CCXLI.—*The Slow Oxidation of Phosphorus. Part II. The Oxidation Products of Phosphorus and Phosphorous Oxide.*

By Christina Cruickshank Miller.

In 1796, Pelletier obtained by the slow combustion of phosphorus in air in presence of water an acid liquid which became known as Pelletier's phosphatic acid. According to Thenard its composition was such that the atomic ratio of combined oxygen to phosphorus was 2·2. Dulong found that the ratio was constant at 2·1, and that the acid liquid was comparatively stable in air (Gmelin, "Handbook of Chemistry," 1849, **2**, 121). Later, Salzer (*Annalen*, 1878, **194**, 28) showed that the liquid contained hypophosphoric, phosphorous, and phosphoric acids, 6—7% of the phosphorus being converted into hypophosphoric acid. It is evident, then, that in moist air at the ordinary temperature phosphorus is not converted entirely into hydrates of phosphoric oxide for which the ratio combined O : P = 2·5.

Turning to the slow oxidation of phosphorus in dry oxygen at moderate pressures, we find that little has been done to determine the nature of the oxides formed. It is generally assumed that the ultimate product of oxidation is the pentoxide, although no analytical data are given in the literature as a basis for this assumption.

Russell (J., 1903, **83**, 1263), in a study of the oxidation of phosphorus in moderately dry oxygen at 14°, found that above 500 mm. pressure, oxidation was slow and accompanied by a very feeble glow. He thought it probable that lower oxides, P_4O_2 and P_4O_4, were formed, for when the oxidation product was heated in a vacuum, phosphorus tetroxide and amorphous phosphorus were obtained. When the pressure of oxygen was reduced to less than 500 mm., oxidation was brisker and accompanied by a very bright glow. Russell's opinion was that the oxide formed in the first stage was oxidised further to the pentoxide, but no proof of this is mentioned.

Jungfleisch (*Compt. rend.*, 1907, **145**, 325) found that the immediate products of the direct and spontaneous oxidation of phosphorus in oxygen at low pressure were different from those formed at higher pressure. At 18—20 mm. pressure, phosphorus trioxide and a bright yellow compound, supposed to be P_4O, were produced. If the oxidation was carried out in presence of water, the aqueous solution contained the products of the action of water on the oxides formed in the dry gas : 58% of the total phosphorus was converted into phosphorous acid. Jungfleisch stated, however, that in pure oxygen at atmospheric pressure in the cold, phosphoric oxide was the sole product. No analytical results were given.

By the oxidation of phosphorus in oxygen at very low pressure (0·1—0·5 mm.), Kohlschütter and Frumkin (*Ber.*, 1914, **47**, 1088) obtained a red product in which the atomic ratio of oxygen to phosphorus varied from 0·1 to 0·7. On thermal decomposition it gave some crystals of phosphorus tetroxide.

The foregoing papers would lead us to suppose that phosphorus oxidises spontaneously to phosphoric oxide at moderate pressures of oxygen (say, 100—800 mm.), but to lower oxides at high or at very low pressures. Yet with phosphorus in presence of water and air (partial pressure of oxygen 160 mm.), the aqueous solution obtained contains a considerable amount of acids not derived from the pentoxide. Now, if Jungfleisch is correct in stating that phosphorus, water, and oxygen at low pressure give the same solution of acids as is obtained by hydrating the products of the corresponding dry oxidation, it is difficult to see why this relationship should cease at higher oxygen pressure. It seems reasonable to suppose that Pelletier's phosphatic acid corresponds in the oxidation of phosphorus in dry oxygen to the formation of oxides containing at least one constituent lower than phosphorus pentoxide.

Now, I have already shown (*Proc. Roy. Soc. Edin.*, 1926, **46**, 239) that phosphorus tetroxide is formed under certain conditions in the slow oxidation of phosphorus trioxide containing dissolved phosphorus, and, further (preceding paper), that both phosphorus and its trioxide take part in the reaction, oxidation of the latter being effected by ozone liberated during the oxidation of the former. [Phosphorus-free trioxide does not oxidise at all in air or oxygen at the ordinary temperature (Miller, J., 1928, 1847).] It follows that phosphorus tetroxide is a product of oxidation of either phosphorus or phosphorus trioxide, or of both. If Thenard's and Dulong's figures be correct, phosphorus tetroxide cannot, however, under the conditions of their experiments, be the sole final product of the slow oxidation of phosphorus, for their atomic ratio O : P is too large.

On account of the uncertainty of the composition of the final product of the slow oxidation of phosphorus, I have made qualitative and quantitative analyses of the oxides. In addition, I have further examined the oxidation product of phosphorus dissolved in phosphorus trioxide, and have studied the oxidation of pure phosphorus trioxide in ozonised oxygen.

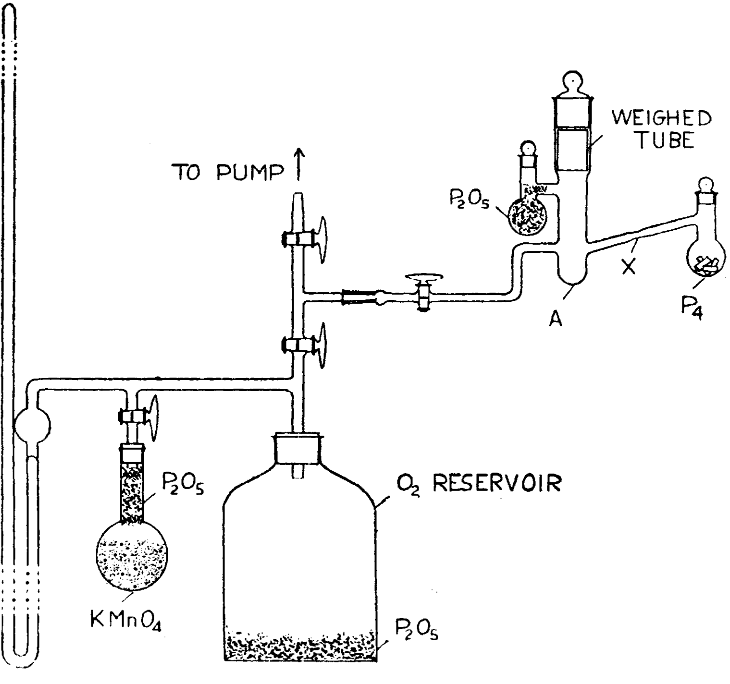
EXPERIMENTAL.

The Oxidation of Phosphorus in Air in Presence of Water.— Pelletier's phosphatic acid was prepared in order to redetermine the atomic ratio of combined oxygen to phosphorus. To a weighing bottle, in which was placed a slice of phosphorus $\frac{1}{4}''$ thick, water was added to a depth of less than $\frac{1}{4}''$. The stopper of the bottle was very loosely inserted, and the whole was set aside at room temperature for at least a day. The phosphorus glowed brightly and ozone was distinctly smelt. The piece of phosphorus was then removed, and the acid solution filtered and analysed. As it contained hypophosphoric, phosphorous and phosphoric acids, the reducing power was found by oxidation with sodium hypobromite, and then the total phosphorus was determined as magnesium pyrophosphate. Hydrogen peroxide was most probably present in the solution, being formed during the oxidation of moist phosphorus, but the amount was negligible (see Leeds, *Chem. News*, 1879, **40**, 70; 1881, **43**, 97). The method of oxidation previously used (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 239) was modified as follows so as to yield more accurate results. To a solution containing less than 0·05 g. of phosphorous acid were added 2 c.c. each of *N*-potassium bromate, 4*N*-potassium bromide, and 2*N*-hydrochloric acid solutions. The more concentrated bromide solution effectively retained the liberated bromine, to the loss of which the principal experimental error was previously attributed. After 5 minutes, 10 c.c. of 0·8*N*-sodium hydroxide solution were added, dilution of the solution being necessary at this stage to ensure complete oxidation. After a further 10 minutes, excess of potassium iodide was added, followed by 6 c.c. of 2*N*-hydrochloric acid, and the liberated iodine was titrated with a dilute standard solution of sodium thiosulphate. The following results were obtained with phosphorous acid and phosphorus-free phosphorus trioxide: Weight of acid taken, 0·0041, 0·0107, 0·0246 g.; weight found by analysis, 0·0041, 0·0106, 0·0245 g. Weight of trioxide taken, 0·0611 g.; weight found by analysis, 0·0611 g. The error in the earlier method was ± 0·3 mg. on the weight of phosphorous acid.

Pelletier's phosphatic acid was found not to be completely oxidised by sodium hypobromite, presumably owing to the presence of hypophosphoric acid. The acid solution was therefore first hydrolysed by evaporation on the steam-bath with a few c.c. of dilute hydrochloric acid, a procedure shown by Salzer (*Annalen*, 1877, **187**, 322) to convert hypophosphoric acid into a mixture of phosphorous and phosphoric acids; oxidation was then effected normally. In two experiments of 2 and 5 days' duration, respectively, the ratio of combined oxygen to phosphorus was 2·195 and 2·18, in agreement with Thenard's result.

The Oxidation Products of Phosphorus in Dry Oxygen.—As a preliminary test, a piece of phosphorus was allowed to oxidise at 15° in oxygen at 400 mm. pressure, so that a small quantity of oxides could be collected in a suitable condition for sublimation in a vacuum. The oxidation product was sublimed at 300°, leaving a slight red residue; in the sublimate the characteristic birefringent crystals of phosphorus tetroxide were visible, but no pentoxide. Experiments on the oxidation of phosphorus were then undertaken in order to determine the quantitative composition of the oxidation product. The method of procedure was to collect in a weighable form the oxides falling from a glowing phosphorus surface, and then to find the atomic ratio of combined oxygen to phosphorus by analysing the aqueous solution obtained from the oxides. Since phosphorus tetroxide would give a mixture of phosphorous and phosphoric acids, the solution was first of all oxidised with sodium hypobromite (the original method referred to on p. 1832 was actually used) and the total phosphorus was determined as magnesium pyrophosphate. Hydrolysis with hydrochloric acid was found to be necessary before oxidation with hypobromite, the increase in reducing power, after hydrolysis, being about 12%.

FIG. 1.



Oxidation of phosphorus in pure dry oxygen at practically constant pressure was carried out at about 11°, the apparatus shown in Fig. 1 being used. Oxygen, generated by heating potassium permanganate, was stored over phosphoric oxide in the large (1500 c.c.) bottle, which was connected to a manometer. The actual oxidation of phosphorus was performed in the tube *A* in which was a small weighed tube for the collection of oxides. To the apparatus were sealed a bulb containing phosphoric oxide and a small distilling flask containing phosphorus, which had been dried in a vacuum over phosphoric oxide. The apparatus was set up as shown, and, after evacuation of tube *A*, left to dry. Phosphorus was then distilled into the lower section of *A* and the distilling flask was removed by sealing off at *X*. The lower part of *A* was cooled in a freezing mixture, and oxygen from the reservoir was added *quickly* (to prevent ignition) to any desired pressure above 500 mm. When oxidation was to be effected below 500 mm. pressure, oxygen was slowly withdrawn until, after a few minutes, the required pressure was reached. This procedure was necessary to prevent ignition. Frequently, when oxygen was quickly added up to 900—1200 mm. pressure, oxidation did not take place; it could, however, be initiated by decreasing the pressure until glowing occurred, and then slowly raising it to the original value. This effect was not produced if tube *A* was dried in a vacuum for a short time only, but prolonged drying of the apparatus apparently prevented oxidation in oxygen at high pressure.

In order to collect the oxides, tube *A* was rotated through an angle of 180° about the ground joint and immersed in water at 11°. From the continuously glowing phosphorus, oxides fell into the weighed tube and, after 2—3 hours, the experiment was terminated. The fact that the glow of the phosphorus was not suppressed showed the absence of an appreciable amount of trioxide, which is an inhibitor of the glow. Tube *A* was cooled to 0° and the oxygen replaced by dry air. The tube with oxides was dropped into a weighing bottle which was immediately weighed, and the oxides, after deliquescence, were analysed in the weighing bottle in the manner indicated.

As expected, there was no evidence of volatile phosphorus trioxide in the dry oxides, which were white with a slight yellow tinge (due probably to a trace of amorphous phosphorus) and were apparently unchanged at temperatures up to 100°. It was noted that the yellow tinge was slightly more pronounced at low oxygen pressures than at high. The aqueous solution contained a very small quantity of a yellow colloidal substance which was not taken into account in the analysis, since its isolation was impracticable and its effect thought to be negligible. As the film of oxides on the oxidising phosphorus had a somewhat yellower tinge than the oxides in the collecting tube, no attempt was made to increase the weight of oxides for analysis by removing from the phosphorus its surface coating of oxides. Prolongation of an experiment did not markedly increase the yield of oxides, presumably owing to the film of oxides on the phosphorus surface which retarded oxidation. If oxidation in tube *A* was effected with air, and an oxygen leak from the reservoir was instituted to make good the loss of oxygen, the falling oxides were yellower than in oxygen. The atomic ratios of combined oxygen to phosphorus found for various experiments are given in the table below:

Expt. No.	Period of drying, hrs.	Oxygen press., mm.	Wt. of oxides, g. × 10^{-4}.	Atomic ratio, O : P.
1	$\frac{1}{4}$	1240	152	2·13
2	3	950	117	2·17
3	20	910	165	2·14
4	3	820	136	2·15
5	20	580	104	2·14
6	20	300	129	2·16
7	44	100	65	2·19
8	70	1210	148	2·16
9	400	480	132	2·17
10	20	(Air)	147	2·09

Despite the considerable range of pressure, the ratios for oxidation in oxygen are fairly constant, the deviation from the mean, 2·16, not exceeding the experimental error. The low value for air, *viz.*, 2·09, was believed to be due to the greater proportion of the yellow substance. The ratio O : P, which resembled that found for the oxidation product in moist air, clearly indicated that neither phosphorus tetroxide nor phosphorus pentoxide was the sole final oxidation product of phosphorus, but pointed rather to the presence of both. The necessity for hydrolysing the acid solution before oxidation also showed the presence of a reducing acid (probably hypophosphoric acid) not derived from phosphorus tetroxide; the latter gives a mixture of phosphorous and phosphoric acids only (Thorpe and Tutton, J., 1886, **49**, 833). As the proportion of this acid was small, however, it was concluded that the principal constituents of the oxidation product of phosphorus in pure dry oxygen at pressures between 100 and 1200 mm. were the tetroxide and pentoxide in almost constant proportion. For the first seven experiments, the weight of oxides obtained was greater than that found by analysis; this was attributed to the absorption of moisture, the amount being roughly sufficient to convert the calculated quantity of phosphorus pentoxide into metaphosphoric acid (the tetroxide is not so hygroscopic). When the apparatus was very thoroughly dried, as in Expts. 8 and 9, the two weights were the same.

In order, if possible, to confirm the foregoing result, the oxides were collected in a narrow tube by suitably modifying tube *A* in Fig. 1. The narrow tube was evacuated, sealed, and heated to 300°. As expected, the oxides sublimed, leaving a small red residue which eventually blackened. The white sublimate consisted of highly birefringent crystals of phosphorus tetroxide and, if the oxidation apparatus had been initially dried as in Expts. 8 and 9, of the pentoxide as well. The result was the same whether the phosphorus had been oxidised in oxygen at 400 mm. or 1000 mm. pressure. Oxides shaken from the surface of the phosphorus gave the same result.

The Stability of Phosphorus Tetroxide in Oxygen.—As phosphorus tetroxide was evidently a final product of the slow oxidation of phosphorus, it was important at this point to study the stability of the oxide in dry oxygen. This oxide in as dry a state as possible was prepared by the oxidation in oxygen of the trioxide containing phosphorus, in presence of concentrated sulphuric acid. The falling oxides were collected in a long narrow tube sealed to the oxidation apparatus referred to below, the narrow tube being constricted at the middle so that the oxides were retained in the upper half. When sufficient had collected, the phosphorus trioxide and sulphuric acid were removed and the oxidation product was sublimed in a vacuum into the second half of the narrow tube, the usual small red residue remaining behind. Oxygen was added to 160 mm. pressure, and the part of the narrow tube containing the oxide was sealed off. The tube was carefully examined under the microscope, and only the characteristic phosphorus tetroxide crystals were detected—under the conditions of the experiment phosphorus pentoxide was not expected to be seen. It was next heated in a small furnace, and cooled down at intervals for examination of the deposited crystals. Only after heating at 350° was a change noted, phosphorus pentoxide crystals being found admixed with those of the tetroxide. After heating at 410°, however, the deposit was almost entirely phosphorus pentoxide. Hence the tetroxide is oxidised in oxygen at a temperature of 350—410°.

Ozonised oxygen, containing 1% of ozone, had no effect on crystals of phosphorus tetroxide at 25°.

The Oxidation Product of Phosphorus dissolved in Phosphorus Trioxide.—Three years ago, I concluded (*Proc. Roy. Soc. Edin.*, 1926, **46**, 239) that, when phosphorus trioxide containing phosphorus was oxidised in presence of concentrated sulphuric acid, in oxygen at 600 mm. pressure and at 25°, the tetroxide was the only product. It has just been shown that phosphorus alone yields the pentoxide as well as the tetroxide, hence the above conclusion may be wrong, or else phosphorus dissolved in phosphorus trioxide does not give the same oxidation product as the element itself. Further experiments on the oxidation of phosphorus trioxide containing dissolved phosphorus were accordingly undertaken in order to find if phosphorus tetroxide was indeed the sole final oxidation product. Phosphorus trioxide was prepared according to Thorpe and Tutton's method (J., 1890, **57**, 545) and distilled before use. Oxidation in oxygen at various pressures was effected at 25° in the apparatus previously described (Miller, *loc. cit.*, p. 240) but, as source of water vapour, pyrophosphoric acid replaced sulphuric acid, which reacts with phosphorus trioxide and might have caused complications.

With pyrophosphoric acid it was more difficult to procure sufficient of the oxidation product for analysis, for, if an experiment was unduly prolonged, moisture acted on the oxides. In a preliminary experiment, the pure white oxidation product obtained under the altered conditions was found to give crystals of phosphorus tetroxide when heated in a vacuum.

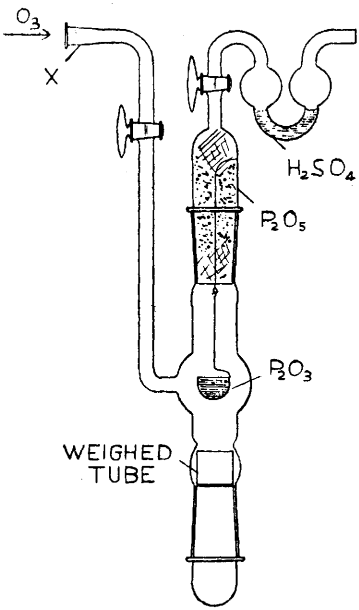
Analysis of the oxides was effected as before. In a representative set of experiments performed at pressures of oxygen between 600 and 1150 mm., the following values of the atomic ratio of combined oxygen to phosphorus were obtained: 2·00, 2·05, 1·89, 2·06, 1·91. The deviation from the ratio 2·00, required for phosphorus tetroxide, in each of the last four experiments exceeded the experimental error, so that the ratios 2·05 and 2·06 indicated the formation of an oxide containing more than two atoms of oxygen to one of phosphorus. The weight of oxides found by analysis was lower than that actually obtained, showing that moisture had been absorbed. The results as a whole could be accounted for by supposing that the oxidation product contained phosphorus tetroxide and pentoxide (+ water), with phosphorous acid (phosphorus trioxide + water) as impurity. In order to settle the question of the real composition of the uncontaminated oxidation product, three more experiments were made in which the utmost care was taken to exclude superfluous moisture. Thus, the weighed tube in the oxidation apparatus was reduced in size so as to decrease the surface on which phosphorus trioxide might give a film of phosphorous acid, and the apparatus was dried over-night at 100° before use. Pyrophosphoric acid was again the source of water vapour, and dry oxygen, the pressure of which was varied from 400 to 1000 mm., was passed into the apparatus as before. The experiments, each of 3 hours' duration, were performed at 25°. The yields of oxides were very small (2—4 mg.), but they were probably uncontaminated with phosphorous acid. The atomic ratio O : P had the values 2·14, 2·23, and 2·20; average, 2·19. This indicates that the oxides obtained from phosphorus dissolved in phosphorus trioxide are not essentially different from those obtained from phosphorus alone.

If the temperature of experiment was raised, or the pressure of oxygen lowered, the value of the ratio decreased, as was to be expected, since phosphorous acid will be more readily formed at higher temperatures and lower pressures. A final experiment was performed at a temperature at which the trioxide ignited (90°). The oxide analysed was the white product that fell freely from the burning trioxide, and did not include the red substance formed, presumably by thermal decomposition, on the basin containing the trioxide. Analysis showed that the oxidation product, for which the ratio O : P was 2·44, consisted almost entirely of phosphorus pentoxide, the slight reducing power being due to the small amount of lower oxides formed during the short pre-ignition period.

The Origin of the Oxidation Products of Phosphorus Trioxide containing Dissolved Phosphorus.

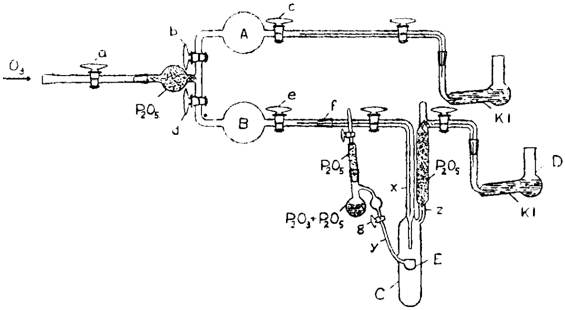
It has now been found that the oxidation products of phosphorus in presence and absence of water, and of phosphorus dissolved in phosphorus trioxide, contain phosphorus and oxygen in much the same atomic ratio. As already pointed out (p. 1831), oxidation in the last case is due to phosphorus and phosphorus trioxide, ozone produced by the oxidation of the element in moist oxygen reacting with the trioxide. The following investigations were carried out in order to determine the nature and extent of this secondary reaction: (*a*) The oxidation product of phosphorus trioxide in ozonised oxygen was analysed quantitatively and qualitatively; (*b*) the amount of ozone required for the oxidation of phosphorus trioxide was found; (*c*) the total amount of oxygen absorbed by phosphorus in presence of phosphorus trioxide was determined.

FIG. 2.



(a) *Oxidation of Phosphorus Trioxide by Ozonised Oxygen.*—Phosphorus-free trioxide was oxidised at 25° by ozonised oxygen (containing about 1% of ozone) in the all-glass apparatus shown in Fig. 2. The apparatus was attached at *X* to a drying tube with phosphoric oxide, which at its other end was connected to a Siemens ozoniser. The latter communicated with the oxygen reservoir shown in Fig. 1. The upper part of the apparatus was charged with phosphoric oxide, and a small weighed tube was inserted for the collection of oxides. The apparatus was left evacuated for at least a day, dry oxygen was then passed in to atmospheric pressure, and the small basin containing phosphorus trioxide was quickly inserted. Ozonised oxygen was passed through the apparatus at atmospheric pressure at the rate of 3 c.c./min., the oxides falling into the weighed tube. After 1—1½ hours, the passage of ozone was discontinued, the basin of phosphorus trioxide removed, and the apparatus thoroughly evacuated at 30—40° to remove the trioxide as vapour. Dry air was passed into the tube, and the pure white oxides were removed, weighed, and analysed as before. The aqueous solution of the oxides contained no yellow substance (compare p. 1834), nor was hydrolysis with hydrochloric acid necessary before oxidation with sodium hypobromite (compare p. 1832). In two experiments, with a yield of oxides of 0·0134 and 0·0362 g., the atomic ratio of combined oxygen to phosphorus was 2·18 and 2·21, practically the same value as was found for slowly-oxidising phosphorus. The oxides were next collected in a suitable manner for sublimation in a vacuum. They sublimed in the customary fashion, giving the clear, cube-shaped, birefringent crystals of phosphorus tetroxide, and, when special precautions had been taken to exclude moisture during oxidation, crystals of phosphorus pentoxide as well. Consequently, when phosphorus trioxide is oxidised in ozonised oxygen, phosphorus tetroxide and pentoxide are formed, and the atomic ratio of oxygen to phosphorus in the oxidation product as a whole is practically the same as that found for oxides derived from slowly-oxidising phosphorus.

FIG. 3.



(b) *Determination of the Amount of Ozone taking Part in the Oxidation of Phosphorus-free Phosphorus Trioxide.*—In the method ultimately adopted, two bulbs of equal capacity were charged with ozonised oxygen of the same composition, at the same high pressure. The pressure in each bulb was then slowly reduced to atmospheric, the gas from one bulb passing through a potassium iodide solution for estimation of the amount of ozone present, and that from the other passing over the phosphorus trioxide, of which the oxidation products were analysed for reducing power and phosphorus content.

The apparatus shown in Fig. 3 was connected with a Siemens ozoniser which communicated with the oxygen reservoir shown in

Fig. 1. The volumes of the bulbs *A* and *B* between the taps were identical (56 c.c.). The tube *C*, in which phosphorus trioxide was oxidised, was made from glass tubing 2 cm. wide, and was 10 cm. long. A small distilling flask for phosphorus trioxide was sealed to *C* so that the freshly distilled, dry trioxide could be run into the cup *E* without introducing moisture. Ozonised oxygen could be introduced just above the surface of the trioxide in the cup by means of the entry tube shown. To the apparatus were attached two tubes containing potassium iodide solution for absorbing ozone. The volume of the apparatus between tap *c* and the point where the ozone reached the absorbing liquid was the same as that between tap *e* and the point, near the trioxide, where ozone entered tube *C*.

The whole of the apparatus, except the two absorption bulbs, was fitted together as shown. The phosphorus trioxide in the distilling flask was mixed with a little phosphoric oxide and the flask was evacuated. Into the rest of the apparatus ozonised oxygen was passed and left over-night so as to eliminate traces of substances that might react with ozone. Afterwards the apparatus was left evacuated for 1—3 days, and dry oxygen was next passed into it to atmospheric pressure. The part to the left of taps *c* and *e* was once more evacuated, and tap *a* closed. From the reservoir, oxygen at a pressure of 1300 mm. was slowly passed into the Siemens ozoniser, and when the pressure here was a maximum the reservoir was shut off and tap *a* opened, so that bulbs *A* and *B* were charged with the same ozonised oxygen to the same pressure. The process was repeated until the pressure of gas in the bulbs was about 1300 mm. Taps *a*, *b*, and *d* were closed. Phosphorus trioxide was distilled into the small bulb above tap *g* and then by means of dry oxygen, at a pressure above atmospheric, forced down into the cup until that was full. The two absorption bulbs were attached and charged with a neutral, 2% solution of potassium iodide. The tube *C* was immersed in water at 25° and ozonised oxygen was slowly passed at the same rate from each of the bulbs *A* and *B*, so that all the entering ozone was used up and the cloud of oxides formed never reached as far as the capillary, *z*, leading to the drying tube. This capillary served to retain the small quantity of oxides borne by the gas stream. Bulbs *A* and *B* were recharged with ozone as often as desired. After 2—4 hours taps *c* and *e* were closed and the apparatus to the left of these was evacuated. Dry oxygen was passed in, and the ozone remaining to the right of the taps was then forced out. The absorption tubes were removed, dilute sulphuric acid was added to both solutions, and the liberated iodine was titrated with a dilute standard solution of sodium thiosulphate. The solution from tube *D* contained neither iodine nor phosphate. The amount of iodine liberated in the first solution was therefore a measure of the amount of ozone used in the oxidation of phosphorus trioxide.

The amount of phosphorus trioxide oxidised was next determined. Tube *C* was disconnected at *f* and tilted so that a considerable amount of perfectly clear trioxide could be run back into the evacuated distilling flask. If any of the oxidation product was dissolved in the trioxide, its amount was negligible. The remainder of the phosphorus trioxide was removed as vapour by prolonged evacuation of the apparatus. During evacuation the apparatus was sealed off at x and y, in order to avoid possible leakage at taps, and then heated in water at 50—60°. When removal of phosphorus trioxide was as complete as possible, air was slowly passed into tube *C* from which the drying tube was then cut off at z. The seals at x and y were also broken and the reducing power of the oxides was ascertained whilst in the apparatus. A blank experiment was similarly performed, and then the total weight of phosphorus in the oxides was determined as usual.

Although the oxidation product, which was assumed to have the composition $PO_{2\cdot19}$, was contaminated with a little phosphorus trioxide, the above results were sufficient for the calculation of the actual weight of phosphorus trioxide *oxidised*. In two experiments the molecular ratio of phosphorus trioxide to ozone ($P_4O_6 : O_3$) was 1·9 : 1 and 2·1 : 1. Therefore when phosphorus-free trioxide is oxidised by ozonised oxygen 2 mols. of phosphorus trioxide are oxidised for every mol. of ozone reacting. Now, in order to convert $2P_4O_6$ into the oxidation product of composition $PO_{2\cdot19}$, 5·5 atoms of oxygen are required; of this, a molecule of ozone can supply 3 atoms at most, so that oxygen as well as ozone takes part in the reaction. If P_4O_8 * and P_4O_{10} are the sole constituents of the oxidation product represented by $PO_{2\cdot19}$, for every mol. of P_4O_8 there must be approximately 0·6 mol. of P_4O_{10} present. The simplest equation that represents the oxidation process is

$$8P_4O_6 + 4O_3 + 5O_2 = 5P_4O_8 + 3P_4O_{10},$$

where the amount of ozone used up is equivalent to the amount of phosphorus pentoxide produced. The presence of phosphorus tetroxide in the final oxidation product was not due to incomplete oxidation, owing to an insufficient supply of ozone, for the tetroxide is not attacked by ozone at 25° (p. 1836). At present it is impossible to say how the ozone molecule behaves in the oxidation of phosphorus trioxide, nor can anything definite be said regarding the different stages of the reaction. It has still to be found whether

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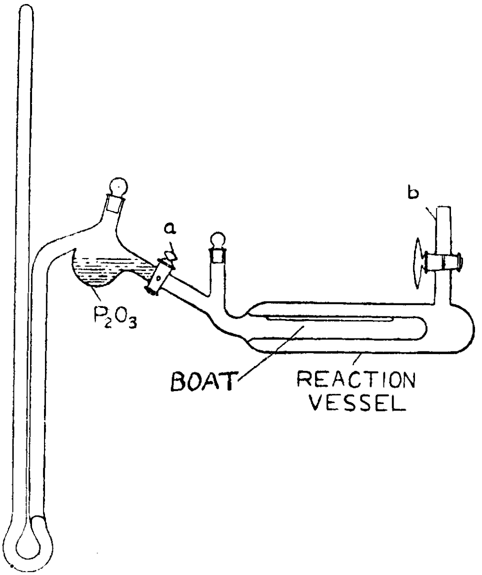
* This formula is used for simplicity, the more probable formula being P_8O_{16} (West, J., 1902, **81**, 923).

variation of the experimental conditions (temperature, oxygen pressure, etc.) affects the mode of oxidation.

(c) *Estimation of the Total Amount of Oxygen absorbed by Phosphorus in Presence of Phosphorus Trioxide at* 25°.—In order to find the total amount of oxygen absorbed by phosphorus in presence of phosphorus trioxide, a known weight of phosphorus dissolved in pure phosphorus trioxide was oxidised in oxygen in presence of a small amount of water vapour. As the phosphorus trioxide was used up by moisture before the whole of the phosphorus was oxidised, it was necessary to add, at intervals, small quantities of phosphorus-free trioxide until oxidation was complete. The apparatus shown in Fig. 4 was connected up at *b* with an oxygen reservoir provided with a manometer, as indicated in an earlier paper (Miller, *loc. cit.*, p. 1849). The mercury manometer (Fig. 4) was shut off from the reaction vessel in case the mercury should affect the reaction, and for convenience the pure phosphorus trioxide was stored in the bulb included in the manometer section. 2—3 G. of pure phosphorus trioxide were placed in the bulb, and the manometer section was evacuated and charged with dry oxygen to a known pressure of about 300 mm. Below the boat in the reaction vessel were put 8 c.c. of a 97% solution of orthophosphoric acid as a source of water vapour. Air was then displaced by dry carbon dioxide, and

FIG. 4.



a weighed amount (0·8—0·9 g.) of phosphorus trioxide, saturated with phosphorus at 25°, was introduced into the boat. The apparatus was attached to the oxygen reservoir and quickly evacuated. From the reservoir of oxygen at a known pressure, oxygen was then passed into the reaction vessel to a pressure of about 300 mm. The whole apparatus was kept at 25°, and while oxidation proceeded the reaction vessel was gently rocked to prevent film formation on the liquids. As the rate of oxidation was approximately known (Miller, *loc. cit.*, p. 1853), the pressure during oxidation could be kept most of the time within certain limits by addition of oxygen at intervals. When most of the phosphorus trioxide was used up, more was added by momentarily opening tap *a*. After two days, when oxidation was practically complete, the reservoir pressure was noted and the reservoir disconnected. Tap *a* was permanently opened, and any further slight pressure change was noted. Pressure was constant after another two days. In a blank experiment, with phosphorous acid replacing phosphorus and phosphorus trioxide, no oxygen was absorbed in four days. The volume of every part of the apparatus was known for all pressures, so that the total amount of oxygen used in the oxidation could be calculated. In two experiments, about two-thirds of the total oxygen was absorbed between 300 and 200 mm. pressure, and the remainder below 200 mm. The weight of phosphorus oxidised was calculated from the weight of phosphorus-saturated phosphorus trioxide used (100 g. of trioxide dissolve 1·71 g. of phosphorus at 25°). On the assumption that both phosphorus and phosphorus trioxide gave an oxidation product of the composition $PO_{2\cdot19}$, the relative amounts of the element and the trioxide oxidised were found to correspond to a molecular ratio ($P_4 : P_4O_6$) of 1 : 4·8 and 1 : 5·4. Hence at 25°, in oxygen at an average pressure of 200 mm., about 5 mols. of phosphorus trioxide are oxidised for every mol. of phosphorus. If the oxidation of the trioxide is due to ozone produced in the oxidation of phosphorus, and if 2 mols. of phosphorus trioxide are oxidised per mol. of ozone, as at 760 mm. oxygen pressure (p. 1841), then the above 5 mols. of phosphorus trioxide require for oxidation 2·5 mols. of ozone, derived from the oxidation of 1 mol. of phosphorus.

Van 't Hoff (*Z. physikal. Chem.*, 1895, **16**, 411), who studied the oxidation of phosphorus at 50° in air at atmospheric pressure and in presence of a dilute solution of indigo as acceptor, found that for every atom of phosphorus oxidised 0·6 atom of "active" oxygen reacted with the indigo (see below). This is equivalent to the production of 2·4 mols. of ozone per mol. of reacting phosphorus, practically the same result as that just found under entirely different conditions.

The oxidation of phosphorus trioxide or indigo during the slow oxidation of phosphorus is an example of an induced oxidation, a type of secondary reaction common in autoxidation processes. A quantitative study of induced oxidations has revealed that, under favourable conditions, for every atom of oxygen taken up by the autoxidisable substance (inductor), an atom of (" active ") oxygen is rendered available for the substance acting as acceptor. This relationship is usually explained by supposing that the primary reaction results in the formation of a peroxide, which then gives up half of its oxygen to the acceptor. When ozone is formed in the oxidation of phosphorus, oxygen itself is supposed to act as acceptor, the following equations being as a rule adopted to explain the mechanism:

$$2P + O_2 = P_2O_2; \; P_2O_2 + O_2 = P_2O + O_3.$$

These equations do not represent experimental facts, however, for both van 't Hoff's result and my own show that the amount of active oxygen or ozone produced per phosphorus atom oxidised exceeds by 20—25% the amount indicated in the equations.

I have assumed that ozone formation precedes the oxidation of phosphorus trioxide, but it may be that oxidation is effected by "active" oxygen, which in other circumstances would give rise to ozone. In order to find if the oxidation of phosphorus trioxide was induced during the oxidation of phosphorus in dry oxygen (no ozone is produced) I heated a bulb, containing phosphorus-saturated phosphorus trioxide and oxygen, at the temperature at which a glow just appeared (oxidation is negligible in absence of glowing). Unfortunately, this condition could not be maintained long owing to the ready ignition of the phosphorus. It is therefore not yet possible to say whether the oxidation of phosphorus in dry oxygen induces the oxidation of phosphorus trioxide, or whether moisture has a bearing on the nature and extent of the induced oxidation.

The Mechanism of the Reaction between Phosphorus and Oxygen.

Since the final oxidation products of phosphorus in dry oxygen consist, as I have shown, mainly of the tetroxide and pentoxide, and the same oxidation products, in similar molecular ratio, are given by phosphorus trioxide under suitable conditions, it is extremely likely that phosphorus trioxide is formed as an intermediate product in the oxidation of phosphorus. Now I have indicated that phosphorus trioxide exerts an inhibitory effect on the glow of phosphorus, from which it follows that if the intermediate compound accumulates in the system during oxidation glowing should cease.

This, however, was not observed, so that the trioxide if formed must undergo immediate further oxidation. But phosphorus trioxide does not oxidise in oxygen at the ordinary temperature unless ozone is present. In the oxidation of phosphorus, therefore, either phosphorus trioxide is oxidised by active oxygen (or ozone) simultaneously formed in the reaction, or newly formed molecules of phosphorus trioxide are sufficiently activated to undergo further oxidation. The latter course seems to be more likely considering that immediate oxidation of the trioxide occurs.

Since the oxidation of phosphorus is accompanied by chemiluminescence, a phenomenon of frequent occurrence in autoxidation processes, it is evident that certain atoms or molecules in the system are sufficiently excited by the energy liberated in the reaction to emit light. According to Petrikaln (*Z. Physik*, 1928, **51**, 395), the spectrum of glowing phosphorus is due to phosphorus trioxide, the molecules of which are excited by a transference of energy by radiation or collision from newly formed pentoxide molecules. This is doubtful, however, for the oxidation products of phosphorus do not contain a surplus of trioxide. If phosphorus trioxide is responsible for light emission it is more likely because a small number of the excited trioxide molecules, produced at an intermediate stage in the oxidation reaction, instead of oxidising further, return to the inactive state with emission of light. The validity of Petrikaln's result is, however, open to question, for his oxide, which was prepared by Biltz and Gross's method (*Ber.*, 1919, **52**, 762), contained phosphorus. Until his experiments are repeated with pure phosphorus trioxide, the possibility exists that phosphorus itself is responsible for the characteristic emission. An examination of the absorption and emission spectra of pure phosphorus trioxide is contemplated.

Summary.

A qualitative test of the oxidation products of phosphorus in dry oxygen revealed that phosphorus tetroxide was a constituent. As phosphorus oxidising in moist air at the ordinary temperature gave a product of the composition represented by $PO_{2.19}$, the oxidation products of phosphorus in dry oxygen were analysed quantitatively. At all the pressures of oxygen tried (100—1200 mm.), and at a temperature of 11°, the oxidation product was of practically the same composition, the atomic ratio O : P being 2·16. It contained phosphorus tetroxide and pentoxide, a trace of amorphous phosphorus, and a small quantity of a substance responsible for the appearance in the aqueous solution of either hypophosphoric acid or a substance resembling it in properties. Phosphorus trioxide was not detected.

Phosphorus tetroxide was stable in oxygen at the ordinary temperature, but underwent oxidation to pentoxide when heated at 350—400°. It was unattacked by ozone at 25°.

Phosphorus-saturated trioxide, which absorbed oxygen at 25°, in presence of a small quantity of water vapour gave an oxidation product of the composition represented by $PO_{2.19}$. Phosphorus trioxide took part in the oxidation, being oxidised, presumably, by ozone liberated in the oxidation of the phosphorus.

When pure phosphorus trioxide was oxidised at 25° by ozonised oxygen, the oxidation product had again the composition represented by $PO_{2.19}$, and the tetroxide and pentoxide were the sole constituents. One molecule of ozone was required for the oxidation of two molecules of phosphorus trioxide (P_4O_6). When phosphorus was oxidised in presence of phosphorus trioxide, and a small amount of water vapour, five molecules of phosphorus trioxide were oxidised for every molecule of phosphorus (P_4) undergoing oxidation.

It was indicated that phosphorus trioxide is most probably formed at an intermediate stage in the oxidation of phosphorus; but it does not accumulate in the system, and probably undergoes oxidation while in an activated state. Active molecules of phosphorus trioxide may be responsible for the chemiluminescence exhibited by slowly-oxidising phosphorus, but this point has still to be settled.

I have much pleasure in acknowledging my indebtedness to Sir James Walker, F.R.S., who has given me great encouragement during my investigations.

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[*Received, June* 19*th*, 1929.]