

XXIII.—*Action of Phosphoryl Chloride on Phosphorus Pentoxide.*

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IN 1871, Gustavson, in a preliminary note (*Ber.*, **4**, 853), described the existence of a viscous mass obtained by heating a mixture of phosphoryl trichloride with phosphorus pentoxide in equal molecular proportions at  $200^{\circ}$  for 36 hours. This substance he regarded as either metaphosphoryl chloride,  $\text{PO}_2\text{Cl}$ , or as a mixture of this substance with its polymers. In this preliminary note, Gustavson made no attempt to prove whether this viscous mass was homogeneous or not. Geuther, in his memoir on the "Mutual Reactions of the Chlorides and Acids of Phosphorus" (*J. pr. Chem.* [2], **8**, 359), attempted to prepare this compound by heating metaphosphoric acid with phosphorus pentachloride. He was not able to obtain any compound agreeing with the chloride  $\text{PO}_2\text{Cl}$ , but found phosphoryl trichloride as the only product. More recently, Thorpe and Tutton (*Trans.*, 1890, **57**, 572), by the action of chlorine on phosphorous oxide,  $\text{P}_4\text{O}_6$ , obtained phosphoryl trichloride and a viscous substance having the appearance and composition of Gustavson's chloride. As the properties of this singular substance appeared to be worthy of a more extended investigation, I have, at Professor Thorpe's suggestion, undertaken to make a more detailed examination of the compound.

To begin with, I repeated Gustavson's experiment. A mixture of phosphoryl trichloride and phosphorus pentoxide, in equal molecular proportions, was heated in a sealed tube at  $200^{\circ}$ . After 20 hours

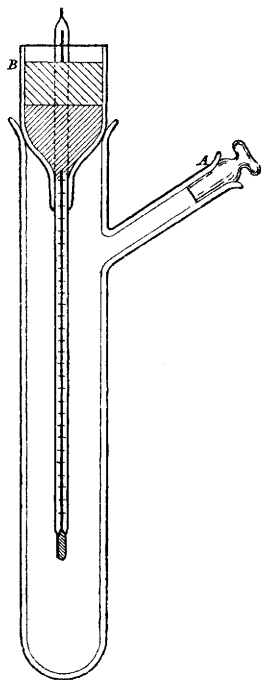
heating, the greater part of the phosphorus pentoxide was dissolved, the whole forming a light-brown, viscous mass. But some portions of the oxide remained unaltered, and even after 120 hours at 200—215°, some unattacked pentoxide remained. The composition of this mass is practically given by the proportions of the two substances put into the tube; but since, owing to its peculiar properties, solvents could only be made to act on a small surface, and since it could be neither distilled nor crystallised, it was impossible to decide whether this mass was really one substance or several. It was noticed, however, that it gave off phosphoryl trichloride at 150°, or 50° below the temperature at which it was formed. This showed that the reaction in the tube was reversible, and suggested an increase in the mass of the phosphoryl trichloride relatively to that of the oxide. Hence in later experiments the amount of the trichloride varied from 2 to 4 mols. to 1 of the pentoxide. Under these conditions, on heating at 200°, the phosphorus pentoxide slowly dissolves, the solution being complete in from 40 to 80 hours. Further heating does not appear to affect the properties of this solution. On account of its exceedingly hygroscopic properties, it is best kept in small, sealed glass bulbs.

If the product is distilled\* in a small, weighed distillation flask, pure phosphoryl trichloride (b. p. 107°) distils over. The distillation of the oxychloride after a time ceases, the thermometer rising suddenly. As the exact composition of the product introduced into the flask is known, the weight of the residue will show how many molecules of the oxychloride have combined with one of the pentoxide, and it is found that equal numbers of molecules of the two substances have combined. All the excess of oxychloride above this proportion distils over, and the residue remaining in the flask, a straw-coloured, viscous mass, has therefore the empirical composition  $P_2O_5$ ,  $POCl_3$ , or  $(PO_2Cl)_n$ . In its appearance and behaviour on distillation, this mass resembles the substance obtained by the action of chlorine on phosphorous oxide. If instead of distilling the product it is kept at 105—108°, and a slow stream of air passed over it, the same substance is obtained. As these results pointed to the formation of a compound polymeric with  $PO_2Cl$ , an attempt was now made to determine its molecular weight by some cryoscopic method. The choice of solvents is somewhat restricted.

\* In distilling this substance with a thermometer, or in passing a current of air over it, neither ordinary nor india-rubber corks can be used. A useful flask for distilling this or similar corrosive liquids is made by sealing on to the neck of an ordinary Wurtz flask about four inches of glass tubing of such a width that the thermometer or leading tube just slides in it. The thermometer is fixed in position by a small piece of india-rubber tubing.

Phosphoryl trichloride was finally chosen as the most convenient. It melts at about  $0^{\circ}$ ; since there is already an excess of oxychloride present, the product is perfectly miscible: further, this excess does not interfere with the melting point, so that the depression produced is due only to the compound present. On the other hand, phosphoryl oxychloride is a difficult substance to keep in a pure state during the time required for a determination; it rapidly absorbs moisture from the air and from corks of any kind. The arrangement used is shown in Fig. 1. A glass tube B was drawn out at one end to nearly

FIG. 1.



fit the thermometer, the latter being fixed in first with sulphur and then with a layer of paraffin on the top as shown by the shading, and the whole ground into the main tube. The thermometer was by Geissler, graduated to  $\frac{1}{5}^{\circ}$  C., and reading by estimation to  $0.01^{\circ}$  C., a sufficiently good approximation for the purpose. As the molecular depression of phosphoryl trichloride has not hitherto been determined, preliminary experiments were made with phosphorus trichloride—a substance not known to have any chemical action on the oxychloride, and which can easily be obtained in a pure state.

A quantity of pure phosphoryl trichloride was prepared by heating phosphorus pentoxide with phosphorus pentachloride in sealed tubes at  $120^{\circ}$ . After a preliminary distillation, the resulting liquid still contains dissolved hydrogen chloride; the latter may be separated either by a current of dry air at  $105^{\circ}$ , or more conveniently by prolonged boiling with a reflux condenser in an apparatus composed wholly of glass. The pure substance is distilled directly into the freezing-point apparatus; its melting point, when freed in this way from dissolved gas, is  $+0.80^{\circ}$ . The phosphorus trichloride was purified just before use in a similar manner. The results are tabulated below.

| No. of experiment. | Weight of $\text{POCl}_3$ taken. | Weight of $\text{PCl}_3$ added. | Depression produced. | 1/concentration. | Depression / concentration. |
|--------------------|----------------------------------|---------------------------------|----------------------|------------------|-----------------------------|
|                    | grams                            | grams.                          | C.                   |                  |                             |
| (I) .....          | 41.62                            | 0.90                            | $1.20^{\circ}$       | 46.2             | 55.5                        |
| (II) .....         | 41.62                            | 3.30                            | 4.20                 | 12.6             | 53.0                        |
| (III) .....        | 44.21                            | 1.37                            | 1.62                 | 32.3             | 52.3                        |
| (IV) .....         | 44.21                            | 3.30                            | 4.02                 | 13.4             | 53.9                        |

The last two observations were made on fresh preparations. The whole four lie on a straight line within the error of experiment, so that up to concentrations of 8 per cent. the depression of the freezing point is proportional to the concentration. Hence, 1 gram-molecule of phosphorus trichloride, dissolved in 100 gram-molecules of phosphoryl trichloride, produces a depression of the freezing point of  $0.48^{\circ}$ , a number differing considerably from the  $0.63^{\circ}$  of Raoult. From this we deduce the latent heat of fusion to be  $20.3$  cal., using van't Hoff's formula  $\lambda = \frac{0.02T^2}{M \cdot \delta\theta}$ . So far as I am aware, this constant has not been directly determined.

The observations on the product were—

| No. of experiment. | Weight of $\text{POCl}_3$ . | Weight of stuff added. | Depression produced. | 1/concentration. | Depression / concentration. |
|--------------------|-----------------------------|------------------------|----------------------|------------------|-----------------------------|
|                    | grams                       | grams                  | C.                   |                  |                             |
| (I) .....          | 44.52                       | 0.393                  | $0.39^{\circ}$       | 113.3            | 44.2                        |
| (II) .....         | 45.30                       | 0.826                  | 0.84                 | 54.8             | 46.1                        |

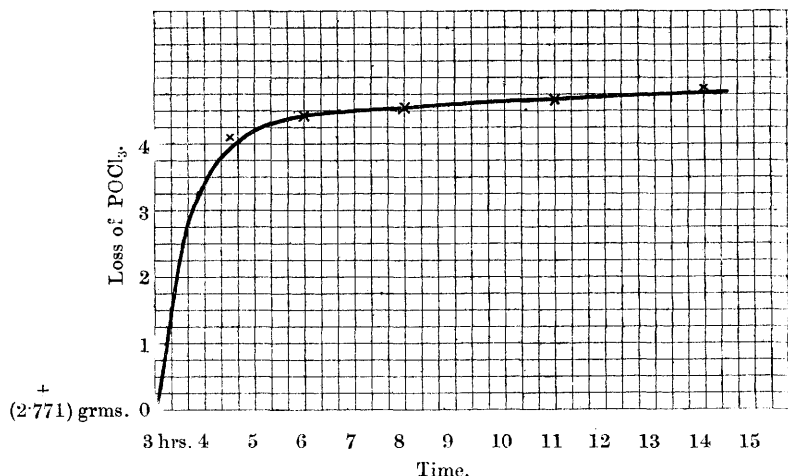
On the assumption that the oxychloride passing over on distillation is uncombined, this gives a molecular weight of 163.  $\text{PO}_2\text{Cl}$  requires

98.4;  $P_2O_4Cl_2$ , 196.8. But further investigation showed that the straw-coloured mass left on distillation is not a single substance, but contains at least two compounds. Hence, even if the further assumption be made that each of the substances present exerts its own osmotic pressure independently of the others, or, in other words, that Dalton's law of pressures holds for such a solution, the result is only the mean molecular weight of two or more compounds.

The residue obtained on distillation was now further examined. If it consists merely of a solution of phosphorus pentoxide in phosphoryl trichloride, then, on treating it with a neutral solvent, such as dry carbon bisulphide, the oxychloride will dissolve, leaving a residue free from chlorine, and the carbon bisulphide solution will contain phosphorus and chlorine in the ratio of 1 : 3.42. If it consist of a single compound, such as  $(PO_2Cl)_n$ , it will either be altogether insoluble, or will dissolve. If only slightly soluble, the ratio of phosphorus to chlorine must be the same in both residue and solution, 1 : 1.14. The viscous residue was treated with small quantities of dry carbon bisulphide, until nothing further was dissolved. The solution, on treatment with water, gives the whole of its phosphorus as orthophosphoric acid, and has the ratio of phosphorus to chlorine at 1 : 2.28, agreeing with  $P_2O_3Cl_4$ , the pyrophosphoryl chloride of Geuther and Michaelis. The residue in the flask, after the extraction of the pyrophosphoryl chloride, has the invariable ratio of phosphorus to chlorine of 1 : 0.79.

It has already been mentioned that the substance commences to dissociate at  $150^\circ$ . At low temperatures ( $105$ — $108^\circ$ ), and in a very slow stream of air, that is, with a high partial pressure, the dissociation is practically *nil*. At the same temperature, in a rapid stream of air, equivalent to a reduction of the pressure, more phosphoryl chloride is lost. The same result is obtained with the higher pressure at  $150^\circ$ . The curve shows the loss of weight with time in a slow, steady stream of dry air at  $150^\circ$ ; the curve is of the logarithmic form, usual in cases of dissociation.

If a bulb full of the solution containing excess of phosphoryl trichloride is added to pure dry carbon bisulphide, the liquid is turbid, but, on standing for some time in a well-closed flask, becomes clear, minute drops of liquid being deposited on the sides of the flask. The ratio of phosphorus to chlorine for the original substance being as 1 : 2.367, and for the clear carbon bisulphide solution as 1 : 3.18; it is evident from the previous discussion that, besides the excess of oxychloride, some other compound, containing less chlorine, has gone into solution. As before, the reaction of this solution with water agrees with the supposition that pyrophosphoryl chloride is present, since here again only orthophosphoric acid is formed. The insoluble



drops, precipitated on the sides of the flask, after being washed with fresh bisulphide, give, on analysis, practically the same ratio of phosphorus to chlorine as before, namely, as 1 : 0.82.

In another experiment, where the ratio of phosphorus to chlorine for the original substance was 1 : 2.67, the clear solution gave 1 : 3.01, and the well washed residue, which weighed 14.7 per cent. of the whole, as 1 : 0.79. A different preparation gave for the same ratio, original substance 1 : 2.14, clear solution as 1 : 2.65. Hence, on treating the contents of the tube directly with carbon bisulphide, some pyrophosphoryl chloride, together with the excess of phosphoryl trichloride, goes into solution, leaving a residue of constant composition, for which the ratio of phosphorus to chlorine is 1 : 0.81. From the value of the ratio found in the carbon bisulphide solution, the relative proportions of pyrophosphoryl and phosphoryl chlorides have been calculated. It differs in different preparations, and agrees with no simple reaction. It is quite evident from this that the reaction is a complicated one, and is not represented by the equation  $\text{P}_2\text{O}_5 + \text{POCl}_3 = 3\text{PO}_2\text{Cl}$ , given by Gustavson, and reproduced in some of the larger text-books.

Since the boiling points of pyrophosphoryl chloride and phosphoryl trichloride differ by over  $100^\circ$ , it was thought that further evidence might be obtained by fractional distillation in a vacuum. Some of the original product was, therefore, placed in a small Würtz flask with a long condensing tube, which was then rapidly exhausted by the Sprengel pump, and sealed. As each fraction came over, the end of the condenser containing the liquid was fused off, and the liquids

analysed. At  $100^{\circ}$ , the distillate was pure phosphoryl trichloride, an analysis of this fraction giving 69.5 per cent. of chlorine instead of 69.34. At  $180^{\circ}$ , an equal number of molecules of pyrophosphoryl and phosphoryl chlorides came over; this requires the ratio of phosphorus to chlorine to be as 1 : 2.67; found 1 : 2.68.

The chemical reactions of the product obtained by the action of phosphoryl trichloride upon phosphorus pentoxide are not very definite. If it be assumed that all the oxychloride above the proportion  $P_2O_5 : POCl_3$  is uncombined, and the distillation experiments lead to this conclusion, then the reaction with ice-cold water is  $2n(PO_2Cl) + 3nH_2O = nHPO_3 + nH_3PO_4 + 2nHCl$ ; half the phosphorus appearing as metaphosphoric acid and the other half as orthophosphoric acid. With absolute alcohol containing just sufficient sodium ethylate to combine with all the chlorine, the chief product is diethylphosphoric acid,  $PO(OH)(OC_2H_5)_2$ , of which the barium salt and insoluble lead salt were prepared, and the identity of which was determined by analysis.

With glacial acetic acid, the product gives a dark brown solution. On distillation, the whole of the chlorine present passes over as acetyl chloride, leaving a tarry, viscous mass in the flask.

The results arrived at may be summarised as follows:—

- (1.) There is not at present any evidence to show that a substance having the composition  $PO_2Cl$ , or any multiple of this, exists.
- (2.) The reaction of phosphoryl trichloride on phosphorus pentoxide at  $200^{\circ}$  is not represented by the equation  $P_2O_5 + POCl_3 = 3PO_2Cl$ , but is much more complex than this.
- (3.) That at least two compounds are formed in the reaction, one of which is pyrophosphoryl chloride,  $P_2O_3Cl_4$ , and the other, which may prove to be a mixture, is of constant composition, and from its analysis cannot have a simpler formula than  $P_7O_{15}Cl_5$ .
- (4.) I have shown, incidentally, that the molecular depression of the freezing point for phosphoryl trichloride,  $0.48^{\circ}$ , differs considerably from the "normal" or average value given by Raoult,  $0.63^{\circ}$ .

In conclusion, my thanks are due to Professor Thorpe, to whom I am much indebted for advice and assistance throughout this work.

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