

CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS

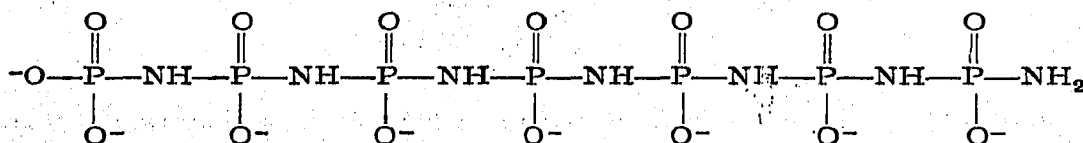
PART VI. THE HYDROLYSIS OF SODIUM HEPTAMETAPHOSPHIMATE AND OCTAMETAPHOSPHIMATE

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STOKES reported that the metaphosphimic acid series ended at the hexamer, and that the heptamer and octamer members existed in a chain form,



although he only isolated the heptamer acid.

STOKES¹ hydrolysed sodium heptametaphosphimate with acetic acid, and found that tetrametaphosphimic acid (characterised by observation of its crystalline form) was formed. STOKES did not isolate the octameric phosphonitrilic chloride or the acid, but found that on hydrolysing the oil (presumably higher cyclic polymers) left after removal of the heptameric phosphonitrilic chloride, a mixture of higher acids was obtained. These acids on further acid hydrolysis, decomposed into tetrametaphosphimic acid, diimidotrimetaphosphate and triimidotetraphosphate.

The possibility of such chain metaphosphimic acids existing in acid solution, is very doubtful since they would be expected to degrade directly to orthophosphate, as do imidodiphosphate or diimidotriphosphate. We believe that these higher acids exist as ring acids, but lack of sufficient material prevented many characterisation tests from being performed. Work is in progress to prepare more of these materials but the yields are extremely low. Analysis of the infra-red spectra of the metaphosphimic acids from the trimer to the octamer show certain interesting trends, and details will be published elsewhere². Paper chromatographic results indicate that the heptameric and octameric acids hydrolyse by paths very similar to the lower acids, and in no way suggest that they have different types of structure.

PREPARATION OF SODIUM HEPTAMETAPHOSPHIMATE AND SODIUM OCTAMETAPHOSPHIMATE

Both these acids were prepared by exactly similar preparations as those described for sodium pentameta-³ and hexametaphosphimates⁴.

Sodium heptametaphosphimate

Found: P, 27.0; N, 11.5.

Calc. for $P_7N_7O_{14}Na_7H_7$: P, 27.8; N, 12.6.*Sodium octametaphosphimate*

Found: P, 27.5; N, 11.8.

Calc. for $P_8N_8O_{18}Na_8H_8$: P, 28.2; N, 12.7.A PAPER CHROMATOGRAPHIC STUDY OF THE HYDROLYSIS OF SODIUM
HEPTAMETAPHOSPHIMATE

Sodium heptametaphosphimate was dissolved in a sodium acetate-hydrochloric acid buffer pH 3.6, and was heated at 60°. Samples were removed at intervals and eluted in BIBERACHER's basic solvent⁵. The species detected, with their R_x values, are given in Table I.

TABLE I

Time (h)	Species (R_x values)
0	HeptaMPm (0.55) only
0.2	HeptaMPm (0.55) + Ortho (1.0)
2	HeptaMPm (0.55) + Ortho (1.0) + trace DITMP (1.45)
6	HeptaMPm (0.55) + Ortho (1.0) + little DITMP (1.45)
24	HeptaMPm (0.55) + Ortho (1.0) + little TMPm (1.20) + DITMP (1.45) + trace ITMP (1.80)
55	HeptaMPm (0.55) + Ortho (1.0) + little TMPm (1.20) + large DITMP (1.45) + ITMP (1.80)
97	HeptaMPm (0.55) + Ortho (1.0) + little TMPm (1.20) + large DITMP (1.45) + ITMP (1.80)

Abbreviations: HeptaMPm = heptametaphosphimate; TMPm = trimetaphosphimate; DITMP = diimidotrimetaphosphate; ITMP = imidotrimetaphosphate; Ortho = orthophosphate.

The hydrolysis was quite rapid compared with that of the lower metaphosphimic acids (trimer excluded) and the formation of orthophosphate after only 0.2 h was particularly noticeable. The orthophosphate increased with time and was present in considerable concentration after 55 h. DITMP was also present in large quantities at 24 h and 55 h, but TMPm was never present in large amounts. As DITMP was detected before TMPm, and this indicates that these are formed by two different mechanisms rather than TMPm being formed as a first step, and then DITMP being formed from the TMPm.

Considerable tailing occurred below the orthophosphate spot, probably due to some chain phosphates, but a spot near the starting line was probably TeMPm, and it was present in similar concentrations to the TMPm.

A PAPER CHROMATOGRAPHIC STUDY OF THE HYDROLYSIS OF SODIUM
OCTAMETAPHOSPHIMATE

Sodium octametaphosphimate was dissolved in a sodium acetate-hydrochloric acid buffer pH 3.6, and was heated at 60°. Samples were removed at intervals and eluted

in BIBERACHER's basic solvent⁵. The species detected, with their R_x values, are given in Table II.

TABLE II

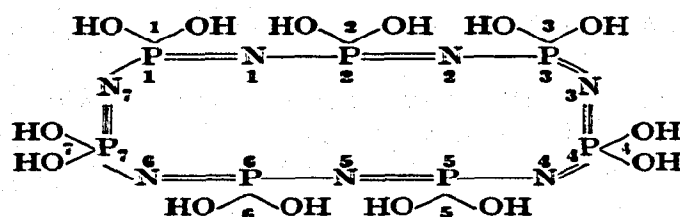
Time (h)	Species (R_x values)
0	OctaMPm (0.50)
0.2	OctaMPm (0.50) + Ortho (1.0)
2	OctaMPm (0.50) + Ortho (1.0) + trace DITMP (1.45)
6	OctaMPm (0.50) + Ortho (1.0) + DITMP (1.45)
24	OctaMPm (0.50) + Ortho (1.0) + trace TMPm (1.20) + DITMP (1.45) + trace ITMP (1.80)
55	OctaMPm (0.50) + Ortho (1.0) + trace TMPm (1.20) + DITMP (1.45) + ITMP (1.80)
97	OctaMPm (0.50) + Ortho (1.0) + trace TMPm (1.20) + large DITMP (1.45) + little ITMP (1.80)

The rate of hydrolysis was comparable to the rate of hydrolysis of the heptameric acid. Orthophosphate was formed almost immediately and after 55 h was present in large quantities. TMPm was again present in only small concentration, and was detected only after DITMP was detected, indicating that TMPm and DITMP are formed by different mechanisms.

Tailing occurred below the orthophosphate spot, and was partially due to OctaMPm, and to chain phosphates, but a small amount of TeMPm was also present.

THE MECHANISM OF HYDROLYSIS

Although HeptaMPm and OctaMPm were only studied qualitatively by paper chromatography, it was shown that the first step of the hydrolysis was a breakdown to a trimeric imidophosphate with production of vast amounts of orthophosphate^{3,4}. Small amounts of TMPm were formed in each case, probably by a mechanism involving bonding across the ring. DITMP was formed in greater concentration, probably through the mechanism involving ring rupture, as for lower metaphosphimates. DITMP was detected before TMPm in the hydrolysis of the higher acid indicating that they were formed by two different mechanisms. The presence of TeMPm is explained by the mechanism involving bonding across the ring similar to that for the preparation of TMPm.



Bonding between P(2) and N(5) gives TeMPm, whilst bonding between P(3) and N(5) will give TMPm. Work is in progress to elucidate the hydrolysis of the higher metaphosphimic acids, but yields of the higher cyclic polymers especially the heptamer and octamer, are very low.

SUMMARY

A preliminary study of the hydrolysis of sodium hepta- and octametaphosphimates in weakly acid solution is described. From paper chromatographic studies, the products of the reaction appear to be trimeric ring imidophosphates, orthophosphate and ammonia. A reaction mechanism is proposed to explain the formation of these products.

REFERENCES

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- ⁴ F. H. POLLARD, G. NICKLESS AND R. W. WARRENDER, *J. Chromatog.*, 10 (1963) 73.
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