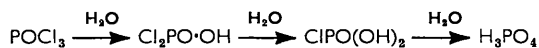


721. *Hydrolysis of Phosphoryl Chloride in Oxygen-18-enriched Water.*

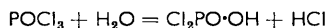
By M. HALMANN and L. KUGEL.

Phosphoryl chloride, dissolved in a large volume of water enriched in oxygen-18 underwent hydrolysis to orthophosphoric acid containing three-quarters of the oxygen-18 excess of the water. Thus, none of the three stages



involved fast reversible formation of an intermediate in which the entering oxygen atom from the water became equivalent to the phosphoryl oxygen atom. The first stage was checked by partial reaction of phosphoryl chloride with oxygen-18 enriched water; the unreacted phosphoryl chloride had not become enriched in oxygen-18.

THE kinetics and mechanism of hydrolysis of phosphoryl chloride have been studied several times.^{1,2} The reaction was shown to proceed in three stages. In the very fast, stage ($t_{\frac{1}{2}} = 10^{-2}$ sec. at 25° in 2 : 1 dioxan-water²), phosphorodichloridic acid is formed,



In dilute aqueous solution, phosphorodichloridic acid undergoes relatively slow hydrolysis² ($t_{\frac{1}{2}} \sim 250$ sec. at 25°) in which both chlorine atoms are replaced simultaneously.² The rate of replacement of the third chlorine atom is thus equal to or faster than that of the second chlorine atom.

A bimolecular mechanism has been suggested for the first two stages of hydrolysis of phosphoryl chloride.² No evidence is yet available as to whether these reactions occur either (a) by synchronous displacements, with simultaneous bond-formation by the nucleophilic reagent (water) and bond-breakage by the leaving group (chloride ion) or, alternatively, (b) by fast reversible addition of water to the phosphoryl group, forming an unstable pentavalent phosphorus intermediate. Experiments on the hydrolysis of dialkylphosphinic halides and dialkyl phosphorohalidates in oxygen-18-enriched water have shown that oxygen exchange between the phosphoryl group and the solvent does not

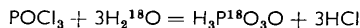
¹ Grunze, *Z. anorg. Chem.*, 1959, **298**, 152; Grunze and Thilo, *Angew. Chem.*, 1958, **70**, 73.

² Hudson and Moss, *J.*, 1962, 3599.

occur.³ On the other hand, hydrolysis of methyl dihydrogen phosphate in acid solution was shown to occur with oxygen-18 being incorporated into the phosphoryl group.⁴ The possibility that such an exchange takes place in one or several of the stages of phosphoryl chloride hydrolysis can therefore not be excluded.

RESULTS

In phosphoryl chloride, any of the three stages of replacement of chlorine by hydroxyl during hydrolysis may occur either with or without oxygen exchange between water and the phosphoryl group. In the absence of any exchange, the required atom % excess of oxygen-18 in the resulting orthophosphoric acid should be three-quarters of the isotopic excess of the water used:



Any exchange should produce phosphoric acid with a higher enrichment in oxygen-18. The results for hydrolysis in dilute aqueous solution (see the Table) give the oxygen-18

Hydrolysis of phosphoryl chloride in water (3.2 ± 0.1 atom % excess of oxygen-18), followed by analysis for oxygen-18 in the phosphoric acid.

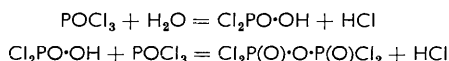
Time (min.)	25	55	71	140	540	1380	2760	10,080
Atom % excess of oxygen-18...	2.4	2.4	2.4	2.6	2.3	2.4	2.5	2.4

Average: 2.4 ± 0.1 atom % excess of oxygen-18.

enrichment in the phosphoric acid product, isolated at various time intervals after mixing normal phosphoryl chloride (0.4 ml.) with enriched water (80 ml.). Before mixing the water was at 0°; after solution of the phosphoryl chloride, it was cooled to room temperature. The absence of any change from 25 min. to 7 days shows that the oxygen exchange between water and phosphoryl chloride, phosphorodichloridic, phosphorochloridic, and phosphoric acids was negligible under the conditions used.

The resulting oxygen-18 excess in the phosphoric acid, $2.4 \pm 0.1\%$, is equal to that required for a simple displacement, *i.e.*, $3.2 \times 3/4 = 2.4 \pm 0.1\%$ excess.

Since the above conclusion depends on analysis of the phosphoric acid for oxygen-18, in which dilution errors tend to give low results, and a slight enrichment may not be detected, a more sensitive test for exchange was carried out. Phosphoryl chloride (55 mmole) was allowed to react with a limited amount of water (55 mmole; 4.6 atom % of oxygen-18); under such conditions, the only expected reactions are ^{1,2}



After 5 hr., the unreacted phosphoryl chloride was recovered; its oxygen-18 content was 0.22 atom %, equal to that of the initial, normal, phosphoryl chloride.

DISCUSSION

Neither the first nor the subsequent stages of hydrolysis of phosphoryl chloride involved fast reversible formation of an intermediate in which the labelled oxygen atom from the water became equivalent to the phosphoryl oxygen atom. This does not exclude some other structure in which both oxygen atoms are bound to the phosphorus, but have non-equivalent configurations. Of the few known stable pentavalent phosphorus

³ Dostrovsky and Halmann, *J.*, 1956, 1004; Halmann, *J.*, 1959, 305.

⁴ Bunton, Llewellyn, Oldham, and Vernon, *J.*, 1958, 3574; Haake and Westheimer, *J. Amer. Chem. Soc.*, 1961, **83**, 1102.

compounds, phosphorus pentachloride has been shown to have a bipyramidal configuration.⁵ For pentaphenylphosphorane, on the other hand, the available evidence favours a tetragonal pyramidal structure.^{6,7} Starting with tetrahedral phosphoryl chloride, addition of water can give rise to several transition states or intermediates in which the entering oxygen atom is not equivalent to the phosphoryl oxygen atom. Possible structures are the trigonal bipyramidal type, with the entering oxygen atom and the leaving chlorine atoms at the apical positions, or tetragonal pyramidal types, with the entering oxygen atom at the single apical position. Analogous structures are possible for the intermediates in the subsequent hydrolysis of phosphorodichloridic acid. The non-occurrence of oxygen exchange during the hydrolysis of phosphoryl chloride may therefore be due to a mechanism involving one of the above intermediates, in which the water and the phosphoryl oxygen atoms are not equivalent, or it may be due to synchronous displacement without the formation of an intermediate.

The stereochemical consequences of reactions involving intermediates of the trigonal bipyramid and of the tetragonal pyramidal types should be different; with suitably substituted substrates R^1R^2POCl , only the trigonal bipyramid should result in inversion of configuration, as was shown by a comparison of the rates of racemisation and of isotopic exchange in the reaction between methyl ethylphenylphosphinate and methoxide ions.⁸ Such a test is obviously not possible for phosphoryl chloride.

EXPERIMENTAL

Phosphoryl chloride (Fluka AG) was purified by distillation in a vacuum system, using stop-cocks and joints lubricated with KEL-F Grease. Analysis for oxygen-18 in phosphoric acid was carried out by precipitation of barium phosphate, which was purified by repeated dissolution in dilute hydrochloric acid and precipitation with sodium hydroxide; the precipitate was then washed with water and dried at 60° in a vacuum oven. It was then sealed together with a mixture of mercuric chloride and cyanide in evacuated tubes with break-seals, heated for 2 hr. at 400°,⁹ and then for 2 hr. at 200° with zinc amalgam.¹⁰ Determination of oxygen-18 in phosphoryl chloride and in water was carried out by distilling 0.02 ml.- and 0.005 ml.-portions, respectively, in a vacuum system, into tubes with break-seals containing a mixture of mercuric chloride and cyanide, and proceeding as above.

This investigation was supported by a Research Grant from the U.S. Public Health Service.

ISOTOPE DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL.

[Received, January 24th, 1964.]

⁵ Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836; Wilmhurst and Bernstein, *J. Chem. Phys.*, 1957, **27**, 661.

⁶ Wheatley and Wittig, *Proc. Chem. Soc.*, 1962, 251; Wheatley, personal communication.

⁷ Degani, Halmann, Laulicht, and Pinchas, *Spectrochim. Acta*, 1964, **20**, 1289.

⁸ Green and Hudson, *Proc. Chem. Soc.*, 1962, 307.

⁹ Anbar and Guttman, *Internat. J. Appl. Radiation Isotopes*, 1959, **3**, 233.

¹⁰ Anbar and Guttman, *Bull. Res. Council Israel*, 1959, **8A**, 146; see also Samuel, *J.*, 1960, 1318, for details of the isotopic analysis.