sidered as susceptible to electrophilic attack to some extent. These results are also consistent with the assignment of the bands in the n.m.r. spectrum.[7,16,17]

The question of formation of other isomers of diiododecaborane arises at this point. Provided that the presence of the first iodine atom does not influence the placement of the second iodine atom, six isomers are expected from the diiodination of decaborane. Three of these, the 5,7-, the 5,8- and the 5,10-isomers are each expected in only 3% of the total yield and therefore were missed easily. The 2,4-isomer by the same token is expected in 31% of the total yield which is fairly consistent

(16) R. E. Williams and I. Shapiro, J. Chem. Phys., **29**, 677 (1958).

(17) NOTE ADDED IN PROOF.—Since this paper was prepared, additional evidence has been obtained supporting the proposition that the four-fold position is susceptible to electrophilic attack. Iodination by iodine and aluminum chloride, i.e., by I⊕, gave the same ratio of iododecaborane isomers,[18] and reaction of decaborane with deuterium chloride and aluminum chloride gave what is apparently 2,4,5,7,8,10-hexadeuteriodecaborane.[19]

(18) M. Hillman, J. Inorg. Nucl. Chem., in press.

(19) J. A. Dupont and M. F. Hawthorne, THIS JOURNAL, **81**, 4998 (1959).

with the experimentally obtained value of 37%. The other two isomers, the 2,5- and the 2,8-, are each expected in about 30% of the total yield. Apparently only one of these isomers was observed.

If the other isomer is not present or is present in much smaller quantities than expected, then it would suggest that the presence of one iodine atom would influence the placement of the second atom, and, intuitively at least, the isomer observed may be considered to be 2,8-diiododecaborane in equal admixture with its enantiomorph. On the other hand, if the properties of the two expected isomers were quite similar then one could easily have been missed even in the quantitative infrared analysis.

Small amounts of several substances were actually obtained with new bands in their infrared spectra, but these were not characterized further.

Dilute Solution Condensation during Hydrolytic Degradation of Imidophosphates at 60°

BY O. T. QUIMBY, A. NARATH AND F. H. LOHMAN

The ultimate product from acid hydrolysis of dilute solutions of these phosphorus-nitrogen compounds, like that of the analogous oxylinked phosphates, is very largely the mono- or orthophosphate. However, during imide degradation appreciable concentrations of new P–O–P links are formed via a condensation of the amide intermediates through the elimination of an ammonium ion. Hydrolysis of trimetaphosphimate ion at pH 3.5 furnishes a striking example of this condensation for a large part of the phosphorus can be recovered at intermediate stages in the form of diimidotrimetaphosphate, i.e., a ring ion with an oxy link in place of one of the imide links. Imide links are usually less stable than oxy links in acid solutions but attain a comparable or greater stability in sufficiently alkaline solution. Imidotrimetaphosphate behaves exceptionally at pH 3.5 where the oxy links break faster than the imide link.

Introduction

When condensed phosphates (P in the V oxidation state) suffer hydrolytic degradation in dilute aqueous solutions, there is but one over-all reaction involved, namely

$$-P-O-P- + HOH \longrightarrow -P-OH + HO-P- \quad (1)$$
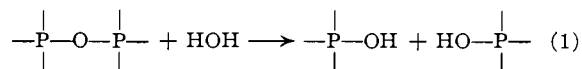
It is essentially irreversible, for if continued long enough, practically all of the phosphorus ends up as orthophosphate. Reaction 1 is reversed if crystalline acid phosphates are heated at 200° or higher.
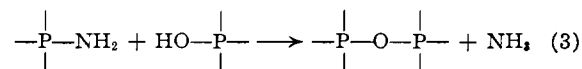
When imide groups replace the oxy bridge in condensed phosphates, hydrolytic degradation presumably first acts to produce amides[1] as indicated by the equation
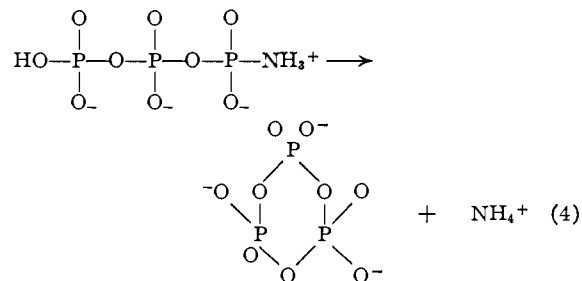
$$-P-\overset{H}{N}-P- + HOH \longrightarrow -P-NH_2 + HO-P- \quad (2)$$
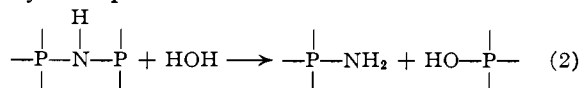
In acidic or mildly alkaline solutions this is not the end of the matter, for the amide may yield P–O–P links[2] by elimination of ammonia

$$-P-NH_2 + HO-P- \longrightarrow -P-O-P- + NH_3 \quad (3)$$

A striking example of amide condensation to form new P–O–P links occurs upon acidifidation of solutions of the chain ion monoamidotriphosphate[3]

$$HO-\overset{O}{\underset{O_-}{P}}-O-\overset{O}{\underset{O_-}{P}}-O-\overset{O}{\underset{O_-}{P}}-NH_3^+ \longrightarrow$$

$$+ NH_4^+ \quad (4)$$

At a pH of 3-4 amidotriphosphate is quickly and almost completely converted to trimetaphosphate at room temperature. The mild acid hydrolysis of trimetaphosphimate briefly described previously[2]

by other investigators, e.g., V. M. Clark, G. W. Kirby and A. Todd, J. Chem. Soc., 1497 (1957); R. W. Chambers, J. G. Moffatt and H. G. Khorana, THIS JOURNAL, **79**, 4240 (1957).

(1) H. N. Stokes, Am. Chem. J., **18**, 629 (1896).

(2) A. Narath, F. H. Lohman and O. T. Quimby, THIS JOURNAL, **78**, 4493 (1956); the generality of reaction 3 is now well substantiated

(3) O. T. Quimby and T. J. Flautt, Z. anorg. allgem. Chem., **296**, 220 (1958).

and more fully described in this paper is presumed to follow a similar path; however, the chain ion intermediates (monoamidodiimidotriphosphate and the two monoamidomonoimidotriphosphates) have not been isolated.

The extent to which reaction 3 may occur is dependent on several factors. Most important is the competition with the hydrolytic reaction

$$-\underset{|}{\overset{|}{P}}-NH_2 + HOH \longrightarrow -\underset{|}{\overset{|}{P}}-OH + NH_3 \quad (5)$$
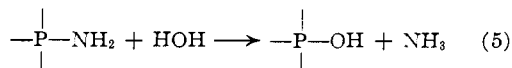
In the following discussion attention will be given to this and other factors such as pH, concentration of reactants, concentration of products and ionic structure.

In the hydrolysis of trimetaphosphimate the nine products which can be separated and isolated by crystallization or chromatography are shown in Fig. 1; amidomonophosphate is also included,
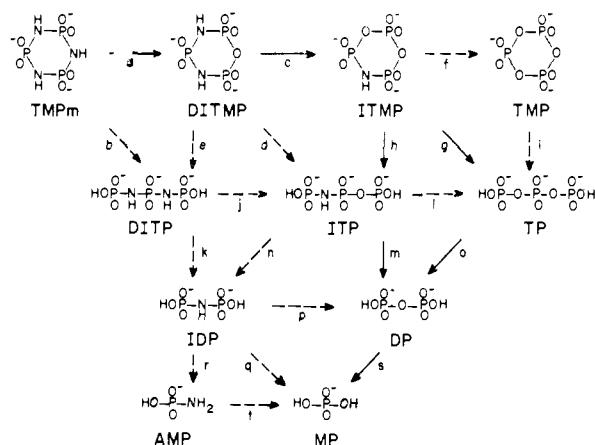

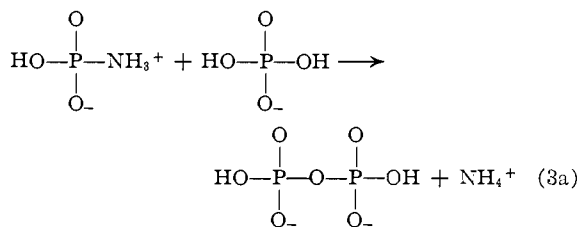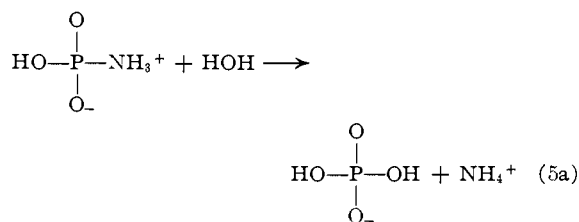TMPm DITMP ITMP TMP

DITP ITP TP

IDP DP

AMP MP

Fig. 1.

even though it was never isolated from the hydrolysates. This paper reports semiquantitative hydrolysis rates for the seven P–N compounds; in addition, some evidence is given on the formation of chain amide intermediates.
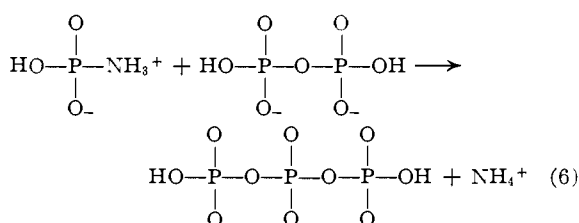
Results

Condensations and Hydrolyses in Formate Buffer at pH 3.6.—Although the present study originated from an attempt to make the chain ion DITP[4] by opening the ring ion, TMPm, the hydrolysis data will be presented for the simplest P–N compound first, namely AMP. The chemical picture will then be built up by proceeding first to the chain dimer, then to chain trimers and finally to ring trimers. Data at pH values other than 3.5 to 3.7 are less complete and will be discussed in a separate section.

Amidomonophosphate.—Even this simple P–N ion (in dilute solutions of $Na_2PO_3NH_2$ in the formate buffer) can and does undergo both reactions 3 and 5. These may be formulated as

(4) Abbreviations used for phosphate ions are: mono MP, amidomono AMP, di DP, imidodi 1DP, tri TP, imidotri 1TP, diimidotri DITP, trimeta TMP, imidotrimeta 1TMP, diimidotrimeta DITMP and trimetaphosphimate TMPm (cf. Fig. 1). All were used as sodium salts.

$$HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-NH_3{}^+ + HOH \longrightarrow$$

$$HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-OH + NH_4{}^+ \quad (5a)$$

$$HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-NH_3{}^+ + HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-OH \longrightarrow$$

$$HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-O-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-OH + NH_4{}^+ \quad (3a)$$

Presumably some triphosphate could also form by extension of (3a) thus

$$HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-NH_3{}^+ + HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-O-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-OH \longrightarrow$$

$$HO-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-O-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-O-\underset{\underset{O_-}{|}}{\overset{\overset{O}{||}}{P}}-OH + NH_4{}^+ \quad (6)$$

However, the amount of TP formed by (6) must be practically negligible at all stages in the hydrolysis of 0.02 M AMP, for chromatograms show that the concentration of the necessary DP intermediate never reaches a level equivalent to 5% of the phosphorus present. Since reaction 6 can be neglected the rate of AMP conversion can be measured by formation of ammonia or of MP + DP as well as by amide disappearance. Lacking a convenient method of determining DP, only data for ammonia formation and amide disappearance have been utilized (Table I). The reaction is so fast that neither method gives more than a rough estimate of the rate of AMP disappearance, which has a quarter-life of about 1.8 minutes.

TABLE I

HYDROLYSIS OF 0.02 M AMIDOMONOPHOSPHATE

Duration of hydrol., min.	% of N present as NH₄⁺	% of N present as amide[a]
0	1.9, 0.6	99, 98
2.5	30, 32	67, 69
5	61, 53, 56	47, 48
10	86	19

[a] The determinations of N still present as amide were done on separate runs in which more care was taken to avoid hydrolysis during warming the solution to 60°.

That DP was rarely detected in the chromatograms of any of the above hydrolysates is not surprising, for the highest rate of DP formation by reaction 3a would take place when the AMP was about half gone so that the solution would then be 0.01 M in both AMP and MP. Under these conditions the molar ratio of water to monophosphate is over 5000. Unless there is some special directing

influence a very large part of the AMP disappearance will occur by reaction 5a and the possible concentration of DP must be quite low.

DP formation was detected qualitatively as follows: An aqueous slurry 0.35 M in NaHPO$_3$-NH$_2$ was adjusted to pH 3.5 with acetic acid, heated quickly to about 70° and stirred at this temperature for 15 minutes. After a short settling period, a portion of the clear supernatant liquid (ca. $^1/_5$ of total volume) was removed and shown to contain much MP. The remaining slurry was stirred for an additional hour at 70°. Upon adding water to increase the volume by 50%, a clear solution soon resulted. Addition of ethanol then precipitated DP as Na$_4$P$_2$O$_7$·10H$_2$O. The precipitate was identified by X-ray diffraction and nitrogen analysis. Absence of nitrogen ruled out sodium imidodiphosphate whose decahydrate gives nearly the same X-ray pattern[5] as Na$_4$P$_2$O$_7$·10H$_2$O. This was confirmed by paper chromatography on hydrolysates of 0.02 M AMP in the presence of 0.02 to 0.10 M MP at 60° and pH 3.5.

Imidodiphosphate.—Since hydrolysis of IDP initially yields AMP and MP

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH + H_3O^+ \longrightarrow$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-NH_3^+ + HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH \quad (7)$$
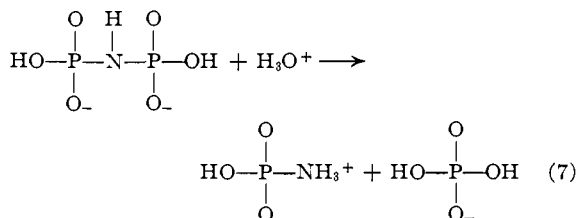
the only new analytical problem is distinguishing the presence of undecomposed IDP from the DP formed by reaction 3a. The two chain dimers can be separated by means of a neutral chromatogram.[6] As shown by the data of Table II, the

TABLE II

HYDROLYSIS OF 0.02 M IMIDODIPHOSPHATE

Duration of hydrol., min.	% of N present as NH$_4^+$	% of P present as MP	$100\, C/C_0$ or % IDP remaining (Chromatog.)
0	1.0	1.4	100
5	12,8		70
10	26,41	46	36
20	60	68,71	..
40	82,79	82	..
60	79,81	90	..
240	86	90	..

rate of IDP disappearance determined chromatographically is nearly twice that calculated from ammonia appearance assuming one IDP molecule destroyed for each molecule of ammonia formed. Qualitatively this is as would be expected, for the concentration of AMP formed by reaction 7 is initially low and hence the rate calculated from ammonia formation must be less than that based
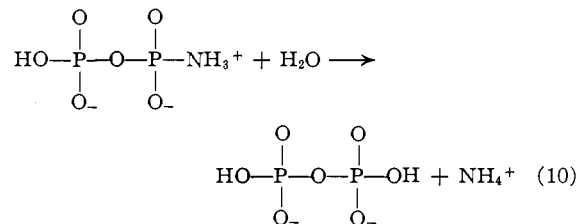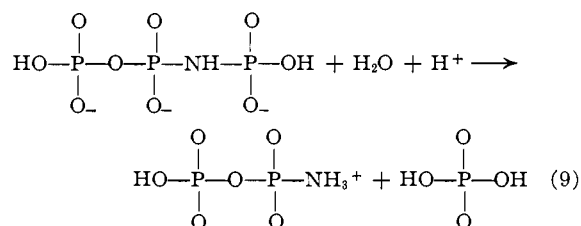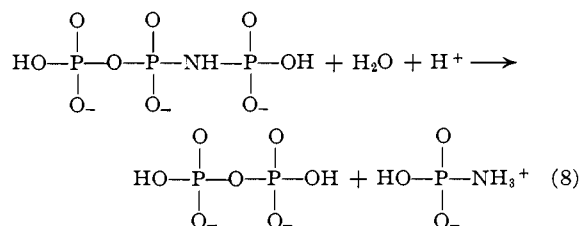
upon a direct measure of IDP disappearance. From the chromatographic data the quarter life of IDP is estimated as 3.5 minutes.

Both nitrogen conversion to ammonia and phosphorus to MP are quite rapid for the first 20–30 minutes but slow down greatly thereafter. This is attributed to the N-rich, chromatographically-immobile species in the sample of imidodiphosphate made via the phosphorus pentachloride-hydroxylamine reaction.[7] Apparently this sample contained only about 80% IDP. The 20% of impurity would not affect the chromatographically-determined quarter life, which is based on the ratio of chromatographically determined IDP concentrations, C_0 at zero hydrolysis time, C after t minutes of hydrolysis.

Chain Imidotriphosphates.—If cleavage of its P–O–P link is ignored, the main steps in the hydrolysis of the monoimidotriphosphate ITP can be represented by equations 8, 5a, 9 and 10.
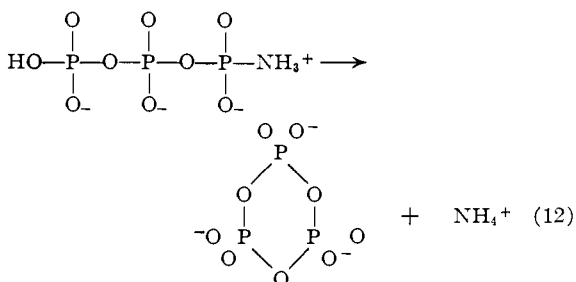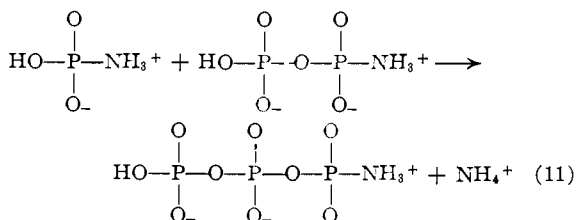
$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-NH-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH + H_2O + H^+ \longrightarrow$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH + HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-NH_3^+ \quad (8)$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-NH-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH + H_2O + H^+ \longrightarrow$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-NH_3^+ + HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH \quad (9)$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-NH_3^+ + H_2O \longrightarrow$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}-OH + NH_4^+ \quad (10)$$

The chromatographic determinations of ITP disappearance (col. 4, Table III) indicate a quater-life of 25 minutes. Since practically all imide nitrogen had become ammonium ion in 4 hr., the ITP concentration must be zero at this point. This is confirmed by the qualitative chromatograms.[7] MP formation was quite rapid at first, due to cleavage of the P–NH–P link, but it slowed down considerably after the first hour or two, when DP had become the main hydrolyzing species, as shown by the qualitative chromatograms.[7]

(5) R. Klement and G. Biberacher, Z. anorg. allgem. Chem., **283**, 246 (1956).

(6) F. H. Lohman and O. T. Quimby, unpublished results, Research & Development Department, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati 39, Ohio.

(7) Material on reagents, methods and photographs of chromatograms, supplementing this article, has been deposited as Document number 6013 with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and remitting $6.25 for photoprints or $2.50 for 35 mm. microfilm in advance check or money order payable to: Chief, Photoduplication Service, Library of Congress.
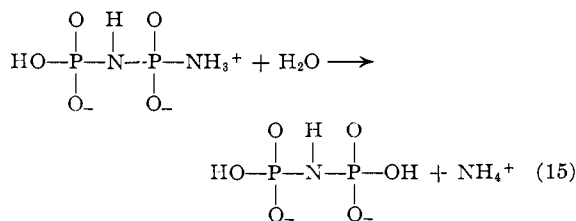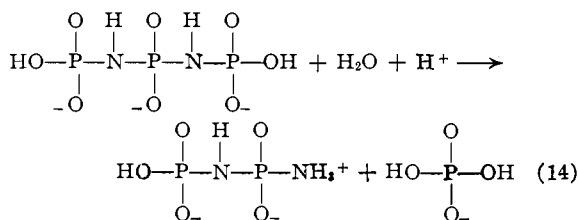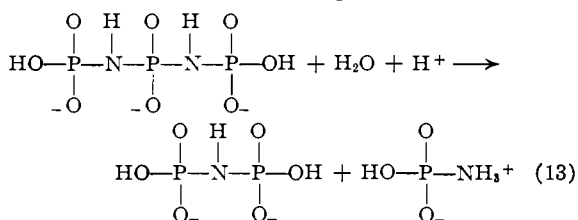
TABLE III

HYDROLYSIS OF 0.02 M IMIDOTRIPHOSPHATE

Duration of hydrol., min.	% of N present as NH₄⁺	% of P present as MP	100 C/C_0 or % ITP remaining (Chromatog.)
0	0.25	3.9	100
15	...	..	86
30	42	27	67
60	62	34	..
240	99	45	..
480	...	48	..

By analogy with the DITP hydrolysis (see below), one would expect the formation of some TMP from the amide intermediates of reactions 8 and 9 as

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ + HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}O\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ \longrightarrow$$

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}O\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}O\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ + NH_4{}^+ \quad (11)$$

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}O\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}O\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ \longrightarrow$$

$$\begin{array}{c} O\ O^- \\ P \\ \diagup \diagdown \\ O \quad\quad O \\ {}^-O\ P\quad\quad P\ O \\ O \diagdown \diagup O^- \\ O \end{array} + NH_4{}^+ \quad (12)$$

No TMP was detected by the ammoniacal chromatograms on hydrolysates from 0.02 M ITP. Hence less than 5% of the total P was present as TMP. However, a three-hour hydrolysis of 0.2 M ITP at 60° in the same buffer gave a mixture with 5–10% of the P present as TMP. This is directionally as would be expected, for the concentration of amide intermediates would be greater at the higher concentration and hence relatively more of the P could suffer condensation *via* equations 11 and 12.

In the case of DITP, the main hydrolyses can be represented by reactions 5a, 7, 13, 14 and 15. From the chromatographic determinations in column 4 of Table IV, the quarter-life of DITP is

$$HO\text{—}\overset{O}{\underset{_-O}{\overset{|}{P}}}\text{—}\overset{H}{\underset{_-O}{\overset{|}{N}}}\text{—}\overset{O}{\underset{_-O}{\overset{|}{P}}}\text{—}\overset{H}{\underset{O_-}{\overset{|}{N}}}\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}OH + H_2O + H^+ \longrightarrow$$

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}\overset{H}{\underset{O_-}{\overset{|}{N}}}\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}OH + HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ \quad (13)$$

$$HO\text{—}\overset{O}{\underset{_-O}{\overset{|}{P}}}\text{—}\overset{H}{\underset{_-O}{\overset{|}{N}}}\text{—}\overset{O}{\underset{_-O}{\overset{|}{P}}}\text{—}\overset{H}{\underset{O_-}{\overset{|}{N}}}\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}OH + H_2O + H^+ \longrightarrow$$

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}\overset{H}{\underset{O_-}{\overset{|}{N}}}\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ + HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}OH \quad (14)$$

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}\overset{H}{\underset{O_-}{\overset{|}{N}}}\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}NH_3{}^+ + H_2O \longrightarrow$$

$$HO\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}\overset{H}{\underset{O_-}{\overset{|}{N}}}\text{—}\overset{O}{\underset{O_-}{\overset{|}{P}}}\text{—}OH + NH_4{}^+ \quad (15)$$

estimated at about 8 minutes. The DITP disappears completely in about 2 hr., as shown by conversion of imide to ammonium ion (Table IV) and by the qualitative chromatograms.[7] As previously noted for ITP, the rate of MP formation decreases markedly after 1–2 hr. because the hydrolyzing species is then mainly DP.[7]

TABLE IV

HYDROLYSIS OF 0.02 M DIIMIDOTRIPHOSPHATE

Duration of hydrol., min.	% of N present as NH₄⁺	% of P present as MP	100 C/C_0 or % DITP remaining (Chromatog.)
0	0.5	0.8, 0.6	100
8	6.3	11.7	76
15	19	17	61
30	44	44	28
60	80	73, 73, 72, 70	..
120	96	82, 85	..
180	..	88, 85	..

ITMP is readily detected in chromatograms[7] for the later hydrolysates from 0.02 M DITP solutions; this is in accord with the greater abundance of amide intermediates from a compound containing two P–NH–P links. This trimeric ring ion forms by reactions analogous to equations 11 and 12.

Ring Imidotriphosphates.—The nitrogen-free analog of these compounds is TMP. Its hydrolysis rate at pH 3.5 and 60° has been estimated by extrapolation of the data of Healy and Kilpatrick,[8] giving a first order reaction rate of 2 × 10⁻⁴ min.⁻¹. This extrapolated rate is supported by a chromatographically determined value of 1.9 × 10⁻⁴ min.⁻¹ in the molar formate buffer (footnote to Table V).

TABLE V

HYDROLYSIS OF 0.02 M IMIDOTRIMETAPHOSPHATE

Duration of hydrol., min.	% of N present as NH₄⁺	% of P present as MP	100 C/C_0 or % ITMP remaining (Chromatog.)
0	0	0.45	100
75	2.9	0.63	..
240	5.5	1.41	..
465	11	2.6	..
960	17, 14[a]	7.3[a]	86[a,b]
1455	29	8.8	
1740	23[a]	10.3[a]	70
1920	35	10.1	

[a] All other runs in the table were made with the ITMP sample that contained 15–20% DITMP, but these runs were made on another sample containing about 5% DITMP, about 5% DP and a trace of MP. [b] TMP, run beside this sample of ITMP in another tube at the same pH and temperature, decreased from 0.02 M to 0.0167 M in 4 hr., corresponding to a first order k = 1.9 × 10⁻⁴ min.⁻¹.

(8) R. M. Healy and M. L. Kilpatrick, THIS JOURNAL, 77, 5258 (1955); see correction *ibid.*, 79, 6576 (1957).

The first step in the hydrolysis of ITMP can be represented as yielding either monoamidotriphosphate (16) or ITP (17).

$$HO{-}P{-}O{-}P{-}O{-}P{-}NH_3^+ \quad (16)$$

$$HO{-}P{-}O{-}P{-}NH{-}P{-}OH \quad (17)$$
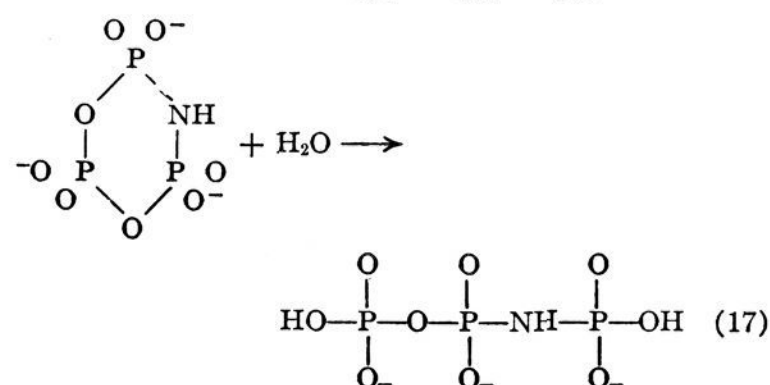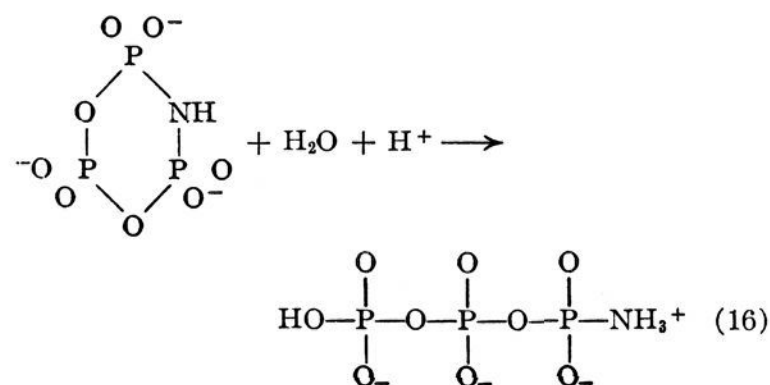
From the ease with which monoamidotriphosphate forms TMP in acid media[3] coupled with the relatively minor amount of TMP (15-20% of total P) detected by the ammoniacal chromatograms of ITMP hydrolysates,[7] it is believed that most of the hydrolysis proceeds by reaction 17. Since this involves rupture of a P–O–P link, it is not surprising that the rate of disappearance of ITMP is so low and so nearly equal to that of TMP (Table V). Several qualitative chromatograms on hydrolysates of TMP and ITMP confirmed the quantitative data in Table V in showing that the two ring ions decrease in concentration at about the same rate. Hence, the rate data cited above for TMP strengthen the quantitative data for ITMP. Among the ten hydrolyzable compounds of Fig. 1, the only other to hydrolyze so slowly is DP.

From the chromatographic determinations of ITMP disappearance in Table V, its quarter-life is about 1400 min. Note further that the imide nitrogen is converted only very slowly to ammonium ion and that the appearance of MP is even slower.

A sample of DITMP purified by ion exchange plus crystallization was used for the hydrolysis studies. The first step in the hydrolysis of this salt can be represented by one of the reactions

$$HO{-}P{-}N{-}P{-}N{-}P{-}OH \quad (18)$$

$$HO{-}P{-}O{-}P{-}N{-}P{-}NH_3^+ \quad (19)$$

$$HO{-}P{-}N{-}P{-}O{-}P{-}NH_3^+ \quad (20)$$
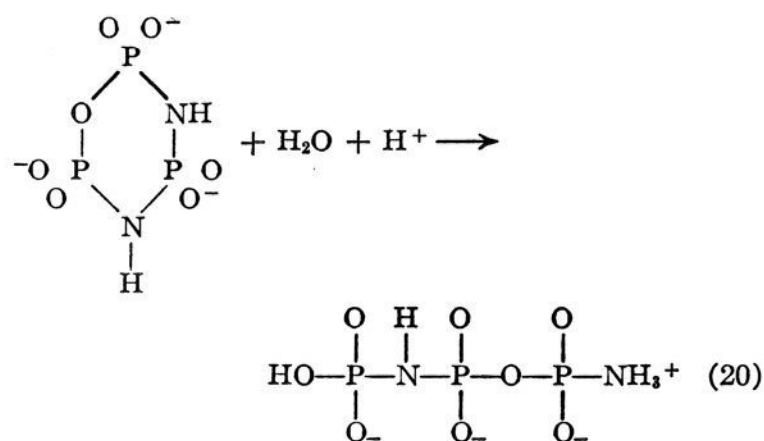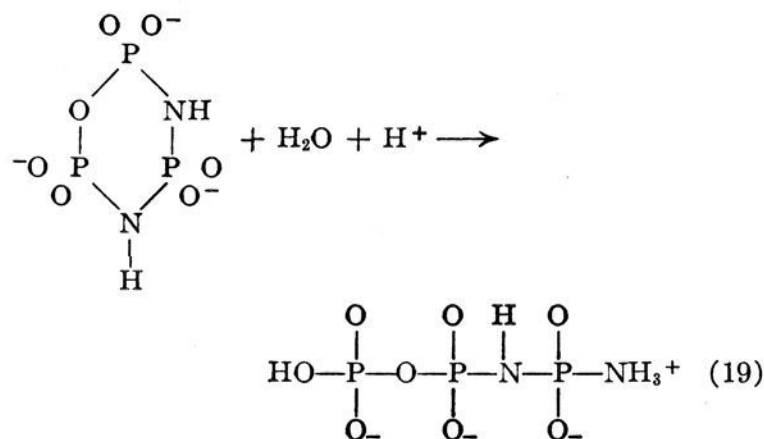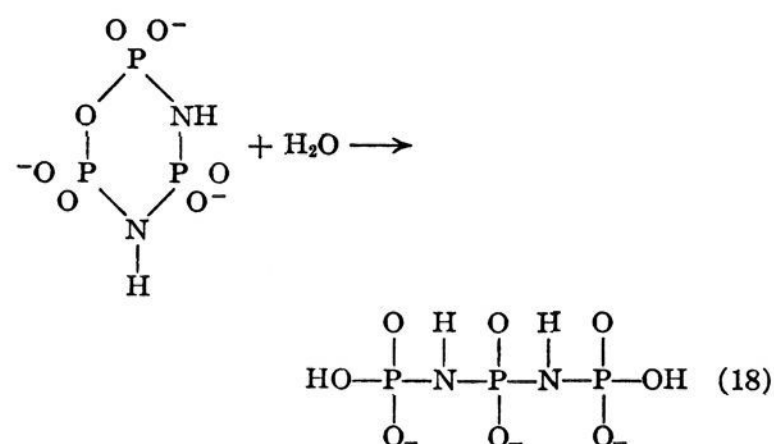
If much DITP were formed via (18) there would be rapid and extensive degradation to lower phosphates as already shown in the chain hydrolysis section. Since experience[7] clearly shows that most of the DITMP becomes ITMP (see also Fig. 2 for
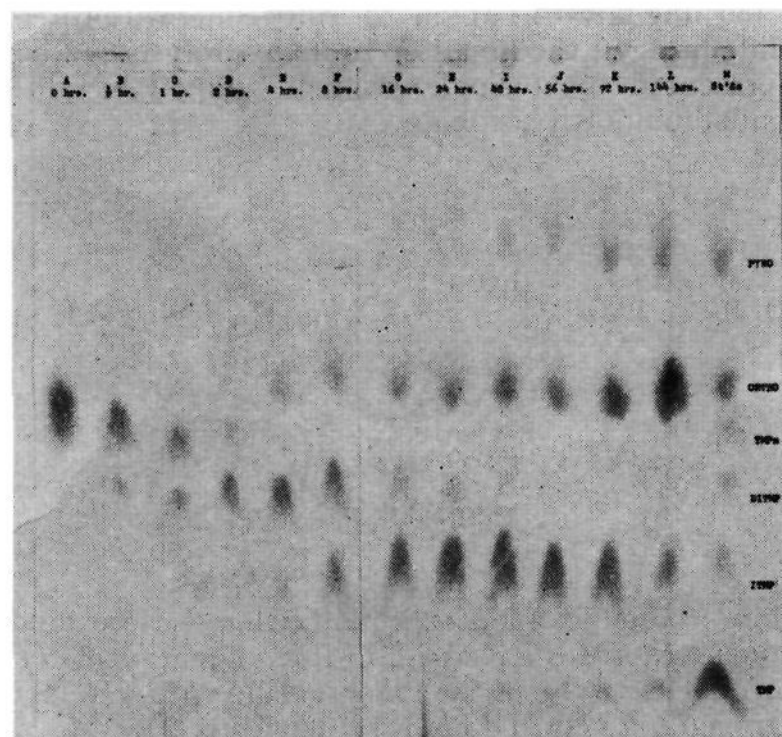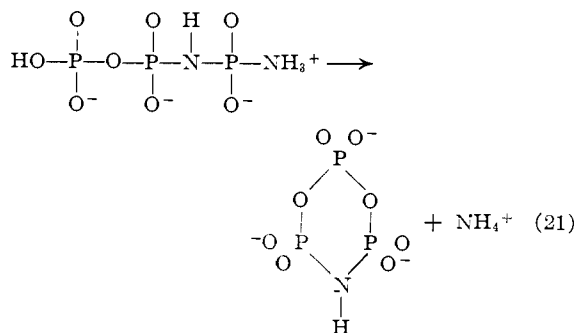

Fig. 2.—Descending alkaline chromatogram on products from hydrolysis of trimetaphosphimate at pH 3.5 and 60°. Sample sizes in gammas of P are: A–L, 7.5 for each TMPm hydrolysate; M, Standards 1 MP (ortho), 1 DP (pyro), 2 TMP, 2 ITMP, 4 DITMP, 4 TMPm.

TMPm hydrolysates at 4–48 hr.), it is believed that the first step involves reactions 19 and 20. These intermediates can never be present in appreciable concentration or they would rapidly lose amide and then suffer the rapid degradation already described for the chain ITP. Instead, each eliminates ammonium ion, forming ITMP, e.g.

$$
\begin{array}{ccccccc}
& O & & O & H & O \\
& \| & & \| & | & \| \\
HO-P-O-P-N-P-NH_3{}^+ & \longrightarrow
\end{array}
$$

(ring structure) $+ NH_4{}^+$ (21)

$$
\begin{array}{ccccccc}
O & H & O & H & O \\
\| & | & \| & | & \| \\
HO-P-N-P-N-P-NH_3{}^+ & \longrightarrow
\end{array}
$$

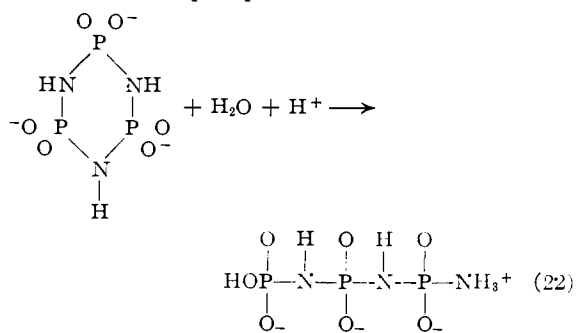(ring structure) $+ NH_4{}^+$ (24)

The quantitative chromatographic data (column 4, Table VI) show that DITMP has a quarter life of about 170 minutes. As would be expected from the mechanism cited, DITMP yields ammonia faster than ITMP (cf. Table V) but yields MP at nearly the same rate.
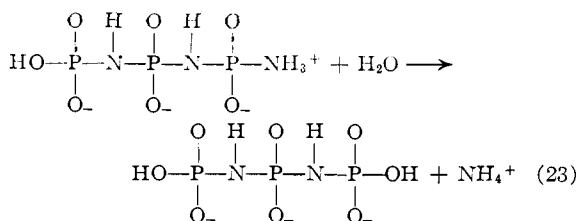
TABLE VI

HYDROLYSIS OF 0.02 M DIIMIDOTRIMETAPHOSPHATE

| Duration of hydrol., min.	% of N present as NH$_4{}^+$	% of P present as MP	100 C/C$_0$ or % DITMP remaining (Chromatog.)
0	0	0.03	100
90	4.1	0.45	83
240	14.6	1.16	..
255	..	1.45	70
465	17.7	2.50	..
1455	41	8.1	..
1920	49	10.6	..

Turning now to TMPm, the ring trimer with three imide bridges, the first step in its hydrolysis can be represented by a single product, namely, mono-amidodiimidotriphosphate.

(ring structure) $+ H_2O + H^+ \longrightarrow$

$$
\begin{array}{ccccc}
O & H & O & H & O \\
\| & | & \| & | & \| \\
HOP-N-P-N-P-NH_3{}^+ & (22)
\end{array}
$$

This product can be expected either to lose ammonia to form the chain DITP via equation 23 or to condense to form the trimeric ring with one less nitrogen, namely, DITMP via equation 24.

$$
\begin{array}{ccccc}
O & H & O & H & O \\
\| & | & \| & | & \| \\
HO-P-N-P-N-P-NH_3{}^+ & + H_2O \longrightarrow
\end{array}
$$

$$
\begin{array}{ccccc}
O & H & O & H & O \\
\| & | & \| & | & \| \\
HO-P-N-P-N-P-OH & + NH_4{}^+ & (23)
\end{array}
$$

Since DITP would rapidly degrade to MP and DP as already indicated, and since the early trimetaphosphimate hydrolysates contain little phosphorus present as MP or DP (Table VII, Fig. 2), one must
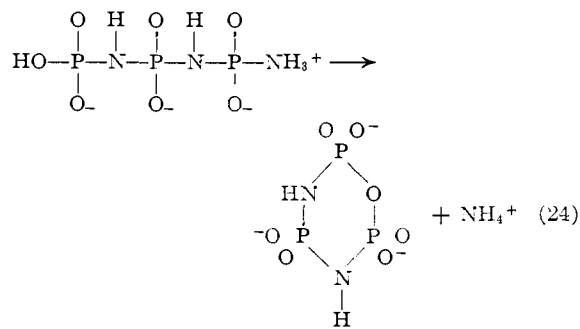
conclude that comparatively little of the phosphorus follows the route indicated by equation 23. In addition, the preparative methods[7] for DITMP and DITP clearly show that most of the TMPm phosphorus goes first to DITMP, the ring with one less nitrogen.

TABLE VII

HYDROLYSIS OF 0.02 M TRIMETAPHOSPHIMATE

Duration of hydrol., min.	% of N present as NH$_4{}^+$	% of P present as MP	100 C/C$_0$, or % TMPm remaining (Chromatog.)
0	1.2	0	100
30	10	0.90	75, 71
60	16	2.3	48, 47
120	26	5.6	
240	38	9.2	
4320	81	32.5	

The rate of TMPm disappearance indicates a quarter-life of about 25 minutes. The formation of ammonium ion from TMPm (Table VII) is considerably faster initially than from DITMP (Table VI). Comparing TMPm to DITMP with regard to rate of MP formation shows that the former is more inclined to lose its amide without reforming a ring; the result is that TMPm degrades more via DITP to MP than does DITMP via ITP to MP.

Qualitative chromatograms (Fig. 2) indicate that most of the TMPm has disappeared in two hours and nearly all is gone in four hours. DITMP is clearly evident after thirty minutes of hydrolysis, reaches a maximum in the 2–4 hr. period, is largely gone in 48 hr., is evident in mere traces at 72 hr. ITMP is detectable in 2 hr., is at a maximum in the 24–72 hr. period and still accounts for 30–35% of the P at 144 hr., the longest time tested. TMP becomes evident in 24 hr., attains a maximum concentration of 5–10% of the P at 72–144 hr. MP is detectable in 1 hr. and grows continually thereafter accounting for 45–50% of the P at 144 hr. DP becomes detectable in 16 hr. and increases to a maximum of 10–15% of the P in 144 hr.

Comparative Hydrolysis Rates at pH 3.5.— Tabulation of hydrolysis rates on imide- and oxy-linked dimers and trimers (Table VIII) reveals four trends:

   a. Among imide-linked chains IDP hydrolyzes faster than either trimer (ITP or DITP), whereas the reverse trend has long been known for the oxy-linked dimer (DP) and trimer (TP).

TABLE VIII

EFFECT OF pH ON QUARTER LIVES OF IMIDE- AND OXY-LINKED PHOSPHATES AT 60°

Compd.	Struc. type	pH 1	pH 3.5	Quarter life, min. pH 8	pH 11	Source of data
AMP	Uncond.	1.5	1.8	18	...	NH_3 formation
DP	Chain	500	1.5×10^3	15×10^3	$>5 \times 10^6$	Ref. 9, 10
TP	Chain	20–40	400	4×10^3	1×10^4	Ref. 10
IDP	Chain	ca. 10^a	3	30–40	300–400	Neutral or alk. chrom.
ITP	Chain	...	25	...	...	Neutral chrom.
DITP	Chain	...	8	20–30	(1.2 to 4) $\times 10^3$	Neutral chrom. or NH_3 formation
TMP	Ring	45	1.5×10^3	1.2×10^4	100	Ref. 14, alk. chrom.
ITMP	Ring	...	1.4×10^3	(9 to 12) $\times 10^3$	...	Alk. chrom.
DITMP	Ring	...	170	(3 to 9) $\times 10^4$	...	Alk. chrom.
TMPm	Ring	8^b	25	(1 to 2) $\times 10^5$	$>2 \times 10^5$	Qualitative alk. chrom.

[a] By orthophosphate formation the quarter life is greater than 6 but much less than 30 min. [b] By rate of ammonia nitrogen formation, assuming one TMPm ion to disappear for each NH_4 ion formed.

b. DITP disappears about three times as fast as ITP; relative abundance of imide links accounts for a factor of but two.

c. Among imide-linked rings, replacement of an imide by an oxy link increases the quarter life by a factor of 7–8.

d. Imide links are more stable in rings than in chains; this is most emphatically shown by comparing the mono-imido ring and chain (ITMP and ITP).

The data of Table VIII may also be examined in terms of the sequence of atoms along the chains or around the ring for suggestions of their effect on the rate of hydrolysis of the imide-link. The fastest rate is observed when the imide link is flanked by terminal –OH's as in IDP. Interposition of another imide, i.e. –P–N–, between the first P–N–P and the terminal –OH as in DITP reduces the rate per imide by a factor of 6. Similar interposition of an oxy link, i.e. –P–O– as in ITP, reduces the rate somewhat more (factor of 8 overall). When the terminal –OH's of ITP are eliminated entirely as in ITMP, there is a further reduction in rate by a factor of 56 (470-fold slower than IDP). Replacement of an imide- by an oxy-link reduces the rate per imide by a factor of 4 to 4.5 in the rings but only by a factor of 1.5 in the chains.

Rate of Species Disappearance vs. pH.—Rough measurements of hydrolysis rates have been made at 60° for most of the P–N compounds at pH 8 (only ITP omitted) and for a few at pH 1 and 11 (0.02 M solution in each case). These estimates, as quarter lives, are also given in Table VIII together with values for P–O–P compounds. Both imide and oxy links disappear slower as the pH rises. However, imide links in chain ions have distinctly shorter quarter lives unless the pH is rather high, e.g., 13 or higher. Here IDP and DITP compare favorably with DP in stability and probably are more stable than TP in such alkaline systems, because they contain enough sodium ions to cause a small increase in TP hydrolysis.[10] The stabilizing effect of alkalinity on the ring ions in DITMP and TMPm seems to come into play at pH values as low as 8. However, judgment should be reserved until the hydrolysis

of these compounds has been more fully studied at pH 8 and above (see detailed discussion below under "Condensation vs. pH").

The amide of AMP is lost more rapidly than the chain imides, but like them is more stable at high alkalinities. Thus, Stokes observed that in boiling concentrated KOH, AMP converts its amide to ammonia at the rate of but 3% per hour.[11]

Attempts to prepare IDP by boiling alkaline hydrolysis of ITP have shown that the latter's P–O–P link is comparable in hydrolytic stability to those of TP. For either of these triphosphates, substantially complete conversion to an equimolar mixture of mono- and diphosphates occurs within an hour of refluxing in 30% NaOH.

TMPm, the least stable ring at pH 3.5, is already the most stable when the pH has risen to 8.0 and remains so at higher pH's. Mild autoclaving fails to alter TMPm in strongly alkaline solutions; more drastic autoclaving converts it to MP and ammonia. For all ring ions except TMPm, however, the stability must decrease again at pH's sufficiently above 8.0, because the ring P–O–P links break readily in alkaline media.

For the acid region Table VIII coupled with Fig. 2 suggests an explanation of why the hydrolysis of TMPm in boiling and highly acid solutions requires considerable time to convert all nitrogen to ammonium ion and still more time to convert all phosphorus to MP[12]: TMPm itself is soon gone and DITMP soon thereafter, but ITMP loses its imide rather slowly and one of its degradation products, namely, DP hydrolyzes to MP rather slowly. For rapid conversion of TMPm nitrogen to ammonium ion, boiling 50% H_2SO_4 has been found effective,[12] perhaps because of its high boiling point. For rapid conversion of the phosphorus to MP, boiling solutions of 50% H_2SO_4, 15% HNO_3, or aqua regia are effective, but boiling 18% HCl is slow,[12] approaching complete hydrolysis asymptotically.

Condensation vs. pH.—The extent of the condensation reactions has not been appraised at pH 1 and 11. However, at pH 8 six of the seven P–N compounds (only ITP omitted) were examined at various stages of hydrolysis by means of qualitative chromatograms,[7] so that qualitative comments are possible.

(9) D. O. Campbell and M. L. Kilpatrick, THIS JOURNAL, **76**, 893 (1954).

(10) J. R. Van Wazer, E. J. Griffith and J. F. McCullough. ibid., **77**, 287 (1955).

(11) H. N. Stokes. Am. Chem. J., **15**, 198 (1893).

(12) K. E. Lemmerman, unpublished results 1952–1954, Research and Development Department, The Procter & Gamble Company.

In the hydrolysis of AMP, IDP and DITP there is essentially no change in the relative extent of hydrolysis and condensation. Thus, DP is a little more evident in the hydrolysates of AMP at pH 8 than at 3.6, but again the product is overwhelmingly MP. In the hydrolysis of IDP no more DP is evident at pH 8 than at 3.6. In the hydrolysis of DITP more ITMP and less DP are evident than at pH 3.6, but the main product, even in intermediate stages, is MP in both cases.

In the case of the imide–containing ring ions, significant changes in the chemistry are apparent.[7] In the hydrolysates of ITMP there appears to be no TMP formed at pH 8.0, that present as impurity gradually disappearing as hydrolysis proceeds. The DITMP impurity is so stable that it appeared not to change in the longest hydrolysis time studied (56 days). The net result appears to be conversion of ITMP to a nearly equimolar mixture of MP and DP.

In the 64 days allowed for hydrolysis of DITMP, very little change occurs as judged by neutral and alkaline chromatograms,[7] which show only minor amounts of MP. However, the acid chromatograms suggest that something has happened to the DITMP, for these show an appreciable decrease in DITMP level and significantly *more MP* than shown by the other chromatograms; in addition, a new and unknown phosphorus-bearing ion yields a spot on the acid chromatogram at a position midway between those typical of MP and DP. These observations suggest the formation at pH 8 of a reaction product from DITMP which chromatographs like DITMP with neutral and alkaline solvents but suffers degradation in the acid chromatographic solvent to MP and some new phosphorus-bearing species. The new ion does not involve the borate of the buffer, for an unbuffered DITMP solution subjected to hydrolysis at pH 8 behaves similarly.

In the hydrolysis of TMPm at pH 8.0 a little DITMP appeared to form immediately upon contact between the buffer solution and the crystals of $Na_3P_3(NH)_3O_6 \cdot 4H_2O$ at room temperature. However, it increases only very slightly during 64 days at 60° (neutral and alkaline chromato-

grams)[7]. This may again be the product suggested above as forming from DITMP at pH 8, for acid chromatograms on these TMPm hydrolysates also show a weak phosphorus spot at a position between those of MP and DP.

In rather acid solutions (pH 1) all species tested hydrolyzed faster than at pH 3.5 with the exception of IDP. Its quarter life, though only approximately determined at pH 1 is at least twice as long as at pH 3.5. This is a rather unexpected result encountered near the conclusion of the study and no explanation is as yet apparent.

Discussion

A question not entirely resolved in the present study is whether, in the mild acid hydrolysis of TMPm or of DITMP, the rings actually form chain amide intermediates. An alternative explanation could be given thus: water or hydronium ion in some way reacts with TMPm to form an intermediate complex from which ammonium ion escapes without there having been a real opening of the ring. The authors have been inclined to the former view because of the following evidences:

1. A monoamide of a chain trimer, namely, monoamidotriphosphate[3] does very readily eliminate ammonium ion and form the ring trimer in high yield when placed in mildly acid solutions.
2. Ring trimers are formed during the hydrolysis of chain trimers and hence must be built up from amide intermediates of mono-, di- and triphosphates (*cf.* DITP and ITP hydrolysis at pH 3.6).
3. The simplest P–O–P compound (DP) is formed by reaction of AMP with MP.

The fact that hydrolysis of TMPm or of DITMP always leads to some lower phosphate degradation products, especially MP, cannot distinguish between the two types of reaction.

Attempts to isolate a chain amide from the ammonolysis of TMPm have not been successful. Even at 100° concentrated NH_3 seems not to react with TMPm.[3]

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