

CHROMATOGRAPHIC STUDIES OF PHOSPHORUS COMPOUNDS

PART XI. THE REACTION OF SODIUM HYDROXIDE WITH PHOSPHORYL CHLORIDE

F. H. POLLARD[†], G. NICKLESS* AND J. D. MURRAY*Department of Chemistry, The University, Bristol (Great Britain)*

(Received September 27th, 1965)

The hydrolysis of orthophosphoryl chloride with water has been studied by several early authors¹⁻³, and more recently by GRUNZE *et al.*^{4,5} and HUDSON AND MOSS⁶. The latter concluded that the primary product of hydrolysis is dichlorophosphoric acid. Furthermore, he claimed that by self-condensation of this acid and condensation with monophosphoric acid, chloro-derivatives of polyphosphoric acids can be formed. VAN WAZER⁷ *et al.* suggest that condensed acids are produced but with little or no chlorine in their structure.

We have applied paper and anion-exchange chromatographic techniques to investigate the reaction occurring when POCl_3 and sodium hydroxide solution are mixed in various mole ratios.

EXPERIMENTAL

Method

The correct amount of 1 N NaOH solution was placed in a small conical flask surrounded by an ice-water mixture. The solution was stirred using a magnetic stirrer. After 15 min the POCl_3 (purified by distillation) was added by means of a syringe pipette. There was some agitation between the immiscible liquids and then a sudden evolution of hydrogen chloride vapour occurred. Liberation of HCl continued slowly but upon heating the rate of evolution increased.

When the POCl_3 :NaOH mole ratio was 50:1, a white precipitate was evident after the sudden HCl evolution. However, if the mixture was refluxed above 100° for one hour or longer, the precipitate disappeared, and now there was seen a clear viscous phase beneath a transparent labile liquid.

A white precipitate was also produced when the mole ratio was 25:1 but after one hour's refluxing, a viscous mixture was produced with no separation of phases. When the ratio was 100:1, no white precipitate was formed initially, but the viscous and labile layers were evident after refluxing. If excess NaOH was present, an homogeneous solution resulted after HCl evolution which was not noticeably affected by heat.

Deceased October 16th, 1965.

* To whom enquiries should be addressed.

Analysis

(1) *Paper chromatography.* The white precipitates and viscous phases were dissolved in distilled water and neutralised to restrict degradation. The labile phases were found to react with water and so were applied directly to the chromatogram.

Descending methods of elution were used with Whatman No. 541 chromatographic paper. Many solvents with different ratios of components and different pH's were tried. The most successful was BIBERACHER's basic solvent⁸. After drying, the chromatograms were lightly sprayed with KARL-KROUPA's reagent⁹ and then they were redried. The developed spots were identified as far as possible by comparison with a standard mixture of condensed phosphates which was developed on the same chromatogram.

(2) *Anion-exchange chromatography.* The neutral solutions obtained from the white precipitates or viscous phases were diluted sufficiently so that 1 ml containing 0.01 g of phosphorus could be introduced on to a column of Dowex 1X8 resin of mesh 100-200. The resin was contained in a column of length 50 cm, diameter 1.0 cm. This was eluted with potassium chloride buffered to pH 11.4 with ammonia. A linear gradient was employed by placing the reservoir and mixing vessel (which were both of 1 l volume and equal diameter) on the same horizontal level with the strong KCl solution (55 g/l) siphoning from the reservoir over into the weak KCl (5 g/l) in the mixing vessel.

The collected 10 ml fractions were warmed with 10 ml of concentrated nitric acid for one hour to convert all phosphate species to monophosphate. Then, after cooling, the solution was made up to 100 ml with distilled water after 5 ml of 5 g/l ammonium metavanadate solution (containing 2% conc. HNO_3) and 10 ml of 10% ammonium molybdate solution had been added. The optical density of the resulting phosphovanadomolybdate complex was measured by comparison with a blank using an Unicam spectrophotometer S.P. 500. Species were identified as far as possible by comparison of retention volumes with those of standard condensed phosphates and also by addition of a known quantity of a standard to the neutral solution under investigation.

RESULTS AND DISCUSSION

While the paper chromatographic findings were purely qualitative, the results derived from the anion-exchange investigation may be described as semi-quantitative. As the POCl_3 and NaOH were immiscible, the relative amount of each product depends to some extent on the surface area common to both components. The area of interface is not reproducible, therefore the results cannot be completely quantitative.

The transparent and labile phases resulting before and after refluxing gave rise to spots corresponding to mono-, di- and triphosphates and trimetaphosphate (Table I). It was also found that a spot of pure POCl_3 produced spots corresponding to the same species (reaction must occur in moist air or solvent vapour; streaking would have resulted if the liquid solvent had reacted with the POCl_3). Indeed the transparent liquid present with the white precipitate had the appearance and characteristic odour of POCl_3 while the labile phase produced after refluxing although having a similar smell was a less dense liquid—this was more likely dichlorophosphoric acid.

TABLE I

CONDENSED PHOSPHATES DETECTED BY PAPER CHROMATOGRAPHY

$POCl_3:NaOH$	Phase	Species identified
1:1	Homogeneous solution, unaffected by heat	Monophosphate and trace of diphosphate
25:1	Initial white precipitate. Viscous mixture (after refluxing)	Mono- and diphosphates
50:1	Initial white precipitate	Monophosphate and traces of diphosphate and higher polyphosphates
	Viscous phase (after 1 h refluxing)	Mono-, di-, triphosphates, higher polyphosphates and trimetaphosphate
100:1	No white precipitate. Viscous layer (after 1 h refluxing)	Mono-, di-, triphosphates, higher polyphosphates and trimetaphosphate

Figs. 1, 2 and 3 show the anion-exchange separation of a mixture of polyphosphates, the elution patterns for the white precipitate, and for the viscous phases respectively.

The final large peak in the viscous phase is presumably due to higher polyphosphates which have not separated from one another. Such a separation could most likely be achieved, using a longer column, and a "shallower" gradient elution method.

When the mixture was refluxed for six hours instead of one hour, there was no significant change in the relative quantities of products.

It is interesting that GRUNZE found polyphosphoric acid derivatives were produced after refluxing a $POCl_3-H_2O$ (1:1) mixture for a few hours⁵. The water content of this mixture is approximately the same as in our $POCl_3-NaOH$ (50:1) mixture. Therefore the hydrolyses depend on water content and not OH^- ion concentration. There is no white precipitate formed in the primary step of the water

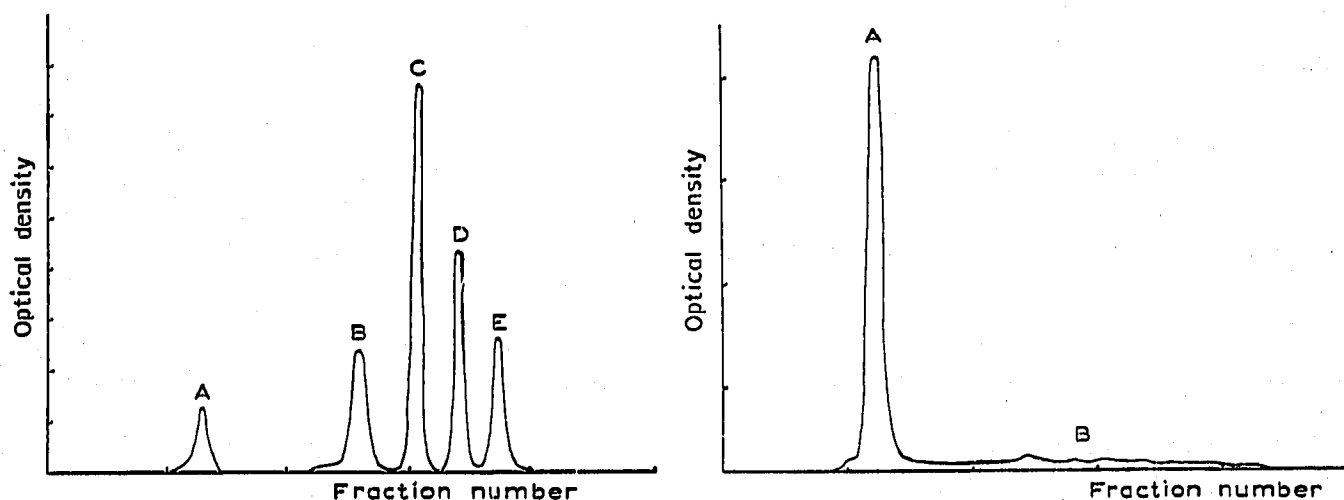


Fig. 1. Chromatographic separation of a synthetic standard mixture of polyphosphates. A = monophosphate; B = diphosphate (pyrophosphate); C = tripolyphosphate; D = tetrametaphosphate; E = trimetaphosphate.

Fig. 2. Chromatogram obtained upon analysis of the white precipitate. A = monophosphate; B = traces of diphosphate and higher polyphosphates.

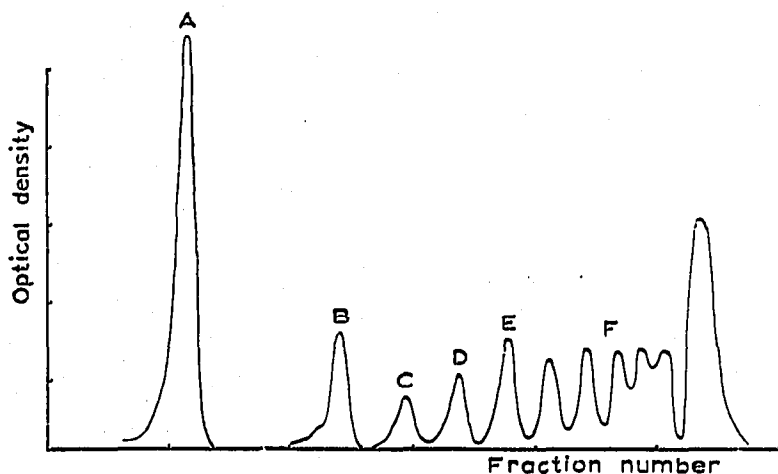


Fig. 3. Chromatogram obtained upon analysis of the viscous phase. A = monophosphate; B = diphosphate; C = tripolyphosphate; D = tetrametaphosphate; E = trimetaphosphate; F = higher polyphosphates (4 or more phosphorus atoms in the chain length).

hydrolysis because acids are produced and not sodium salts of the lower condensed acids which are insoluble in POCl_3 .

GRUNZE also claimed⁵ that polyphosphoric acids were produced when POCl_3 : $\text{H}_2\text{O} < 2$. We checked this water hydrolysis and could identify only mono- and diphosphoric acids for POCl_3 : $\text{H}_2\text{O} = 2$, just as only mono- and diphosphates were produced in the POCl_3 - NaOH (25:1) mixture. As the relative amount of water is increased, one would expect the replacement of $-\text{Cl}$ by $-\text{OH}$ to take priority over the condensation occurring by elimination of HCl molecules.

It must be pointed out that any branched chain products would undergo degradation upon dissolution in water and also if chloro-derivatives were present, they would probably be converted to chloride-free condensed phosphates when the neutralisation was performed with strong base.

SUMMARY

The hydrolysis of phosphoryl chloride with aqueous base has been investigated. Separation and identification of the products by means of paper and anion-exchange chromatography has shown that salts are formed which have a similar composition to the acids formed by hydrolysis with water in neutral solution.

REFERENCES

- 1 C. A. WURTZ, *Ann. Chim. Phys.*, 20 (1847) 472.
- 2 A. BESSON, *Compt. Rend.*, 124 (1897) 1099.
- 3 H. MEERWEIN AND K. BODENDORF, *Ber. Deut. Chem. Ges.*, 62 (1929) 1952.
- 4 H. ROUX, E. THILO, H. GRUNZE AND M. VISCONTINI, *Helv. Chim. Acta*, 38 (1955) 25.
- 5 H. GRUNZE, *Z. Anorg. Allgem. Chem.*, 313 (1961-1962) 316.
- 6 R. F. HUDSON AND G. MOSS, *J. Chem. Soc.*, (1962) 3599.
- 7 J. R. VAN WAZER, L. C. D. GROENWEGHE AND J. H. PAYNE, *J. Am. Chem. Soc.*, 82 (1960) 5305.
- 8 G. BIBERACHER, *Z. Anorg. Allgem. Chem.*, 285 (1956) 86.
- 9 E. KARL-KROUPA, *Anal. Chem.*, 28 (1956) 1091.