730. *Preparation of Pyrophosphoryl Chloride from Phosphoric Oxide and Phosphorus Pentachloride, and a Radiochemical Investigation of the Reaction.*

By P. C. Crofts, I. M. Downie, and R. B. Heslop.

The reaction of phosphoric oxide with phosphorus pentachloride (formed *in situ* from phosphorus trichloride and chlorine) provides an excellent route to pyrophosphoryl chloride. The manner in which the yield depends on the $P_4O_{10} : PCl_5$ ratio suggested that P–O–P linkages are not formed in the reaction and hence that the phosphorus atoms of the pyrophosphoryl chloride must be derived only from the phosphoric oxide. This was confirmed by using $^{32}PCl_5$; practically all the radioactive phosphorus appeared as phosphoryl chloride.

The reaction of phosphoric oxide and phosphorus pentachloride was reported by Oddo[1] to yield some pyrophosphoryl chloride, $Cl_2OP{\cdot}O{\cdot}POCl_2$, together with phosphoryl chloride as the main product. As other methods [2,3] for the preparation of pyrophosphoryl chloride give yields which are usually below 20%, this reaction was re-investigated. It appeared to us that Oddo's low yield of pyrophosphoryl chloride (8%, based on the total phosphorus in the reaction mixture) probably resulted from the proportions of reactants which, according to equation (1), would be expected to give only phosphoryl chloride. At first we considered that the best ratio of reactants would be that of equation (2), in which it is assumed that all the phosphorus, whether originally present as phosphoric oxide or as phosphorus pentachloride, can be converted into pyrophosphoryl chloride.

$$P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$3P_4O_{10} + 8PCl_5 \longrightarrow 10P_2O_3Cl_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$P_4O_{10} + 4PCl_5 \longrightarrow 2P_2O_3Cl_4 + 4POCl_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

If, however, this compound is formed only by partial breakdown of the phosphoric oxide structure, in which P–O–P linkages are already present, whilst the phosphorus pentachloride is converted wholly into phosphoryl chloride, the reaction should be represented by equation (3) and the maximum possible conversion into pyrophosphoryl chloride of the total phosphorus in the reactants is 50%.

The effect of using different proportions of reactants was therefore investigated. A higher yield of pyrophosphoryl chloride than Oddo obtained was got by increasing the ratio of phosphoric oxide to phosphorus pentachloride. Subsequently, in order to avoid the unpleasant operation of weighing out phosphorus pentachloride, the reaction was carried out by passing chlorine into a boiling suspension of phosphoric oxide in a mixture of

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[1] Oddo, *Gazzetta*, 1899, **29**, II, 330.

[2] Geuther and Michaelis, *Ber.*, 1871, **4**, 766; Wagner-Jauregg and Griesshaber, *Ber.*, 1937, **70**, 8; Klement and Wolf, *Z. anorg. Chem.*, 1955, **282**, 149.

[3] Besson, *Compt. rend.*, 1897, **124**, 1099; Becke-Goehring and Sambeth, *Angew. Chem.*, 1957, **69**, 640.

phosphorus trichloride and a diluent (carbon tetrachloride or phosphoryl chloride). The yields of pyrophosphoryl chloride obtained are shown in the Table.

Molar ratio, P_4O_{10} : PCl_5	1 : 2	3 : 8	1 : 4	1 : 4
Diluent	CCl_4	CCl_4	CCl_4	$POCl_3$
Yield (% calc. on total P)	13, 10	23, 27, 22	29, 34	30, 31
Yield (% calc. on eqn. 3)	39, 30	58, 68, 54	58, 69	59, 62

The fact that the highest yields, calculated on total phosphorus, are obtained by using the 1 : 4 ratio of reactants required by equation (3) supports the view that the P–O–P linkages, and hence the phosphorus atoms, in the pyrophosphoryl chloride are derived wholly from the phosphoric oxide. As a further test, the reaction was carried out with phosphorus pentachloride labelled with phosphorus-32. The prediction that, in accordance with equation (3*a*), the products would be inactive pyrophosphoryl chloride and radioactive phosphoryl chloride was found to be essentially true: the radioactivity of the phosphorus in the pyrophosphoryl chloride was less than 0·5% of that of the phosphorus in the phosphoryl chloride.

$$P_4O_{10} + 4^{32}PCl_5 \longrightarrow 2P_2O_3Cl_4 + 4^{32}POCl_3 \quad \ldots\ldots\ldots \quad (3a)$$

The reaction of phosphoric oxide with phosphorus pentachloride, formed *in situ* from phosphorus trichloride and chlorine, provides a simple method for the preparation of pyrophosphoryl chloride in similar yields (calc. on total phosphorus) to those recently reported[4] for the less convenient procedure of heating phosphoric oxide and phosphoryl chloride in sealed tubes at 200° for 48 hours, and in consistently higher yields than are obtained by either of the methods most frequently used.[2,3]

EXPERIMENTAL

Yields are calculated on the basis of equation (3).

Reaction of Phosphoric Oxide and Phosphorus Pentachloride.—A mixture of phosphoric oxide (42·6 g., 0·15 mole) and phosphorus pentachloride (97·8 g., 0·47 mole) was heated at 105° for 8 hr., then cooled and filtered. The solid was washed with carbon tetrachloride, and the combined filtrate and washings were distilled, giving pyrophosphoryl chloride (20·0 g., 34%), b. p. 105°/18 mm.

Reaction of Phosphoric Oxide, Phosphorus Trichloride, and Chlorine in Carbon Tetrachloride.—Some runs were carried out in three-necked flasks but, because of the difficulty of introducing phosphoric oxide into these, a 700 ml. wide-mouthed reaction vessel with a multi-neck flanged lid was found to be more convenient. In a run with this apparatus, chlorine was passed through a boiling mixture of phosphoric oxide (71·0 g., 0·25 mole), phosphorus trichloride (87·5 ml., 1·0 mole), and carbon tetrachloride (100 ml.) until an excess was present. After a further 30 minutes' boiling, the mixture was cooled and filtered and the filtrate distilled, giving pyrophosphoryl chloride (86·5 g., 69%), b. p. 101°/10 mm., n_D^{20} 1·4765, d_4^{20} 1·814. The infrared spectrum (liquid film) contained a fairly sharp, strong band at 1316 cm.$^{-1}$ (P=O stretching), a broad strong band at 966 cm.$^{-1}$, and a broad band of medium strength at 704 cm.$^{-1}$, the last two being associated with the P–O–P group.[5] These frequenies are close to those recently reported[6] for pyrophosphoryl chloride in cyclohexane.

*Reaction of Phosphoric Oxide and Phosphorus-*32 *Pentachloride.*—A 250 ml. three-necked flask was fitted with a reflux condenser protected by a calcium chloride tube, and a tube reaching almost to the bottom of the flask and serving to lead in nitrogen and chlorine through a trap, in which chlorine could be condensed and its volume roughly measured. The apparatus was flushed with nitrogen, and neutron-irradiated red phosphorus (*ca.* 6 mg., *ca.* 3 μc) was introduced through the central neck. Chlorine (5 ml.) was condensed in the trap and allowed to evaporate into the flask where it reacted with the radioactive phosphorus. Phosphorus trichloride (35 ml., 0·4 mole) and carbon tetrachloride (40 ml.) were added from a tap-funnel temporarily fitted to the central neck, and the mixture was boiled for a few minutes until the phosphorus pentachloride (from the radioactive phosphorus and from reaction of part of the

[4] Grunze, *Z. anorg. Chem.*, 1958, **296**, 63.

[5] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1958, p. 318.

[6] Baudler, Klement, and Rother, *Chem. Ber.*, 1960, **93**, 149.

phosphorus trichloride with chlorine remaining in the flask) had dissolved. Phosphoric oxide (28·4 g., 0·1 mole) was added from a dropping device for solids, temporarily fitted to the central neck. The mixture was heated to the b. p. and chlorine, previously condensed in the trap, was passed in slowly until after 1 hr. an excess of chlorine was seen to be present. Boiling under reflux was continued for a further hour, with occasional brief passage of chlorine to resaturate the mixture.

After being kept overnight, the mixture was distilled to a vapour temperature of 90° (50 ml. of distillate). The remaining liquid was decanted from a small quantity of solid into a Claisen flask and distilled, to give fractions (i) b. p. <27°/38 mm. (4·9 g.), (ii) b. p. 27°/38 mm. to 29°/23 mm. (31·0 g.), and (iii) b. p. 29—103°/23 mm. (4·4 g.). The condenser was disconnected, the tip of the side arm of the flask was wiped with filter paper, and a clean condenser, adaptor, and receiver were fitted. Distillation then afforded fraction (iv), pyrophosphoryl chloride (20·6 g., 41%), b. p. 103—106°/23 mm.

The radioactivites of fraction (ii) (phosphoryl chloride containing a little carbon tetrachloride) and fraction (iv) were measured in a Mullard liquid counter, Type MX 124, with a Panax scaler, Type D 657, and were observed to be 39140 and 336 c.p.m. respectively. On the assumption that fraction (ii) is pure phosphoryl chloride and fraction (iv) pure pyrophosphoryl chloride, and with correction for background (18 c.p.m.), lost counts, different densities, and different phosphorus contents of phosphoryl chloride and pyrophosphoryl chloride, the ratio of radioactive phosphorus to total phosphorus in the pyrophosphoryl chloride is calculated to be 0·47% of the ratio of radioactive phosphorus to total phosphorus in the phosphoryl chloride.

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER, 1.

[*Received, April 11th*, 1960.]