

XCIV.—*Phosphorus Tetroxide.*

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INDEPENDENTLY of the lowest oxide of phosphorus, the existence of which as an orange-red powder is maintained by some chemists (Michaelis and Pitsch, *Annalen*, 1899, 310, 45) and disputed by others (Burgess and Chapman, *Trans.*, 1901, 79, 1235), there are three well-defined oxides of phosphorus, all of which are easily obtainable in colourless crystals. Of these, the best known is phosphoric oxide, the molecular weight of which was determined by the vapour density method by Tilden and Barnett (*Trans.*, 1896, 69, 154). The other two have been studied by Thorpe and Tutton and obtained by them for the first time in a state of purity. Phosphorous oxide is easily volatile, and its vapour density is such as to establish conclusively the formula P_4O_6 (*Trans.*, 1890, 57, 545; 1891, 59, 1019). There remains an intermediate oxide having the empirical formula PO_2 or P_2O_4 , which was isolated by Thorpe and Tutton and described by

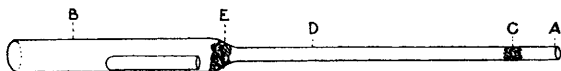
them as a tetroxide (Trans., 1886, 49, 833). The use of this name was based on the supposed correspondence between this compound and the tetroxides of nitrogen and antimony, but inasmuch as the constitution and molecular weight of the latter are unknown, the phosphorus compound is more safely designated phosphorosulphuric oxide, as already indicated by Thorpe and Tutton. The discoverers having stated (*loc. cit.*) that, although the substance is volatile in a vacuum, they had not been able to obtain it in sufficient quantity to determine its vapour density, and there being no probability that they would take up the subject again, it was suggested by Prof. Tilden that I should prepare some of the oxide and determine its vapour density with the aid of the apparatus used by himself and Mr. Barnett. In entering on the inquiry, no difficulties were apprehended apart from those involved in the manipulation of a highly deliquescent substance, and it was expected that the volatility of this oxide would be intermediate between that of the phosphorous and phosphoric oxides respectively.

A supply of phosphorous oxide was prepared by the method devised by Thorpe and Tutton. The only modification found desirable in the apparatus was an alteration in the form of the tube in which the phosphorus was burned, the open end being turned up very slightly so that a rod could be inserted horizontally to clear a way from end to end when necessary. About 130 grams of the pure oxide were made, and collected in tubes each holding about 10 grams.

Phosphorosulphuric Oxide. Preparation and Analysis.

A tube containing about 10 grams of the trioxide was introduced into a thick-walled tube of soft glass of about 13 mm. bore. This tube was previously sealed off at one end and filled with dry carbon dioxide by means of a narrow glass tube passing to the bottom. The stream of gas was kept up for a short time after the trioxide was introduced, the gas tube then withdrawn, and the outer tube corked. The tube was then drawn out to a fine capillary, sealed off, and heated in an inclined position at a temperature of 200—250° for 2 or 3 days. On opening it after cooling, a small quantity of gas escaped, which was evidently phosphoretted hydrogen, and was probably due to the presence of a trace of moisture. The tube contained a solid of a brilliant carmine colour. The end containing the substance was cut off and immediately placed inside a tube, of the shape shown in the figure, full of carbon dioxide. A stream of dry carbon dioxide was passed through from the end *A*, and the tube sealed off at *B*. A plug of glass wool was placed at *E* and another at *C* to prevent loose particles being drawn along the tube into the pump. The carbon dioxide

used was dried by sulphuric acid and phosphoric oxide. The end was then connected to a Sprengel pump by thick-walled tubing and exhausted as completely as possible. The bulb, *B E*, was placed in an iron trough lined with asbestos and covered by an asbestos lid, and then gradually heated by means of burners placed below. Phosphorus distilled away and was condensed at about *D*, but this was driven further along by



means of a Bunsen flame. On further heating, small crystals began to grow, and ultimately a considerable quantity was found between the bulb and *D*. These crystals were colourless, highly lustrous, transparent, and, at first sight, apparently cubical in shape. The distillation was continued until only a small quantity of a reddish-brown (nearly black) substance remained in the bulb. The tube was now allowed to cool, filled with dry carbon dioxide, and the portions containing the crystals and the phosphorus separately sealed off. The crystals of what was presumably the tetroxide were, in some places, stained yellow and were evidently not quite pure. These were redistilled once or twice in another tube until free from coloured particles. Before disconnecting the tube from the pump, the crystals were caused to sublime along the tube and separated into small portions of from 0.5 gram to 2 grams each. Carbon dioxide was then admitted and the small portions sealed off separately. On several occasions, when the oxide had been exposed to the air before redistillation, it was found, after the carbon dioxide had been pumped from the tube and the tube was heated, that a gas was given off which passed through the pump and gave rise to slight explosions as the bubbles escaped into the air. This was probably phosphine, due to the presence of moisture. It was also noticed that in redistilling the tetroxide a stain in the form of a brown or red ring was left on the small tubes at the level to which the tetroxide had reached. The longer the exposure to air or moisture, the greater was the amount of this substance formed. Attempts were made to prevent the formation of the red substance by breaking open the specimen tube inside a rubber tube attached to the end *B* while a stream of dry carbon dioxide was passed through, and in this way the amount was reduced to a very slight stain.

Analysis.—A number of samples were analysed, the results agreeing with those obtained by Thorpe and Tutton, and showing that the empirical formula of the compound is PO_2 . The oxide dissolved slowly in water with a hissing sound and evolution of a faint odour like that of phosphine. The solution was oxidised by nitric acid or bromine water and the phosphorus estimated as magnesium pyro-

phosphate. Using 0.2—0.9 gram for each analysis, the following percentages of phosphorus were obtained: 49.4, 49.1, 49.6, 48.9, and 49.4. The percentage of phosphorus corresponding to the formula PO_2 is 49.2.

Reactions in Aqueous Solution.—1. Silver nitrate solution gave a white precipitate, quickly changing to brown and then black.

2. Barium chloride or barium hydroxide gave a white precipitate, soluble in hydrochloric acid, but not readily soluble in acetic acid.

3. Calcium chloride gave no precipitate at first, but a flocculent, white precipitate on adding ammonia.

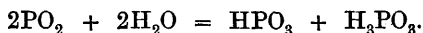
4. Potassium permanganate was slowly decolorised, hot or cold.

5. Mercuric chloride gave a white precipitate, which formed slowly, hot or cold.

6. Lead nitrate gave a white precipitate, insoluble in acetic acid

7. Magnesia mixture gave a white precipitate, which, however, was not crystalline like that given by orthophosphates, and filtered only with difficulty. It probably consisted of magnesium metaphosphate, for, contrary to the statements in many books, metaphosphates give a precipitate with magnesia mixture.

The reactions numbered 1, 4, and 5 agree with the observations of Thorpe and Tutton, except that the precipitate with silver nitrate is described by them as yellow. From these reactions, it appears probable that the phosphorous phosphoric oxide, on solution in water, gives rise to phosphorous and metaphosphoric acids according to the equation,



Attempts to estimate the phosphorous and metaphosphoric acids quantitatively did not, however, yield concordant results. This was probably due to the unsatisfactory methods of estimating these two acids in presence of each other.

An aqueous solution of the oxide neutralised by sodium hydroxide and allowed to evaporate in the air gave a thick syrup with small, perfectly-formed, octahedral crystals, which, when examined under the microscope, were found to be similar to those obtained by neutralising phosphorous acid with soda and evaporating in the same way. The crystals from either solution gave no polarisation colours when examined in polarised light.

Action of Solvents.—Endeavours to find a suitable solvent with the view of determining the molecular weight were unsuccessful. Benzene, naphthalene, phenol, nitrobenzene, chloroform, carbon disulphide, and ether seemed to be entirely without action on the oxide, whilst acetone was turned slightly brown and acetic acid became deep brown. This action seems to resemble that of the commercial pentoxide on acetic acid.

Action of Light and Heat.—A sample of the crystals exposed for twelve months to daylight was unchanged.

Heat seems to cause no chemical change, as the substance sublimes without melting and without decomposition.

Density.—The density of the crystals was determined by means of a mixture of methylene iodide and benzene which seemed to be without action on them. The mean of several determinations gave the density at $22.6^{\circ}/4^{\circ}$ as 2.537. The densities obtained by Thorpe and Tutton for phosphorous oxide were, liquid, $d\ 28.8^{\circ}/4^{\circ}=1.935$, and solid $d\ 21^{\circ}/4^{\circ}=2.135$. The density of phosphoric oxide is given as 2.387.

Vapour Density of Phosphorosulphuric Oxide.

The vapour density was determined by Victor Meyer's method in the platinum apparatus described by Tilden and Barnett (*loc. cit.*).

The samples were prepared for the determinations in the following way. A tin case was made somewhat similar to the wooden case described by Tutton (Trans., 1897, 71, 865), but without wood and without drawer. The windows were of celluloid and clamped in by rubber bands between brass frames. The gloves were also clamped in between brass rings. At the bottom of the box was a glass tray containing phosphoric oxide, and above this was a table of perforated zinc on which were placed the materials and apparatus.

Small vapour density tubes were prepared and fitted with rubber stoppers. These were weighed with and without the stoppers. Other tubes in which these could be placed were sealed off and placed with them on the zinc table in the case. A file, pliers, a piece of wire, and a tube containing the oxide were also placed inside the case, which was then closed air-tight by tightening the clamps. It was left closed for several days so that the contents should be thoroughly dried. The hands were then inserted in the rubber gloves, the tube containing the oxide scratched with a file and opened, and each vapour density tube half filled with the oxide, stoppered with its own stopper, and placed in a larger tube which was also stoppered. The box was then opened and each outer tube sealed off about an inch from the end of the small tube. Each of the outer tubes was then scratched with a file and weighed. When a determination was to be made, the outer tube was broken into two and the pieces kept for subsequent weighing. The weight of the oxide used in any determination was thus found.

The stopper was taken out of the vapour density tube, which was at once placed in position in the vapour density apparatus and the experiment carried out. In this way, the substance in the tube was not exposed to the air for longer than a couple of seconds.

Attempts were made to determine the vapour density at a temperature of about 900° , but at this temperature 0.2 gram of the substance gave only a bubble or two of gas. A contraction of about two or three cubic centimetres then took place. The same result was obtained whether the platinum bottle was filled with nitrogen or with carbon dioxide. A higher temperature was then employed. A special fire-clay jacket was obtained, the gas supply increased, and air forced through by means of a Root's blower driven by a gas engine. A white heat was quickly obtained, and it was found possible to keep the temperature very constant. The temperature actually obtained was above 1400° as indicated by the fusion of a sample of test steel of melting point 1400° . At this temperature, the oxide volatilised immediately, gas was given off readily, and the experiment completed sharply in the ordinary way. The following results were obtained:

Weight of oxide taken.	Uncorrected volume of gas.	Vapour density.
0.2167	11.3 c.c.	231.1
0.1819	9.5	230.7
0.2073	11.4	217.6
0.1551	8.1	237.8

The mean density of the vapour was therefore 229.3, and the molecular weight calculated therefrom 458.6.

As a check on these results, two estimations of the vapour density of mercury were made in the apparatus at the same temperature in the same manner. One experiment gave 102.3 and the other 103.1 instead of 100. It is obvious therefore that the apparatus is capable of giving normal results.

It is, however, difficult to accept the conclusion to which these experiments lead, namely, that the formula of the oxide does not fall into line with the formula of phosphorous oxide, P_4O_6 , and that of phosphoric oxide, P_4O_{10} , but belongs to a more complex type, P_4O_6 , P_4O_{10} , or P_8O_{16} . Nevertheless, it is quite certain that the molecular weight is not intermediate between the molecular weights of phosphorous and phosphoric oxides.

Vapour Density of Phosphoric Oxide.

As the apparatus was available, it seemed worth while to determine the vapour density of phosphoric oxide at a higher temperature than that employed by Tilden and Barnett (*loc. cit.*). The pure oxide was sealed up in tubes as described, and the manipulation was exactly the same as with the phosphorosulphuric oxide. The following are the results obtained:

THE ABSORPTION SPECTRA OF PHLOROGLUCINOL. 929

Weight of oxide taken.	Uncorrected volume of gas.	Vapour density.
0·1374	11·1 c.c.	149·4
0·0744	5·75	153·7
0·1491	12·5	148·9
0·1118	9·2	147·9
0·1309	10·6	150·3
0·0758	6·1	151·3

The mean density of the vapour was therefore 150·2, and the molecular weight calculated therefrom 300·4. This approaches more nearly to the theoretical number 284 than the results obtained in the original experiments at the lower temperature corresponding to a red heat.

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