CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS

PART V. THE HYDROLYSIS OF HEXAMETAPHOSPHIMIC ACID

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STOKES[1] reported that tetrametaphosphimic acid is produced in the hydrolysis of hexametaphosphimic acid, but did not study the hydrolysis products further. Preliminary results of the hydrolysis of hexametaphosphimate are reported here, a more detailed study is being carried out and will be published later.

PREPARATION OF SODIUM HEXAMETAPHOSPHIMATE

Two grams of hexaphosphonitrilic chloride was dissolved in 10 ml of diethyl ether, and agitated with a solution of 5 g sodium hydroxide in 10 ml of water, for about two days, when the ether layer was free from phosphonitrilic halide.

The aqueous solution was separated off and the sodium hexametaphosphimate precipitated as a thick syrup by the addition of 5 ml of ethanol. The precipitate was washed by stirring with 1 ml samples of 60 % v/v aqueous ethanol, redissolved in the minimum of water, reprecipitated with ethanol and rewashed with 60 % v/v aqueous ethanol until free from sodium chloride. Stirring with renewed samples of ethanol, removed water from the sodium salt which was obtained as a white amorphous powder. The sodium salt was filtered off and dried *in vacuo* over sulphuric acid.

Found: P, 26.6; N, 11.4;

Calc. for $P_6N_6O_{12}H_6Na_6$: P, 27.4; N, 12.4.

The salt gave one spot in the three chromatographic solvents (Table I).

TABLE I

Solvent	R_x *value*
GASSNER's acid[3]	0.07
QUIMBY's neutral[4]	0.06
BIBERACHER's basic[5]	0.40

The retention volume of sodium hexametaphosphimate under the conditions reported in ref.[2] was a major peak at 320 ml, and a minor one at 250 ml. Since paper chromatography showed the absence of all other phosphate species, it was decided that the smaller peak must be due to a small amount of a different form of the hexa-

metaphosphimate ion. STOKES[1] postulated that it can exist in both ring and chain forms.

Potentiometric titration of hexametaphosphimate gave three inflection points, which (these are shown in Fig. 1) correspond to 4, 5, 6 replaceable hydrogens, with pK values of 2.80, 6.88 and 9.40 respectively. STOKES[1] prepared sodium salts of the hexamer containing 4.6, 6.0 and 6.4 atoms of sodium, and it appears that a number of

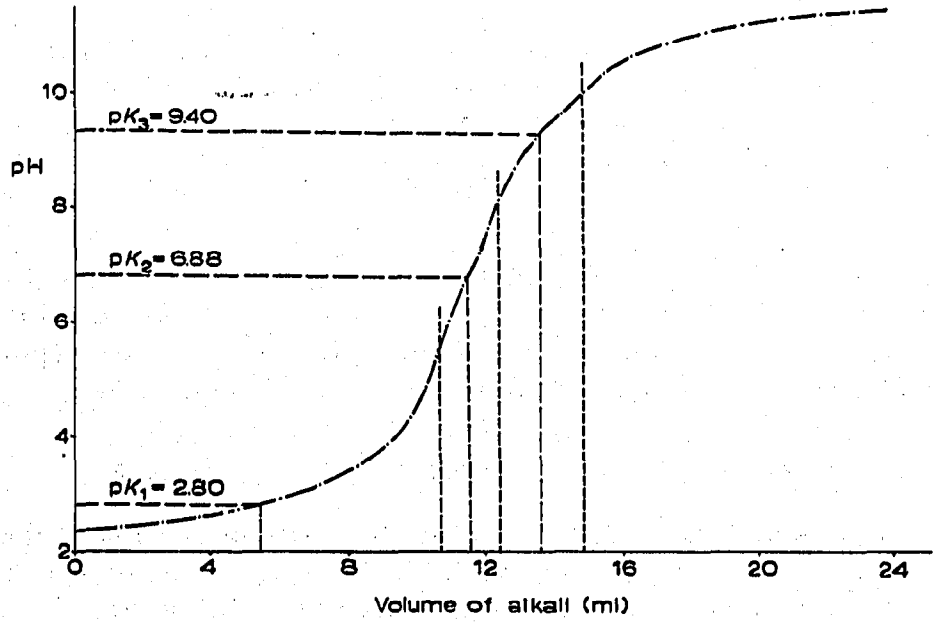


Fig. 1. Potentiometric titration of hexametaphosphimic acid.

salts exist in which the number of metal atoms is not a whole number. As with the pentamer[6], it appears that one, and possibly two units of the ring structure are in a different environment to the others. The appearance of two or three inflection points in the titration curves of the pentamer and hexamer respectively does not necessarily imply that they have chain structures.

PAPER CHROMATOGRAPHIC STUDY OF THE HYDROLYSIS OF SODIUM HEXAMETAPHOSPHIMATE AT 60° AND pH 3.6

Sodium hexametaphosphimate was dissolved in a sodium acetate–hydrochloric acid buffer pH 3.6, and maintained at 60°. Samples were removed at intervals and chromatographed in BIBERACHER's basic[5] and GASSNER's acid[3] solvents. The species detected by the BIBERACHER solvent, with their R_x values are given in Table II.

Samples chromatographed in GASSNER's acid[3] solvent showed large amounts of orthophosphate to be present, with pyrophosphate (R_x 0.76), and a trace of a phosphate species on the starting line.

The hydrolysis appeared to take a similar path to that of the pentamer and tetramer acids in the decomposition to trimeric ring imidophosphates, with the simultaneous production of orthophosphate. Only small quantities of trimetaphosphimate were formed in this hydrolysis, qualitatively much less than for the pentamer.

TABLE II

Time (h)	*Species present*
0	HexaMPm (0.40)
0.2	HexaMPm (0.40)
1	HexaMPm (0.40) + Ortho (1.0)
3	HexaMPm (0.40) + Ortho (1.0) + trace TMPm (1.20) + trace DITMP (1.45)
8	HexaMPm (0.40) + Ortho (1.0) + trace TMPm (1.20) + trace DITMP (1.45) + trace ITMP (1.80)
20	HexaMPm (0.40) + Ortho (1.0) + little TMPm (1.20) + DITMP (1.45) + ITMP (1.80)
48	Same as 20 h but ITMP increasing
100	Little HexaMPm (0.40) + Ortho (1.0) + little TMPm (1.20) + DITMP (1.45) + ITMP (1.80)
200	Ortho (1.0) + little TMPm (1.20) + DITMP (1.45) + large ITMP (1.80)
285	Large Ortho (1.0) + trace TMPm (1.20) + little DITMP (1.45) + large ITMP (1.80)

Abbreviations: HexaMPm = hexametaphosphimate; TMPm = trimetaphosphimate; DITMP = diimidotrimetaphosphate; ITMP = imidotrimetaphosphate; Ortho = orthophosphate.

The tetrametaphosphimate (TeMPm) reported by STOKES is difficult to identify, but the occurrence of a spot on the starting line in the acid solvent could be caused by the highly insoluble tetrametaphosphimic acid.

ION-EXCHANGE STUDY OF THE HYDROLYSIS AT 60° AND pH 3.6

Similar hydrolytic conditions to those used in the paper chromatographic study were employed, and samples were removed at intervals and subjected to ion-exchange separations. The results are shown in Fig. 2.

The elution patterns are rather complex in the fraction numbers 25 to 40. At 18 h, the peaks at fraction 25 and 32 are due to HexaMPm; at later intervals the peak at 25 tended to move forward, whilst that at 32 remained stationary. It is probable that the peak at 25 in these later fractions is probably pyrophosphate, since the HexaMPm has largely disappeared. A DITMP peak could be detected in each case at fraction 36, and although this decreased in size after 186 h, it gave a better resolved peak at that time, due to the corresponding decrease in HexaMPm at fraction 32. It was impossible to say whether TMPm or TeMPm was formed, but the complexity of the elution patterns in this region made their presence a distinct possibility. Trace TMP was found after 186 h.

The high concentration of orthophosphate formed was in agreement with the decomposition of HexaMPm to a trimeric ring plus three orthophosphate groups or their equivalent in chain phosphates. Great accuracy is not possible because of the difficulties of estimating the concentration of DITMP formed.

MECHANISM OF THE REACTION

The hydrolysis of hexametaphosphimate is thought to occur by two mechanisms, one giving DITMP and orthophosphate by a ruptured ring mechanism[2,6,7], and the

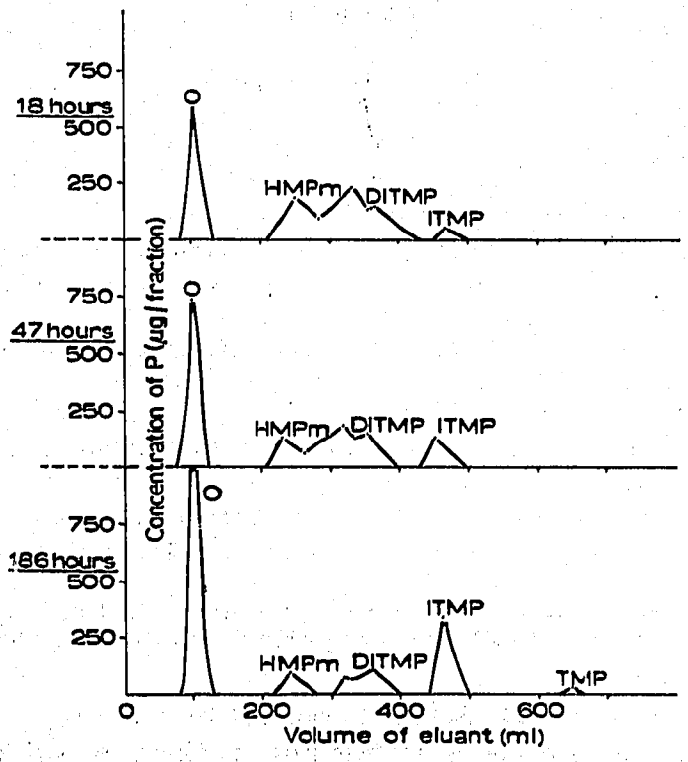
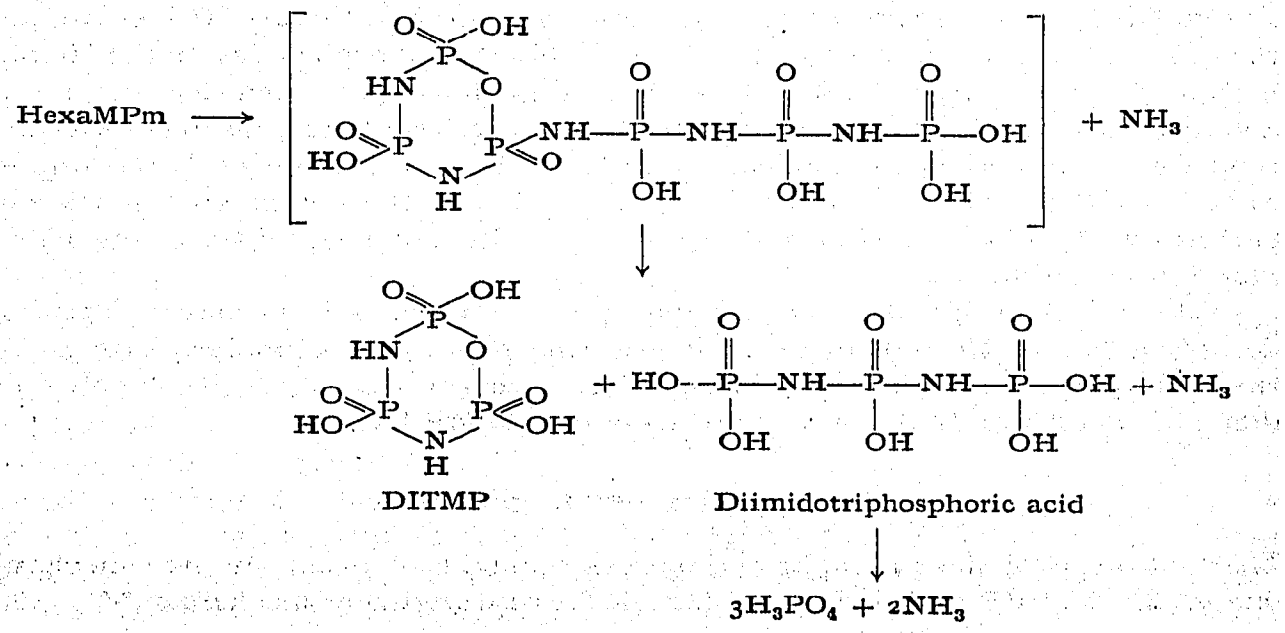


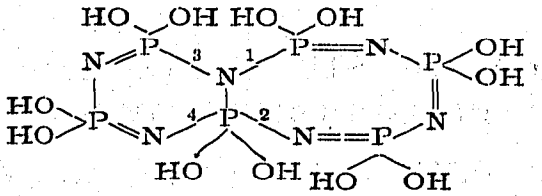
Fig. 2. Elution patterns for the hydrolysis of hexametaphosphimate at pH 3.6 and 60°.

other giving TMPm or TeMPm and orthophosphate involving branching across the ring.

The first of these is essentially the same as that described for the tetramer[7] and pentamer[6] in which the ring breaks, and on reformation does so in such a way that a six-membered ring is formed, and a chain containing three phosphorus atoms remains, which degrades rapidly to orthophosphate or pyrophosphate.

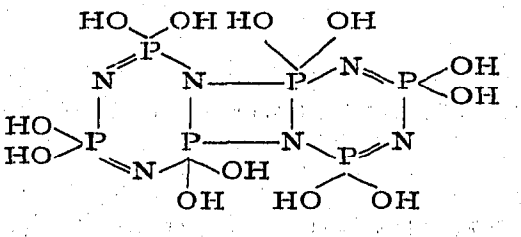


The intermediate postulated as occurring in the second mechanism has the following structure:

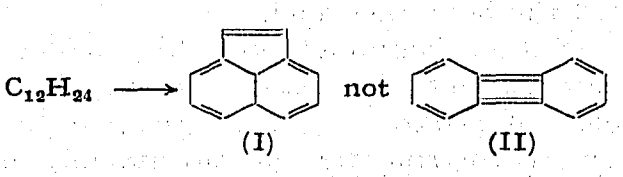


which according to the two P–N bonds which are broken would yield TMPm or TeMPm. Thus 1 and 2 would give TMPm, whilst 3 and 4 would give TeMPm.

It was thought that the hydrolysis of HexaMPm might yield two molecules of TMPm if branching could occur in the ring in two places as shown below, but the low yield of TMPm does not suggest this.



But the organic compound analogous to this structure is very rarely formed, thus cyclododecane condenses to structure I, and not the diphenylene type structure II[8].



(I) (II)

As with the pentamer, there can be little doubt that the first stage of the hydrolysis of hexametaphosphimate is a breakdown to a trimeric ring imidophosphate with the elimination of three molecules of orthophosphate. Again, no definite evidence for the formation of tetrametaphosphimate was obtained.

SUMMARY

A preliminary study of the hydrolysis of sodium hexametaphosphimate in weakly acid solution is described. The products of the reaction are trimeric ring imidophosphates, orthophosphate and ammonia. A reaction mechanism is proposed to explain the formation of these products.

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