates completely^{3,4}. Investigations into the possible similar use of this technique in this case subsequently proved successful not only for the separation of amidophosphates, but also for the linear imidophosphates. This technique was used to elucidate the hydrolytic degradations of MAP, IDP and DITP.

EXPERIMENTAL AND RESULTS

Resin. Dowex 1 × 8, mesh size 100–200 B.S.S.

Column. 50 cm × 0.9 cm diameter.

Eluant. 0.075 M potassium chloride (buffered to pH 11.4), passed through the column for 200 ml, followed by 0.60 M potassium chloride at pH 5.0 dropping into 1 l of 0.075 M potassium chloride at pH 7.8.

Temperature. The column was operated at 1° using a circulating water-jacket.

Analysis of eluant. By collecting 10 ml fractions using a syphon fraction collector, and subsequent treatment by the standard colorimetric method for determination of phosphorus by the phosphovanadomolybdate complex⁴.

In some cases, when absolute quantitative results were not required, analysis was carried out using a Technicon autoanalyser system, a procedure which has been described in great detail elsewhere⁷. Basically the column eluant pumped at 48.0 ml/h was hydrolysed to convert all phosphorus species to phosphate with a sequence of 7.5 N H₂SO₄ for 15 min at 95°, and 10 N H₂SO₄ for 30 min at 95°. The orthophosphate so made was subsequently determined as the phosphomolybdenum blue colour using hydrazine sulphate as reducing solution. The final colour flowed continuously through a colorimeter coupled to a potentiometric recorder.

The type of separation achieved using such a system is given diagrammatically in Fig. 1.

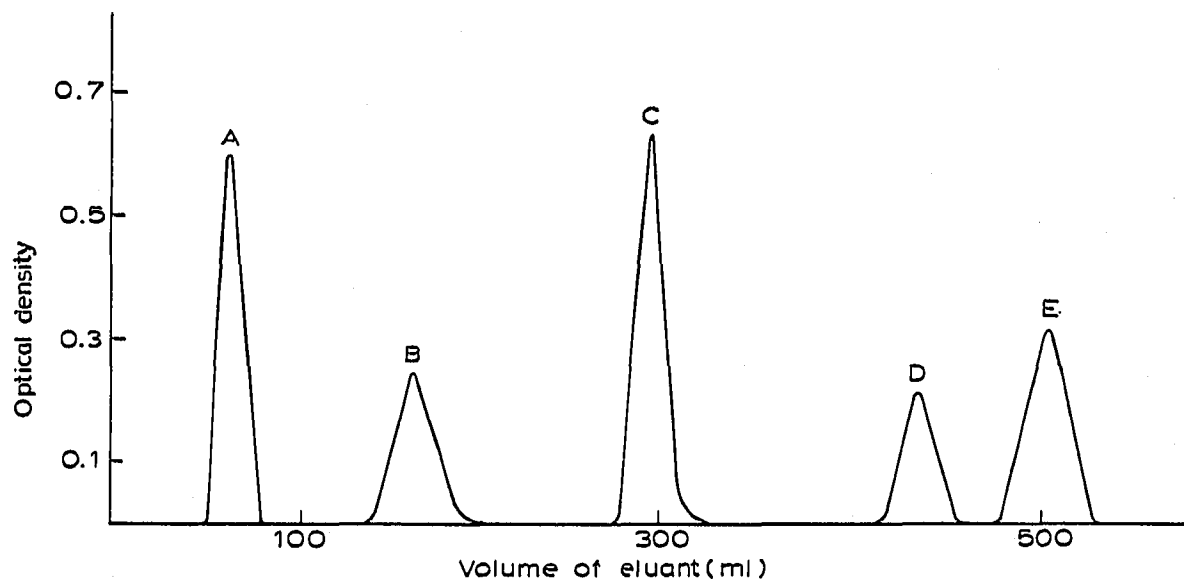


Fig. 1. Separation of amido- and imidophosphates. A = Diamidophosphate. B = Monoamidophosphate. C = Orthophosphate. D = Imidodiphosphate. E = Diimidotriphosphate.

Hydrolysis of amidophosphate

Sodium MAP (supplied by Albright and Wilson Ltd.) was analysed for orthophosphate content and was found to be 99.6% pure. This was thought to be pure enough for further study.

0.10 g samples of sodium MAP were dissolved in 10 ml of acetate-hydrochloric acid buffer pH 4.40 suspended in a water bath at 40.0°. Aliquots of this solution were removed at different time intervals and delivered into 5.0 ml ice-cold 0.1 *N* caustic soda solution. 1.0 ml of this solution was transferred to the anion-exchange column and the elution procedure carried out.

Results. From the graph of $\log a/b$ (where a = total phosphorus concentration at time $t = 0$, and b = total amidophosphate concentration present at time t min) against t (min) was produced a linear relationship for a first order reaction with a velocity constant, k , of $3.60 \cdot 10^{-3} \text{ min}^{-1}$ (see Fig. 2). During the course of the hydrolysis, small

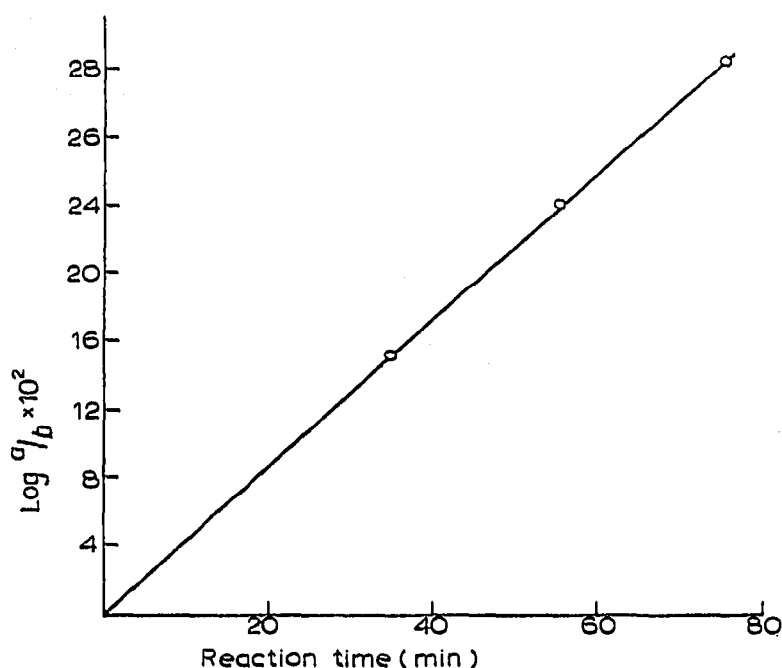


Fig. 2. First order hydrolysis of monoamidophosphate.

quantities of pyrophosphate were detected, but they were neglected in the elucidation reaction kinetics. A typical elution pattern of a reaction mixture is shown in Fig. 3.

Hydrolysis of monoimidodiphosphate

Sodium IDP was prepared and purified by HERBERT of these laboratories⁸. Previous investigations into the hydrolytic degradation of the imidodiphosphate anion^{5,6,9} have indicated the possibility of the replacement of the imido-linkage by oxygen to yield the pyrophosphate anion as well as fission of the imido-link to yield MAP and orthophosphate.

Separation of IDP and pyrophosphate (DP) proved extremely difficult by anion exchange, and a much weaker gradient of the chloride eluant was used.

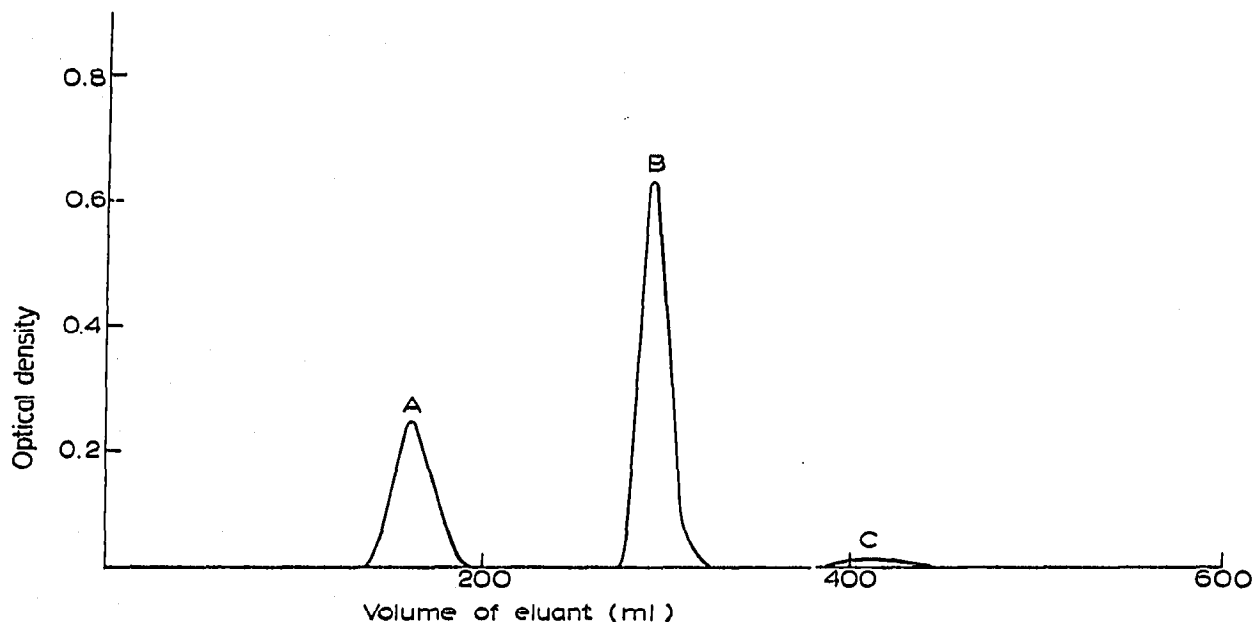


Fig. 3. Elution pattern for the hydrolysis of monoamidophosphate. A = Monoamidophosphate. B = Orthophosphate. C = Pyrophosphate.

Details for the separation of MAP, MP, IDP, and DP, were as given below, and as shown in Fig. 4.

Column. Dowex 1 \times 8, 100-200 mesh.

Eluants. 0.075 M KCl (at pH 11.4) for 200 ml, then 0.25 M KCl (at pH 7.8) dropping into 1 l of 0.075 M KCl (at pH 5.0).

Temperature. The column was run at ca. 1°.

The hydrolysis of imidodiphosphate was carried out under exactly similar conditions of acidity and temperature as for MAP, and the same procedure used for the analysis.

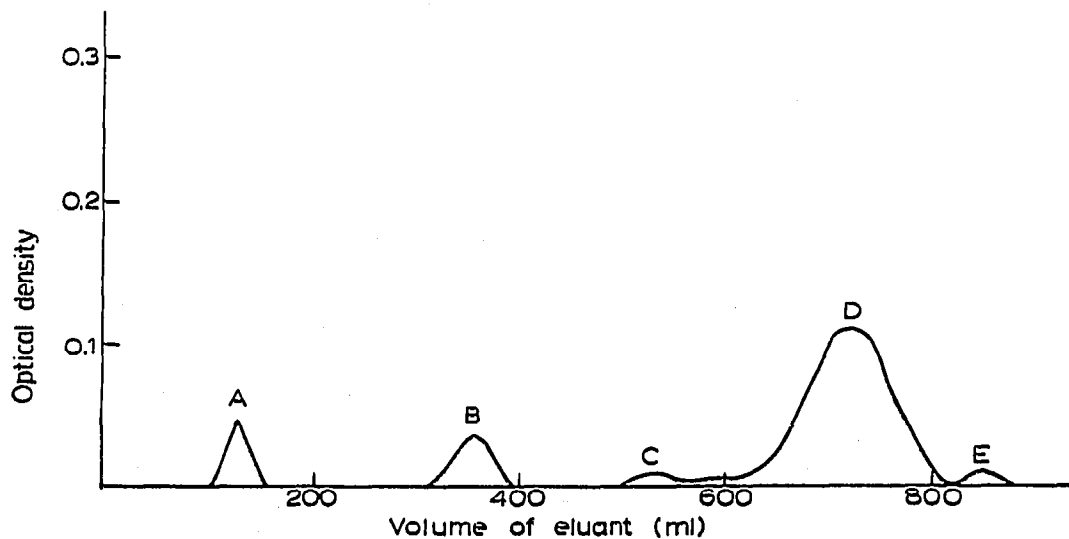


Fig. 4. Elution pattern for the hydrolysis of imidodiphosphate. A = Monoamidophosphate. B = Orthophosphate. C = Forward tailing (decomposition) of D. D = Imidodiphosphate. E = Pyrophosphate.

Results. Sodium IDP was found to hydrolyse very rapidly at pH 4.40, and 40.0° to MAP and orthophosphate. Pyrophosphate was detected, but only in small quantities of the order of 5 %.

The first order reaction velocity constant was evaluated to approximately $1 \cdot 10^{-1} \text{ min}^{-1}$, and is shown in Fig. 5.

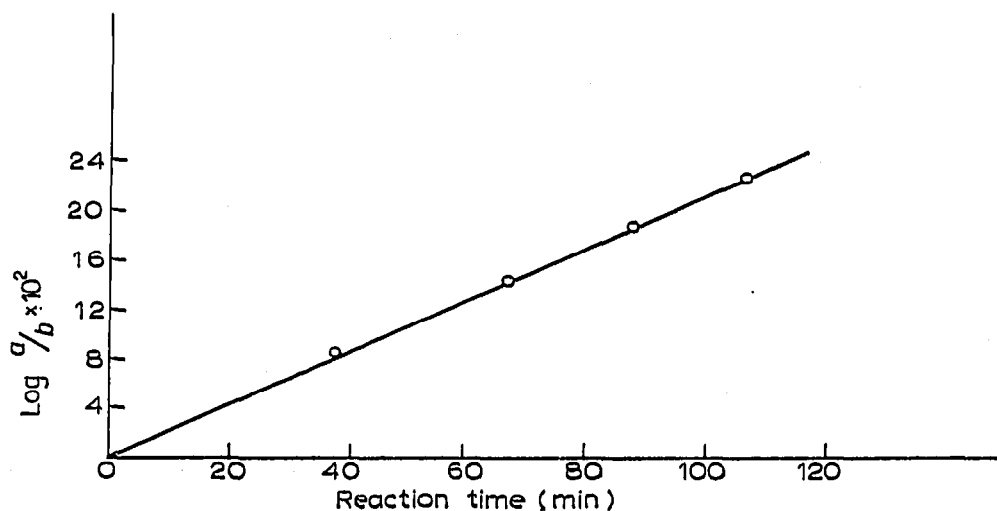


Fig. 5. First order hydrolysis of imidodiphosphate.

Hydrolysis of diimidotriphosphate

Using the separation conditions given in relation to Fig. 1, the hydrolysis of sodium DITP⁸ (prepared and purified in these laboratories by P. A. HERBERT) was investigated at 40.0° and pH 4.40. Analysis of the reaction products was carried out using the Autoanalyser system, and a typical trace for a reaction time of 90 min is given in Fig. 6.

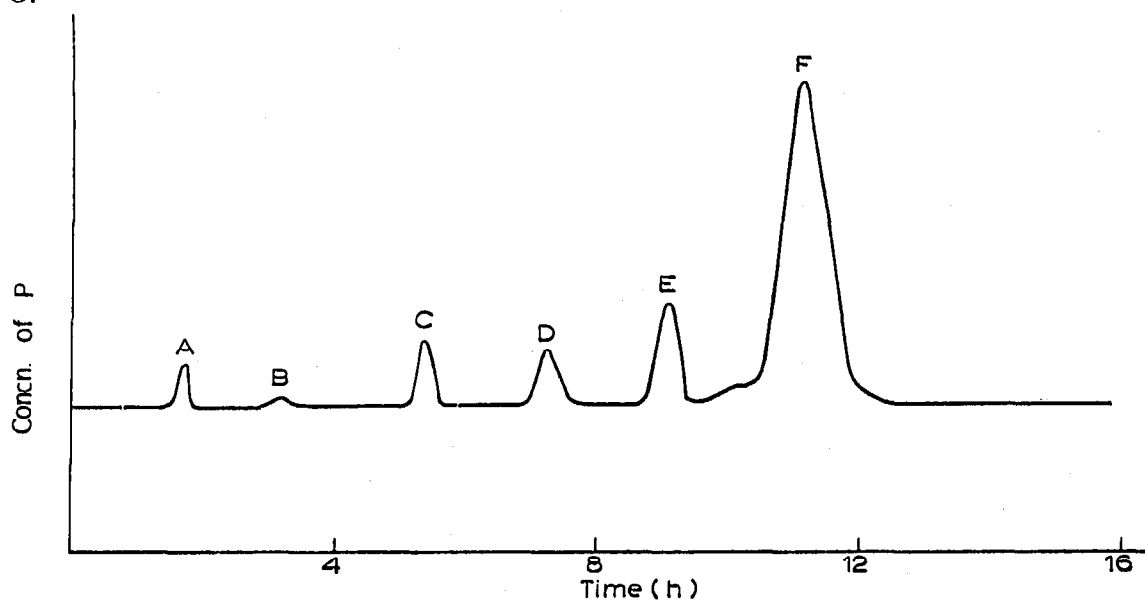
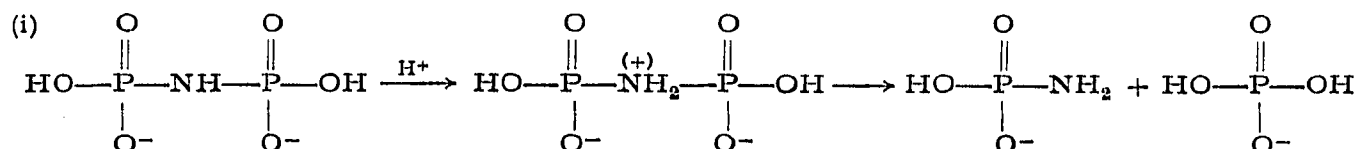


Fig. 6. Elution pattern for the hydrolysis of diimidotriphosphate. A = Diamidophosphate. B = Monoamidophosphate. C = Orthophosphate. D = Unknown species (see text). E = Imidodiphosphate. F = Diimidotriphosphate.

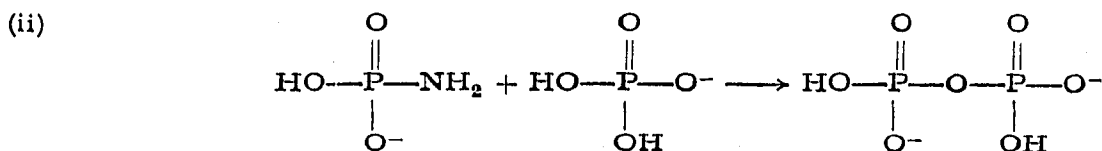
The reaction velocity constant could not be evaluated to any certain degree of accuracy, but the system is being examined in greater detail.

DISCUSSION

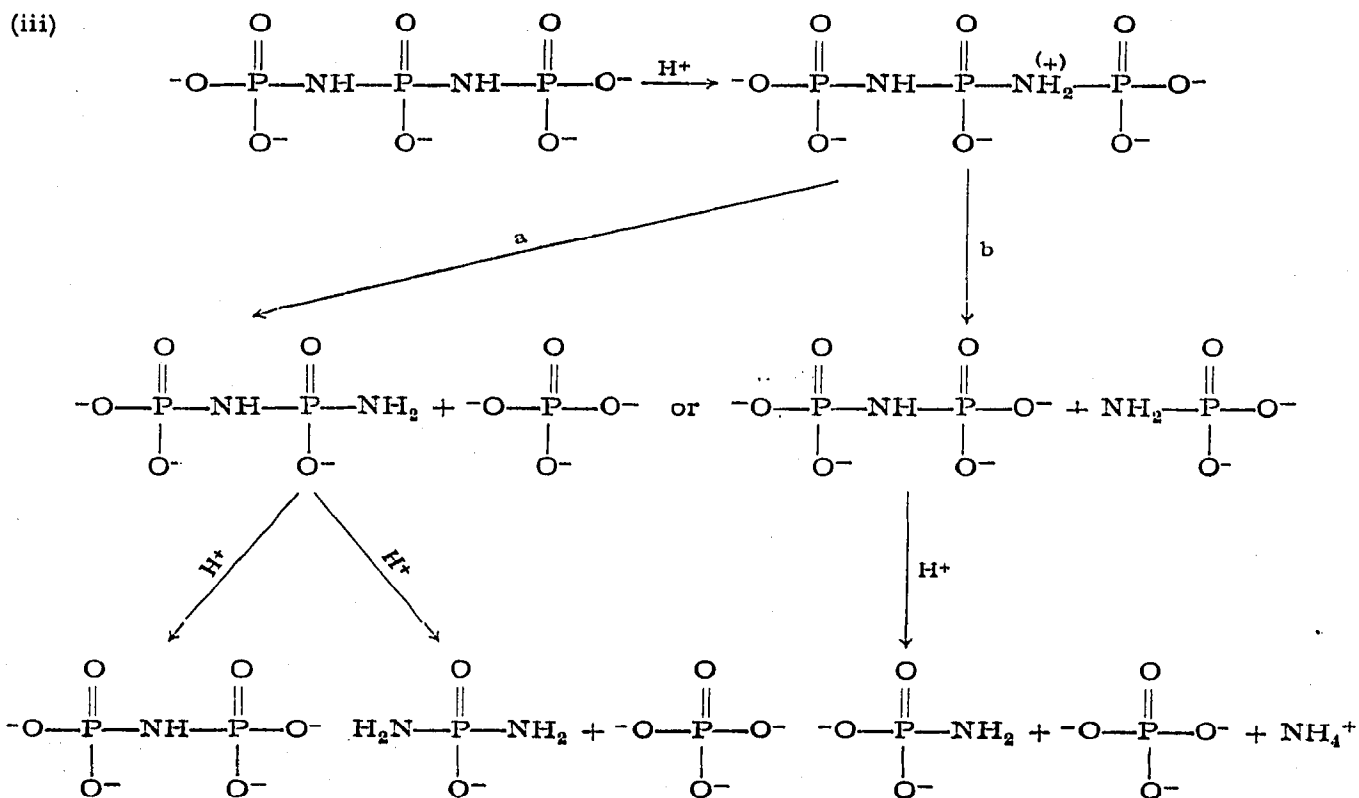
The study of the hydrolytic breakdown of IDP and DITP shows a definite pattern of behaviour for linear imidophosphates in general. IDP breaks down on hydrolysis to amidophosphate, orthophosphate and small quantities of pyrophosphate. The breakdown of the imido linkage therefore occurs primarily by protonation of the $-NH-$ group,



and condensation of amido and orthophosphate occurs to yield pyrophosphate.

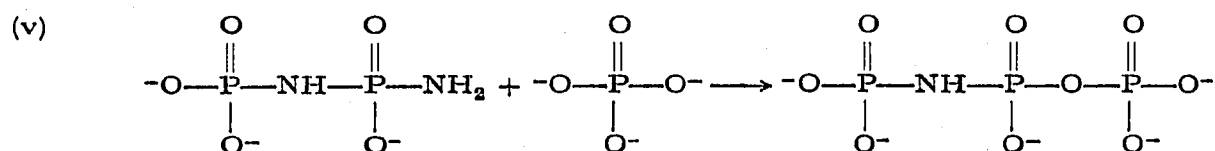
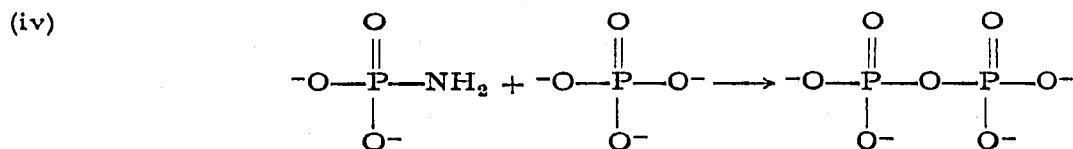


Similarly, DITP hydrolysis by the same mechanism of protonation of one $-NH-$ linkage, and subsequent fission to yield amidoimidodiphosphate and orthophosphate (iiia), or imidodiphosphate and amidophosphate (iiib).



Analysis of the hydrolysis products of the DITP anion (Fig. 6) shows the presence of diamidophosphate and an unknown species (D) which by inference from its faster retention time with reference to imidodiphosphate must be amidodiphosphate. The main reaction path, therefore, seems to be (iiia) and not (iiib).

With the presence of amidophosphate in solutions, small quantities of condensation products are almost certainly formed:



but unfortunately no positive establishment of their existence was found.

Attention must finally be drawn to the stability of monoamidophosphate ($3.60 \cdot 10^{-3} \text{ min}^{-1}$) with reference to the stability of monoimidodiphosphate ($1 \cdot 10^{-1} \text{ min}^{-1}$) under identical conditions. Further studies into the variation of reaction velocity constant with pH are now being carried out, and details will be published later.

ACKNOWLEDGEMENT

Grateful acknowledgement is made to the Department of Scientific and Industrial Research for a Maintenance Grant to one of us (A.M.B.) during the period of this research.

SUMMARY

A study of the hydrolytic degradation of the linear phosphorus-nitrogen acids is outlined and discussed in an attempt to interpret the behaviour of more complex ring imidophosphate acids in solution.

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