CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS

PART II. THE HYDROLYSIS OF SODIUM TRIMETAPHOSPHIMATE

F. H. POLLARD, G. NICKLESS AND R. W. WARRENDER

Department of Chemistry, University of Bristol, Bristol (Great Britain)

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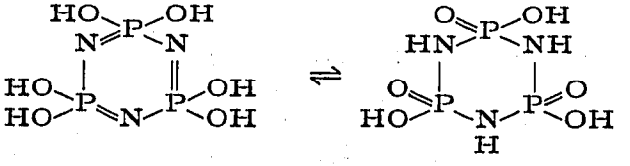
GLADSTONE[1-5] obtained an acid which analysed to $P_2N_2O_5H_6$, by the action of water on an ethereal solution of trimeric phosphonitrilic chloride, and which he regarded as the diamide of pyrophosphoric acid. STOKES[6] interpreted GLADSTONE's results in another way, and pointed out that two molecules of trimetaphosphimic acid (TMPm) with three molecules of water has some empirical formula of $P_2N_2O_5H_6$. The trimetaphosphimic acid is rapidly hydrolysed by the hydrochloric acid formed in the reaction, but alkali metal salts of the metaphosphimic acid are easily prepared by agitation of an ethereal solution of the chloride with an alkali metal acetate or base.

Three atoms of hydrogen are replaceable by alkali metals, while silver is able to replace either 3 or 6 hydrogen atoms. Two tautomeric forms of TMPm are possible:



(a) (b)

STOKES[6] favoured formula (b), and this has been confirmed by potentiometric titration and infra-red spectroscopy[7].

Trimetaphosphimic acid is unstable, but its salts are stable in neutral or alkaline conditions. Treatment in strong acid, however, causes hydrolysis to proceed, the final products being orthophosphate and ammonia[6].

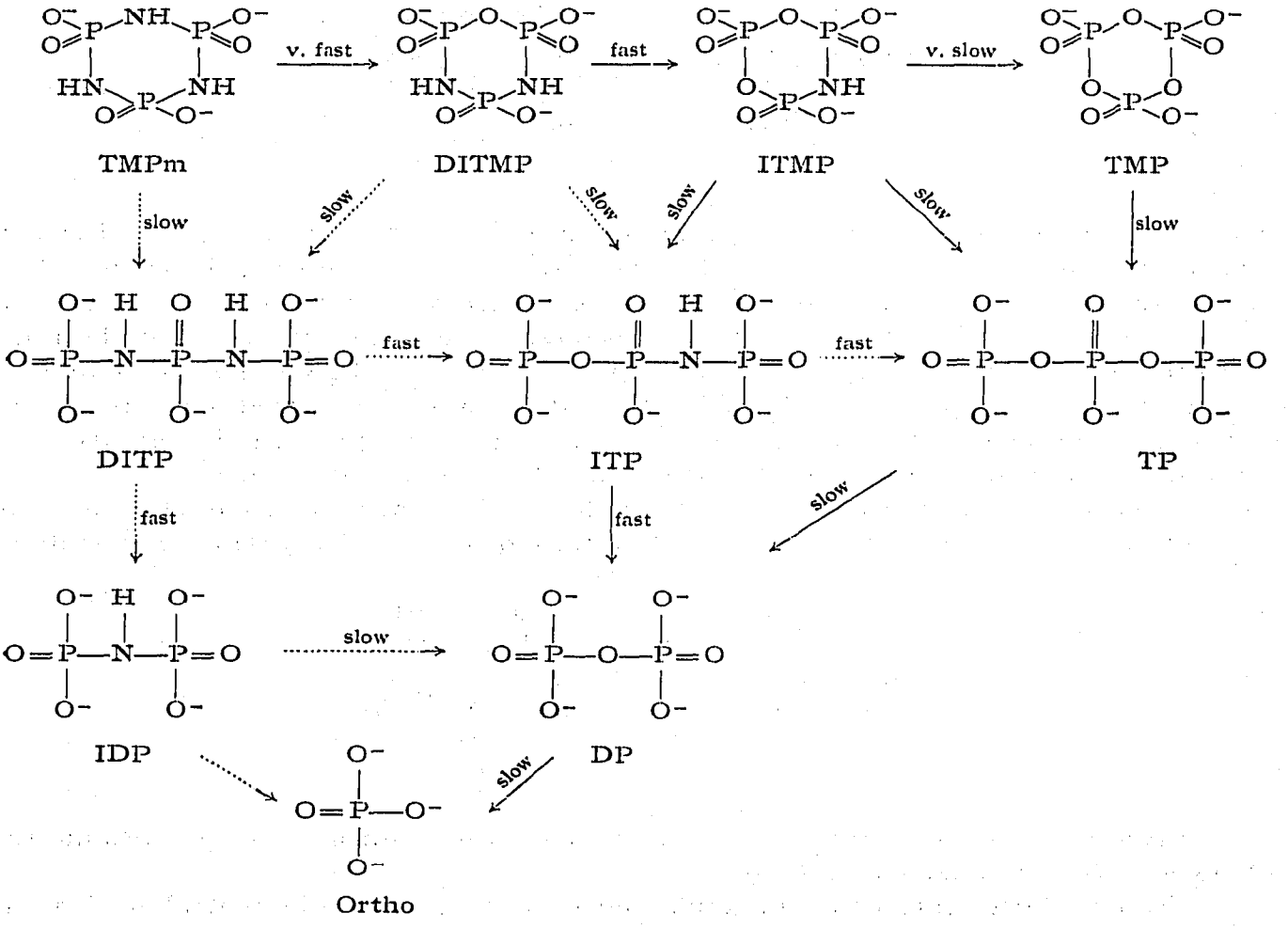
When the reaction is limited, by the choice of suitable conditions, STOKES' analysis[6] of the mixture indicated the presence of:

(i) Unchanged trimetaphosphimic acid $P_3N_3O_6H_6$ (TMPm)
(ii) Diimidotriphosphoric acid $P_3N_2O_8H_7$ (DITP)
(iii) Imidodiphosphoric acid $P_2NO_6H_5$ (IDP)
(iv) Pyrophosphoric acid $P_2O_7H_4$ (DP)
(v) Orthophosphoric acid PO_4H_3 (Ortho)
(vi) Ammonium ions (NH_4^+).

Little further work was carried out on the hydrolysis until NARATH, LOHMAN AND QUIMBY[8,9] found that acid hydrolysis proceeds largely through intermediate

ring compounds with one, two and three oxygen atoms successively replacing the original imide linkages. Possible paths of the decomposition suggested by these workers are outlined below, the main sequence following the solid arrows.

It is interesting to note that the mechanism proposed by STOKES[6] involved the scheme concerned with the broken arrow sequence of reactions. STOKES[6] isolated the first intermediate and DE FICQUELMONT[10] prepared it by a different method, both reporting it to be the chain diimidotriphosphate (DITP) instead of DITMP.



Abbreviation	*Name of acid species*
TMPm	Trimetaphosphimate
DITMP	Diimidotrimetaphosphate
ITMP	Imidotrimetaphosphate
TMP	Trimetaphosphate
DITP	Diimidotriphosphate
ITP	Monimidotriphosphate
TP	Triphosphate
IDP	Imidodiphosphate
DP	Diphosphate
Ortho	Orthophosphate

NARATH *et al.*[9], however, found on repetition of either preparation, only ring products, predominantly DITMP.

This communication describes the hydrolysis of trimetaphosphimate in acid solution through a variety of phosphorus-nitrogen containing acids, finally to orthophosphate and ammonia. QUIMBY, NARATH AND LOHMAN[9] have described the hydrolysis of each of the species included in their scheme for the decomposition of TMPm, and suggested mechanisms for the hydrolysis. The results of this study confirm in detail their results. This work provided a "proving ground" for the paper chromatographic and ion-exchange procedures which were used to study the hydrolysis of the higher polymeric phosphonitrilic chlorides of which we have observations up to the octamer.

A paper chromatographic study of the hydrolysis of sodium trimetaphosphimate

The sodium trimetaphosphimate was prepared by hydrolysis of triphosphonitrilic chloride[6].

The hydrolysis was carried out under exactly the same conditions as those of QUIMBY, NARATH AND LOHMAN[9], namely 60° and in hydrochloric acid, sodium acetate buffered solution at a pH 3.6. The hydrolysis was allowed to proceed for about three weeks and samples were chromatographed in BIBERACHER'S[11] basic, QUIMBY'S neutral[9] and GASSNER'S[12] acid solvents. Although this was carried out as a qualitative study, but using standardised techniques[13], the approximate percentage of total phosphorus present as each species is estimated from the relative size and intensity of the spots (especially with chromatograms eluted with BIBERACHER'S[11] solvent) and shown in Table I.

TABLE I

Time (h)	*TMP* $R_x = 2.40$	*ITMP* $R_x = 1.80$	*DITMP* $R_x = 1.45$	*TMPm* $R_x = 1.20$	*Ortho* $R_x = 1.00$	*Chain phosphates* $R_x = 0.45$
0	—	—	—	100	—	—
0.25	—	—	25	75	—	—
1	—	—	50	50	—	—
2	—	2	64	34	—	—
4	—	8	80	10	2	—
20	—	32	65	—	3	—
30	—	45	47	—	4	4
48	—	60	28	—	6	6
72	3	62	15	—	10	10
91	5	63	12	—	10	10
117	8	60	8	—	15	10
163	8	58	4	—	16	12
192	9	58	2	—	18	13
235	10	56	—	—	20	14
285	10	52	—	—	23	15
331	10	50	—	—	25	15
380	10	45	—	—	28	17
450	10	40	—	—	30	20

Samples of the hydrolysates were chromatographed in the acid and neutral solvents, and in each case they confirmed the results of the BIBERACHER'S chromatograms. The neutral chromatograms showed the development of the ring imidophosphates which were detected. These species, together with their R_x values are shown in

Table II, but of course, species reported as orthophosphate could be mixtures of orthophosphate and chain phosphates.

Samples chromatographed in GASSNER's acid solvent showed increasing amounts of orthophosphate from 4 h to 30 h, and a trace of pyrophosphate after 20 h.

TABLE II

Time (h)	*Species present**
0	TMPm (0.21) only
2	TMPm (0.21) [30] + DITMP (0.30) [60] + trace Ortho (1.00)
4	TMPm (0.21) [10] + DITMP (0.30) [80] + ITMP (0.50) [5] + Ortho (1.0) [5]
20	DITMP (0.30) [60] + ITMP (0.50) [30] + Ortho (1.00) [10]
48	DITMP (0.30) [50] + ITMP (0.50) [25] + Ortho (1.00) [25]

* R_x values are given in parentheses; relative amounts in square brackets.

The hydrolysis of TMPm at 60° at pH 10.0

Sodium trimetaphosphimate was dissolved in a sodium bicarbonate–sodium hydroxide buffer pH 10.0 previously heated to 60°. Samples were removed at intervals to 170 h, eluted in the three chromatographic solvents already mentioned.

No hydrolysis products were obtained during the study, showing the inert nature of the P–N–P bonds in alkaline solution[9].

A paper chromatographic study of the hydrolysis of sodium diimidotrimetaphosphate

Sodium diimidotrimetaphosphate was prepared by two methods[6,10] both of which had previously, but erroneously been described as preparations of sodium diimidotriphosphate.

Found: P, 28.8; N, 8.6. Calculated for $Na_3P_3(NH)_2O_7 \cdot H_2O$: P, 28.9; N, 8.7.

Sodium diimidotrimetaphosphate was dissolved in sodium acetate–hydrochloric acid buffer pH 3.6 at 60°. Samples were removed at intervals and chromatographed in BIBERACHER's basic solvent. An estimation of the approximate percentage of total phosphorus present as each species is given in Table III.

TABLE III

Time (h)	*TMP* $R_x = 2.40$	*ITMP* $R_x = 1.80$	*DITMP* $R_x = 1.45$	*Ortho* $R_x = 1.00$	*Chain species* $R_x = 0.45$
0	—	—	100	—	—
0.25	—	10	90	—	—
1	—	20	80	—	—
2	—	30	70	—	—
4	—	35	65	—	—
20	—	45	50	trace	5
48	—	50	35	5	10
72	5	55	20	10	10
91	5	60	15	10	10
117	7	60	10	12	12
163	9	55	5	15	15
235	10	55	3	17	15
331	12	48	—	25	15
432	13	40	—	30	17

The initial stage of this hydrolysis, DITMP to ITMP was much slower than the stage TMPm to DITMP, the half life of DITMP being about 25 h. Orthophosphate again appeared before TMP in the hydrolysis products.

The hydrolysis of DITMP at 60° and pH 10.0

Sodium diimidotrimetaphosphate was dissolved in a sodium bicarbonate–sodium hydroxide buffer pH 10.0 previously heated to 60°. Samples were removed at intervals and eluted in all the three chromatographic solvents.

The species on all the chromatograms had low R_x values caused by the excess of sodium ions in the buffer solution, making identification of most species impossible. However, from the basic and neutral solvents it was possible to say that no ITMP or TMP were formed, but that chain phosphates, the identities of which could not definitely be determined, were formed. Orthophosphate was detected after about 120 h.

It was concluded that alkaline hydrolysis of DITMP occurs by a different path to the acid hydrolysis, and probably yields chain imidophosphates very slowly through fission of the P–O–P linkage; further work is to be published[14].

An ion-exchange study of the hydrolysis of TMPm at 60° and pH 3.6

BEUKENKAMP, RIEMAN AND LINDENBAUM[15] showed the possibilities of anion exchange chromatography in the separation and quantitative analysis of phosphate mixtures, together with theoretical equations to describe elution characteristics. Later[16], the theory was developed to permit calculation of the positions of elution maxima when eluants of different concentrations were passed successively through the column. A number of advantages, especially those of time and accuracy were introduced by GRANDE AND BEUKENKAMP[17] when they published details of gradient elution technique for the separation of the lower condensed phosphates. The chromatographic separations of the imidophosphates formed in these hydrolyses were effected by a modification of the gradient elution method.

The apparatus used was exactly similar to that described by GRANDE AND BEUKENKAMP. An ion-exchange column, 19 cm long and 2 cm diameter contained in a glass tube fitted with a tap, was used. The column contained 25 g of Amberlite CG-400 resin (100–200 B.S.S. mesh) in the chloride form. It was found that resins from different production batches may differ in the sharpness of peaks obtained, probably due to minor changes in cross-linkage or particle size. The eluant solution for the mixing bottle was 1 l of 0.10 *M* potassium chloride solution buffered to pH 5.0 with a potassium acetate–acetic acid buffer, and the eluant solution for the reservoir was 1.00 *M* potassium chloride solution, also buffered to pH 5.0 with acetate buffer. After elution, the phosphorus was determined by the phosphovanadomolybdate method[18], because of the lack of interference of other ions and the stability of the complex when compared to the more sensitive molybdenum blue methods[19,20].

The retention volumes of the lower condensed phosphates and the imidophosphates were found, and are given in Table IV. In each case a 5 ml solution of the phosphate containing 200–400 μg of P/ml was used.

All the trimeric ring imidophosphate preparations gave single sharp elution peaks, and showed the presence of little or no impurities, but the chain imidophosphates partially decomposed under the conditions of hydrolysis.

TABLE IV

Species	Retention volumes on a 19 cm column	
	Preparation	Retention volume (ml)
Orthophosphate	A. & W.*	100
Pyrophosphate	A. & W.*	250
Triphosphate	A. & W.*	400
Trimetaphosphate	A. & W.*	640
Imidotrimetaphosphate	Ref. 22	450
Diimidotrimetaphosphate	Refs. 6, 10	360
Trimetaphosphimate	Ref. 6	270
Imidodiphosphate	Ref. 23	190**
Diimidotriphosphate	Ref. 24	280**

* Albright & Wilson.
** Partially decomposed under conditions of elution.

From Table III, a quantitative separation of the phosphate species formed in the reaction is possible.

Sodium trimetaphosphimate was hydrolysed at 60° and pH 3.6 in sodium acetate–hydrochloric acid buffer. 5 ml samples were removed at intervals and subjected to ion-exchange separations. The types of separations obtained are given in Fig. 1.

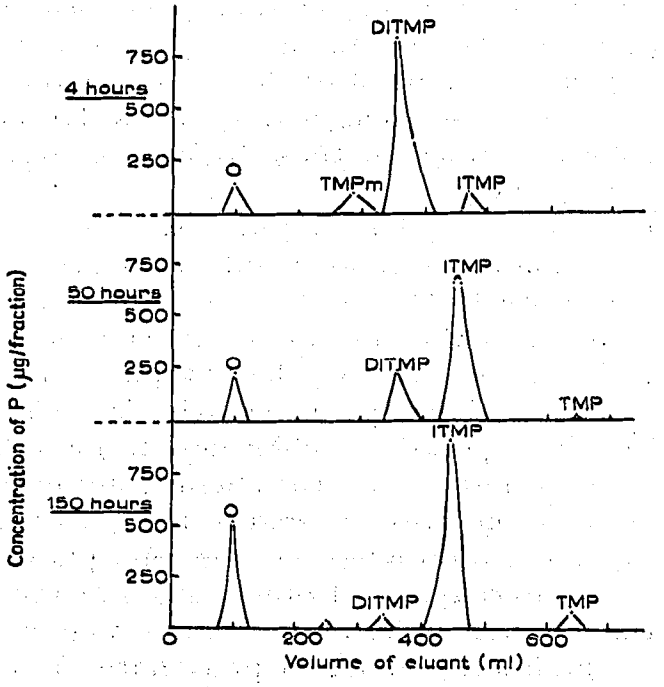
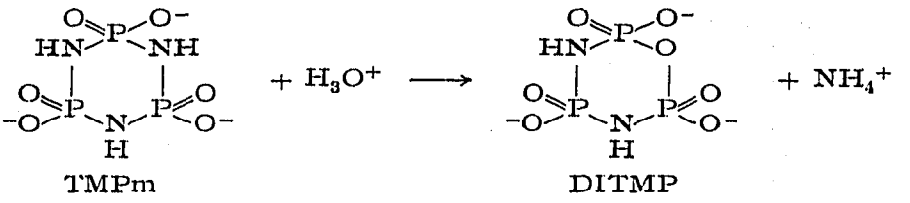


Fig. 1. Elution patterns for the hydrolysis of trimetaphosphimate at pH 3.6 and 60°.

The elution curves confirm the results of paper chromatographic study, except their failure to find any chain phosphate species except pyrophosphate. These quantitative results emphasise the stability of ITMP under these conditions.

Comparison of the rates of hydrolysis of TMPm, DITMP and ITMP

The first stages in the acid hydrolysis of TMPm, DITMP and ITMP all involve the elimination of one molecule of ammonia, whether the mechanism involves a ring or chain intermediate, *e.g.*



TMPm DITMP

The hydrolyses studied by paper and ion-exchange chromatography, were carried out in buffer solutions where the liberated ammonia is absorbed by the buffer without affecting the pH of the solution. However, in unbuffered solutions the liberated ammonia causes the pH to rise, and initially this concentration of ammonia is proportional to the concentration of the imidophosphate species which has been hydrolysed.

Two methods were employed to detect the ammonia being liberated:

(1) A solution of the imidophosphate at 60° was adjusted to pH 3.6 by addition of hydrochloric acid. The hydrolysis was allowed to continue while the pH of the solution was recorded by a potentiometric recorder connected to a conventional recording pH meter. The velocity constants were not calculated from the results due to the non-linear relationship between pH and the amount of ammonia liberated. The relative rates of the hydrolyses are shown in Fig. 2, but the other difficulty is that as the pH rises, the slower the rate of hydrolysis becomes.

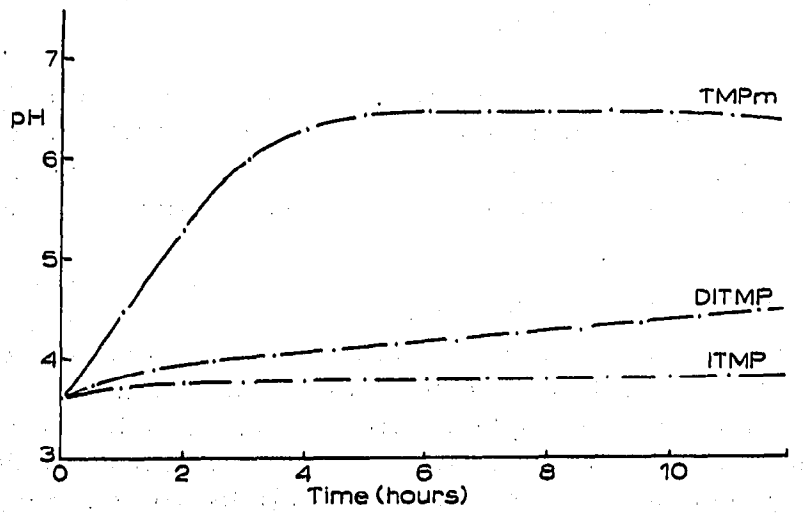


Fig. 2. Rate of change of pH for the hydrolysis of trimeric ring imidophosphates at pH 3.6 and 60°.

(2) A solution of the imidophosphate at 60° was adjusted to pH 3.6 by addition of dilute hydrochloric acid from an E.I.L. Model 24, automatic titration unit. The instrument was then set to adjust the pH to 3.6 by addition of more dilute acid, immediately the pH rose above the detection limits of the apparatus, about ± 0.20 pH

units. The volume of acid added was proportional to the amount of ammonia liberated in the hydrolysis, especially over the initial stages of the reaction (see Fig. 3). Difficulty was encountered with the hydrolysis of ITMP because the formation of

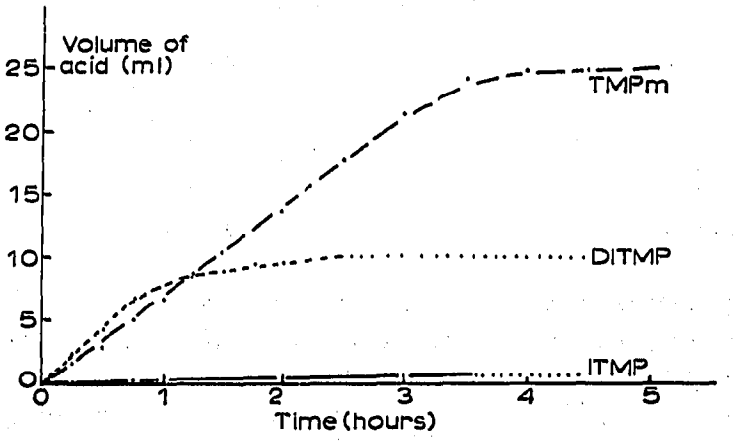


Fig. 3. Rates of hydrolysis of trimeric ring imidophosphates at pH 3.6 and 60°.

orthophosphate (from the decomposition of the imido chain phosphates) caused the pH to drop. Approximate hydrolysis rates were calculated for the initial stages of each reaction, assuming first order reaction kinetics, because of constant pH.

Species	*Reaction rate (min^{-1})*
TMPm	$8 \cdot 10^{-3}$
DITMP	$6 \cdot 10^{-3}$
ITMP	$7 \cdot 10^{-4}$

This work was not meant to provide an accurate study, but to determine approximate reaction rates. The assumption made was that little orthophosphate is formed over the initial stages of the reaction, and hence does not affect the pH of the solution. All these rates are now being carefully checked by quantitative ion-exchange procedures[14].

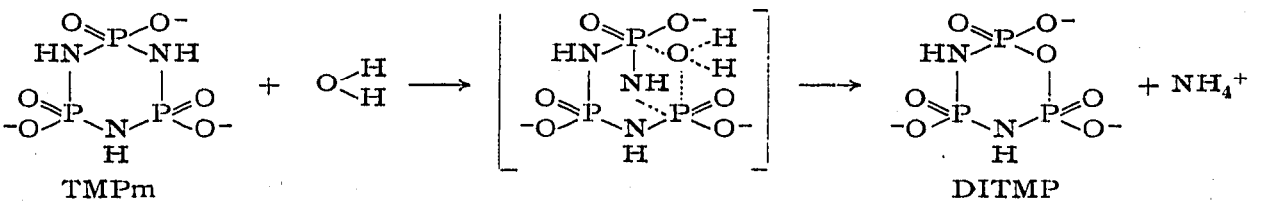
The mechanism for the hydrolysis of trimetaphosphimate

Paper chromatography and ion-exchange chromatography, together with elemental analysis and pH titrations of isolated intermediates, showed that the hydrolysis of TMPm proceeded through ring imidophosphates as reported by QUIMBY, NARATH AND LOHMAN[9]. No chain imidophosphates were detected, but it is possible that small amounts were formed which were hydrolysed very rapidly to orthophosphate. However, failure to detect orthophosphate over the initial stages of the reaction make this unlikely. Two mechanisms can be proposed for the hydrolysis[9]: one involves a chain amidoimidophosphate intermediate, and the other a complex ring intermediate; the former is the one favoured.

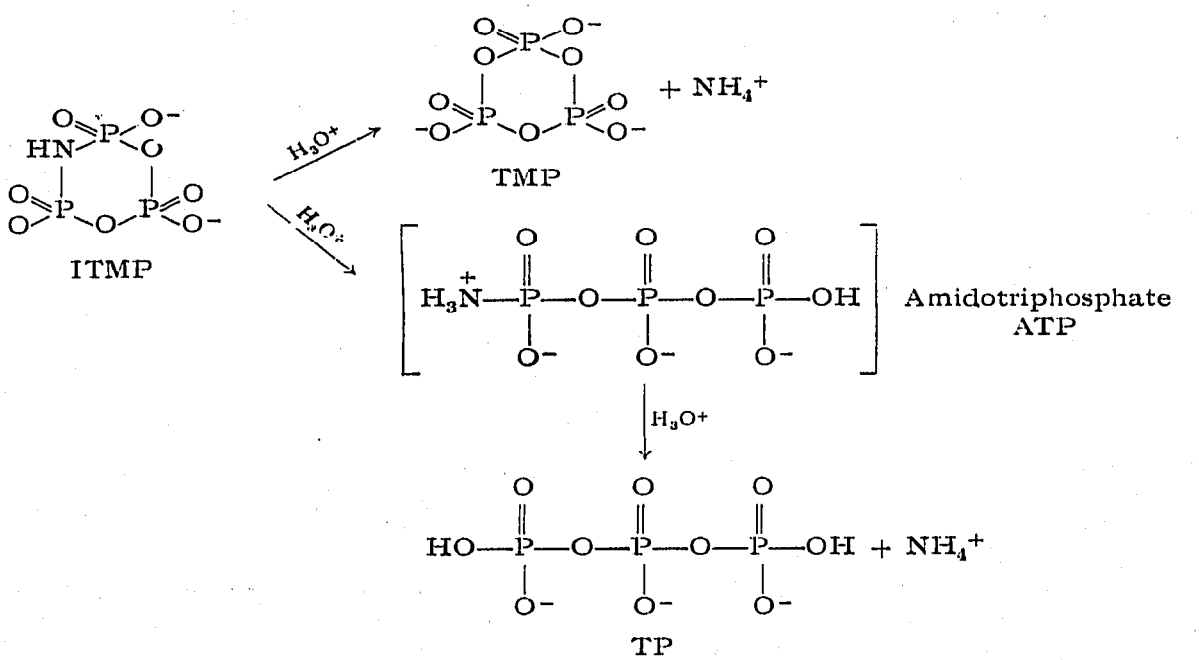
Both these mechanisms have been reconsidered in view of the results obtained from the hydrolysis of TMPm, higher metaphosphimic acids, and a study of molecular

models of the acids. It has been concluded that the actual mechanism probably lies somewhere between the two models, and that it involves the simultaneous breaking and reformation of bonds.

If we consider that a complex ring intermediate is formed, then the first stage of the hydrolysis can be represented as follows:

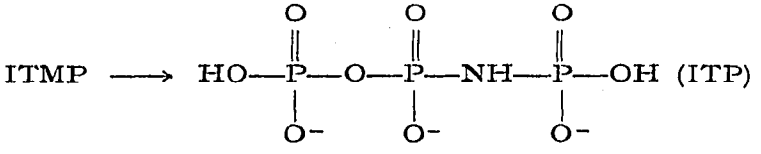


The ring intermediate which, momentarily, contains a four membered ring, could be formed by donation of electron pairs of the oxygen atom of an approaching water molecule into the empty 3*d*-orbitals of the phosphorus atoms. DYATKINA AND SYRKIN[21] have discussed the interaction of electron pairs of one atom with vacant *d*-orbitals of another which occurs in phosphorus compounds and results in the formation of supplementary bonds and increased bond strength. In phosphonitrilic halides, such interaction can occur between an unshared 2*s*-pair of nitrogen and an empty 3*d*-orbital of phosphorus, in addition to the sp^3d-electrons engaged in the formation of five bonds, and this situation also arises in the trimetaphosphimate anion. When we consider the approach of a water molecule competition arises between the 2*s*- and 2*p*-electron pairs of the oxygen atom of the water molecule and the 2*s*-electron pair of the nitrogen for donation into the emty 3*d*-phosphorus orbitals. If this tendency is greater for oxygen, the four membered ring complex will be formed. This would not be stable, it would decompose at the P–N bonds with the resultant formation of DITMP.



ITMP would be formed from DITMP and TMP from ITMP by an exactly similar mechanism. However, TMP is only formed in very small amounts from ITMP, and orthophosphate appears before TMP is detected. Thus ITMP must hydrolyse by two paths, one of which must involve a chain.

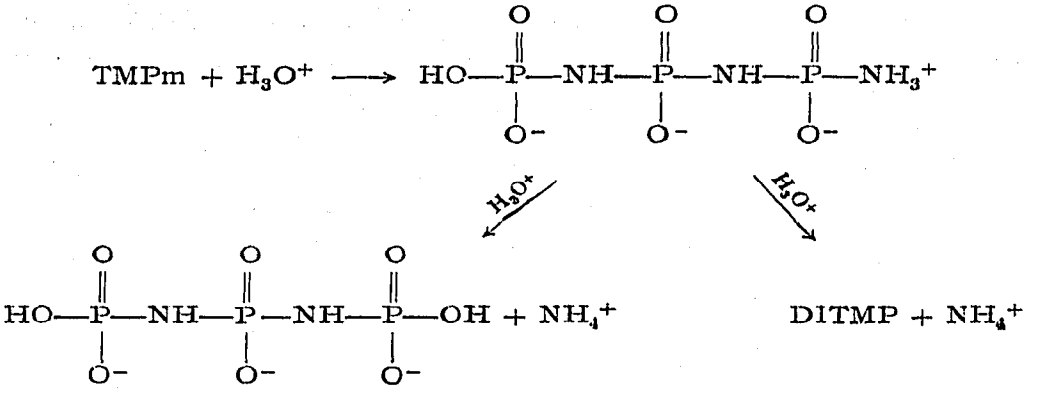
ITMP can either break at a P–N link, or at a P–O linkage, which in a chain form would give:



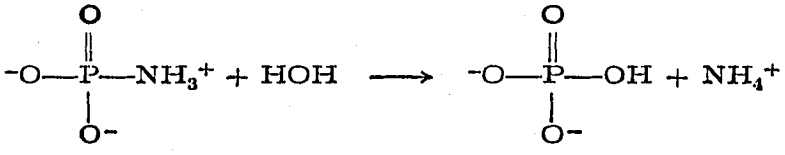
This would easily decompose[14] into pyrophosphate and orthophosphate at pH 3.6, and is most likely in view of the failure to detect triphosphate in the hydrolysis products.

But the strong argument against the complex ring mechanism is that the phosphorus atoms are too far apart for a P–O–P bond to be formed at the same time as a P–N–P bond in a ring compound, even taking into account the large size of the 3*d*-orbitals of the phosphorus atom.

The principal argument against the chain mechanism is that chain imidophos phates are known to degrade rapidly to orthophosphate in acid solution. Only one chain intermediate can be formed from TMPm, monamidodiimidotriphosphate:

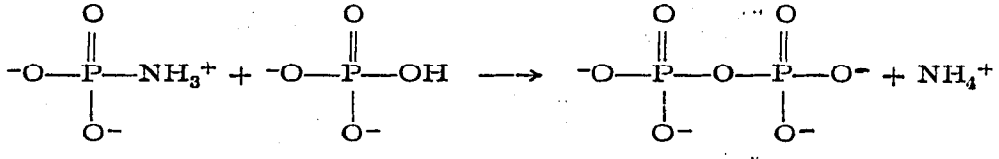


QUIMBY also assumes, and we confirm, that as no orthophosphate is formed immediately, only DITMP is formed. However, it has been shown that the hydrolysis of monamidophosphate which is very fast, yields about 95 % orthophosphate by the reaction:



(1)

whilst a condensation reaction (2) occurs to only 5 %:



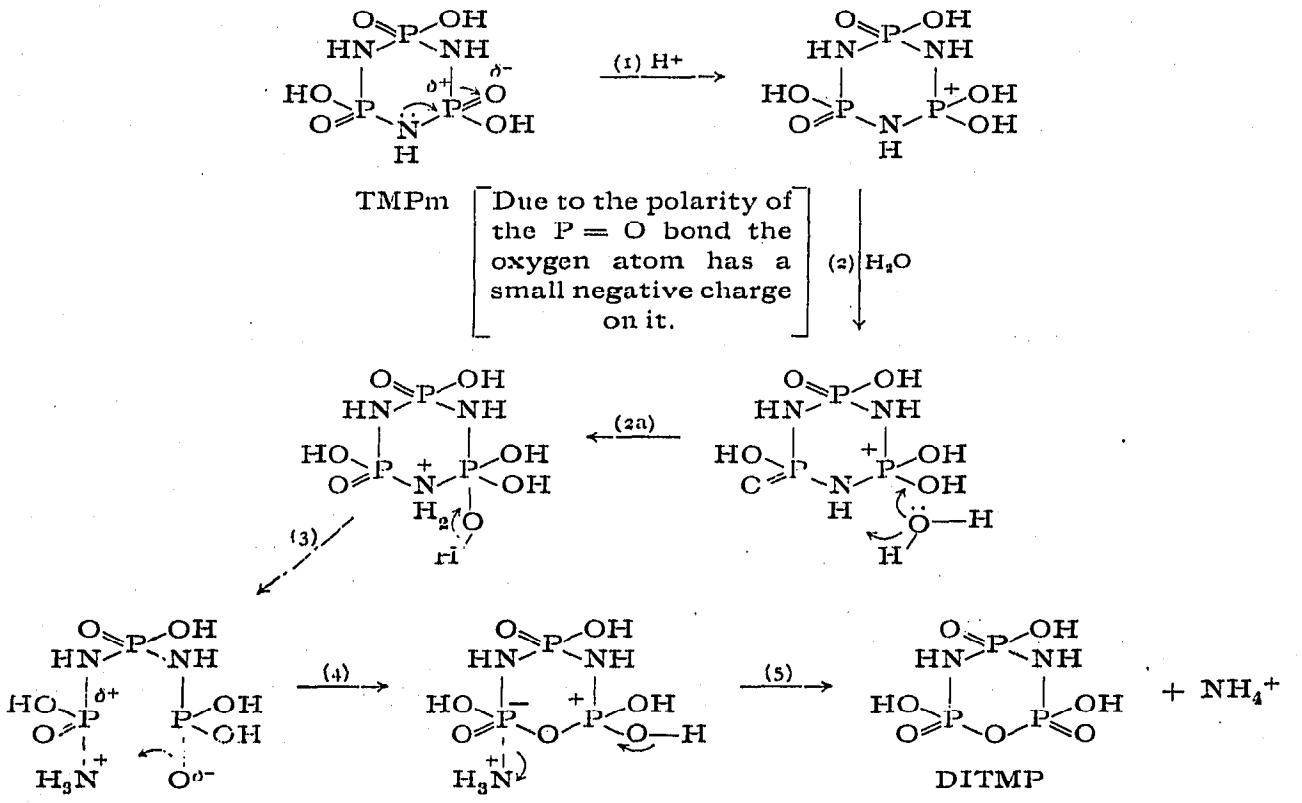
(2)

There appears no reason why the hydrolysis reaction (1) should be any less important than the condensation reaction (2), especially when long chain amidophosphates are considered, and which makes the chain mechanism seem improbable.

Having indicated the advantages and disadvantages of both mechanisms, we suggest a "ruptured ring" mechanism, incorporating ideas from both, in which bond rupture and reformation simultaneously occur.

The major steps in the hydrolysis involve: (1) protonation of a P atom, (2) approach of a water molecule, and (2a) bonding to the P atom, (3) rupture of the P–N bond, (4) formation of a P–O–P bond by electron transfer from the P–O bond on the adjacent P atom, (5) splitting out of the ammonium ion.

A detailed mechanism of the hydrolysis of TMPm to DITMP is given below.



The steps of the mechanism are thought to occur almost simultaneously so that immediately a P–O–N bond is broken, a P–O bond is formed. The mechanism proposes that a P–O bond is first formed by donation of a lone pair of the oxygen of the water molecule (into the empty *d*-orbital of the P atom) before a P–N bond breaks, another P–O bond is then formed, completing the ring before the second P–N bond breaks.

It is proposed that it is the P–O group on the P atom which is active in the reformation of the ring step due to its polarity, electrons being transferred from this bond to form a second P–O bond, with the adjacent P atom which has a small positive charge induced on it by the attacked $-NH_3^+$ group. This mechanism explains the stepwise substitution of oxygen linkages for imide linkages. Similar mechanisms are proposed for the hydrolysis of DITMP and ITMP. The rate of hydrolysis decreases going from TMPm to DITMP to ITMP as expected if the number of imide linkages

available for substitution are considered. ITMP must be hydrolysed by two paths, one yielding TMP by a mechanism similar to that for TMPm to DITMP, and the other yielding ortho- and pyrophosphates. The mechanism of this second path is thought to be attacked at one of the oxygen linkages of the ITMP resulting in cleavage of the ring and formation of ITP, which is immediately hydrolysed to ortho- and pyrophosphates.

Cleavage of a P–O–P linkage is more difficult than a P–N–P linkage. In TMPm, only P–N–P linkages are present and hydrolysis is rapid, DITMP has two imide and one oxygen linkage with the result that attack at the strong oxygen linkage is slight. However, when we come to ITMP, the number of oxygen to imide linkages is 2:1, and attack at oxygen linkages becomes important. The hydrolysis of ITMP to TMP is much slower than DITMP to ITMP due to reduction in imide linkages available for substitution. The fission to ortho- and pyrophosphate is also slow because of stability of P–O–P linkages.

As a general rule in this series, attack at a P–N–P bridge yields a ring compound, but attack at a P–O–P bridge yields a chain compound. Thus acid hydrolysis of DITMP yields ITMP whilst alkaline hydrolysis yields the chain DITP.

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SUMMARY

A mechanism is proposed for the course of the limited hydrolysis of the trimetaphosphimate ion, using the techniques of paper and anion-exchange chromatography as methods of separating the complex series of products which is obtained. As a general rule, attack at a P–N–P linkage in a ring compound yields a ring compound containing a P–O–P linkage instead, whilst attack at a ring P–O–P linkage gives a chain polyphosphate. Thus acid hydrolysis of diimidotrimetaphosphate gives imidotrimetaphosphate, whereas alkaline hydrolysis produces diimidotripolyphosphate.

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