CCXL.—*The Preparation and Properties of Pure Phosphorus Trioxide.*

By Christina Cruickshank Miller.

The luminescence exhibited by slowly oxidising phosphorus trioxide has been frequently commented on and studied since the preparation of the oxide by Thorpe and Tutton (J., 1890, **57**, 545) and their study of its properties. Many have been the attempts to find the relation between the glowing of phosphorus and the glowing of its oxide. Although the best conditions for production of the glow in the two cases are by no means the same, there are several striking points of resemblance; for example, Emeleus (J., 1925, **127**, 1362) established the identity of the ultra-violet band spectra, and Downey (*ibid.*, 1924, **125**, 347) showed that the light from each is capable of ionising oxygen; also Scharff (*Z. physikal. Chem.*, 1908, **62**, 179) found that substances which inhibit the glow of phosphorus likewise inhibit that of the trioxide.

The possibility of the glow being due to phosphorus in the oxide was considered by Thorpe and Tutton but rejected as unlikely. It is now shown, however, that Thorpe and Tutton did not study an oxide free from phosphorus, and that many properties supposed to be characteristic of phosphorus trioxide may, indeed, be due to dissolved phosphorus.

In an earlier paper (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 76) it was shown that there was a connexion between the glowing of phosphorus trioxide and the presence of water vapour. The effect on phosphorus trioxide, in evacuated bulbs, of water vapour derived from certain salt–hydrate mixtures was such as to indicate the possibility of formation of hydrides of phosphorus. It has since been found, however, that the use of hydrated chlorides and sulphates leads to erroneous results owing to the liberation of hydrogen chloride from chlorides and of sulphur dioxide from sulphates. When chlorides are used, gaseous hydrogen phosphide has been definitely proved to be amongst the final products, but its formation is due to complicated reactions which ensue between the hydrochloric acid and the phosphorus trioxide, not to direct action of aqueous vapour on the trioxide. When sulphates are used no hydrogen phosphide is produced. The very slight increase of pressure observed when water itself was the source of moisture is now attributed to carbon dioxide initially dissolved in the oxide and liberated in part by the conversion of phosphorus trioxide into phosphorous acid. In subsequent experiments water vapour at various pressures was obtained by the use of aqueous solutions of orthophosphoric acid, which produced no pressure change in presence of phosphorus trioxide in evacuated bulbs.

The Rate of Oxidation of Phosphorus Trioxide.

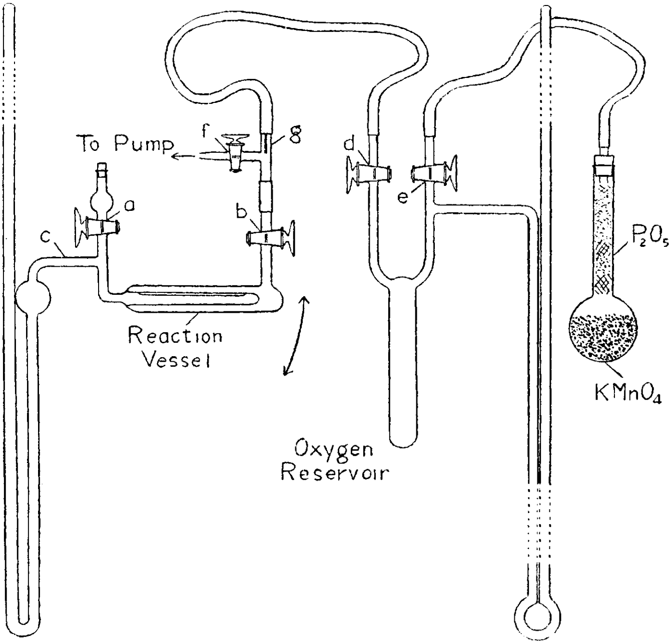
The rate of oxidation in oxygen, at 25°, of phosphorus trioxide, prepared according to Thorpe and Tutton's method and distilled at low pressure over reduced copper gauze, was studied in presence of the following solutions of phosphoric acid :

H_3PO_4 (g. per 100 g. of solution) ...	50	80	90	97
Density at 25°	1·335	1·629	1·743	1·845
Aqueous tension at 25° (mm.)	16·7	4·0	1·2	0·2

(If moisture was excluded from the apparatus oxygen was absorbed at an extremely slow rate.)

The apparatus (shown to the left in Fig. 1) was a slight modification of that used with hydrate mixtures (*loc. cit.*) and consisted of a bulb into one end of which was sealed a glass boat. Phosphorus trioxide was run into the boat at *a* and phosphoric acid into the wide tube at *b*. On to the apparatus was sealed a mercury manometer, and the whole was held pivoted at *c* so that an up and down movement could be effected as shown by the arrow. The volume of the bulb was a minimum, 30 c.c., so as to maintain the saturated vapour pressure of phosphorus trioxide, and the shaking device prevented film formation on the liquids.

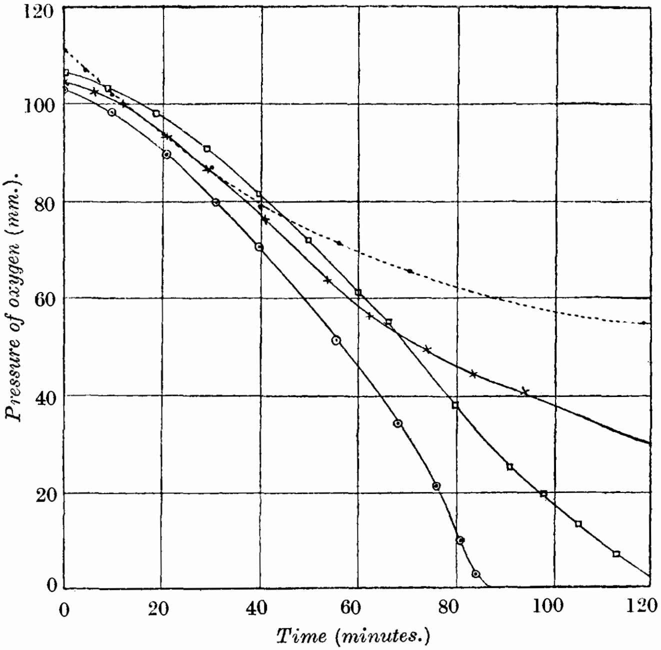
FIG. 1.



In all experiments the same quantities of liquids were used, *viz.*, 0·2 c.c. of phosphorus trioxide and 8 c.c. of a phosphoric acid solution, a choice which did not introduce a marked change in the pressure of water vapour as the oxide was used up. The apparatus containing phosphoric acid was evacuated, and oxygen, generated by heating potassium permanganate, passed in till its partial pressure was 100—110 mm. After the apparatus had been heated to 25°, liquid phosphorus trioxide was run into the boat and pressure readings were made at intervals. The pressure–time curves (Fig. 2) illustrate the nature of the results.

Experiment 1. When the pressure of water vapour was very low—0·2 mm.—oxygen was absorbed at a slowly increasing rate until all had gone in $1\frac{1}{2}$ hours. During oxidation, glowing and flashing took place in the vapour phase, the luminescence always tending to be away from the phosphorus trioxide source, *i.e.*, not above the boat. Luminescence was all the time of the same nature, but brighter at lower pressures, and it faded and disappeared abruptly when nearly all the oxygen was used up. Most of the phosphorus trioxide seemed to be oxidised.

FIG. 2.



⊙ *Pressure of water vapour* 0·2 *mm.*; □ 1·2 *mm.*;
× 4·0 *mm.*; 16·7 *mm.*

Experiment 2. The rate of absorption of oxygen in presence of 1·2 mm. pressure of water vapour was similar to that in Expt. 1, but the rate fell off after about 70 minutes. The glow phenomena up to this point were also similar, except that glowing took place to a slight extent above the boat. After 90 minutes, when the rate of oxidation was slower, there was permanent glowing round numerous solid particles in the boat. This was not observed when the pressure of water vapour was very low. No phosphorus trioxide remained.

Experiment 3. When the pressure of water vapour was 4 mm. the rate of oxidation for 40 minutes was similar to that in the two preceding experiments. The glow tended very early to pass above the boat, and steady glowing showed at numerous points in the boat, earlier than in Expt. 2. The passing of the glow to the boat coincided with a reduction in the rate of absorption of oxygen and with the disappearance of phosphorus trioxide.

Experiment 4. With a high pressure of water vapour, flashing occurred after a few minutes above the boat, and in 10 minutes steady glowing took place in the boat. The phosphorus trioxide was practically all used up. After ½ hour the only glowing was that round the solid particles in the boat, and the fairly rapid initial rate of oxygen absorption had given way to a very slow absorption.

In these experiments it was found that the bulk of the phosphorus trioxide was converted into phosphorous acid, which did not absorb oxygen under the conditions prevailing. When the pressure of water vapour was high, this conversion was very rapid, and the subsequent slow rate of oxygen absorption was therefore not due to phosphorus trioxide. In all experiments, after the oxygen was used up, a small, insoluble residue, consisting of minute particles surrounded by liquid, remained in the boat; this was apparently phosphorus, for it glowed in air. The glowing previously observed in the boat was around these particles. As a test, 40 mg. of phosphorus were disintegrated in 2 c.c. of a 50% solution of phosphoric acid and part of the mixture was oxidised as in Expts. 1—4. Glowing took place round the solid particles and the pressure fell at a measurable rate, depending on the quantity of mixture present and on the amount of liquid surrounding the particles. The appearance of phosphorus in the boat in Expts. 1—4 was attributed to phosphorus originally dissolved in the phosphorus trioxide and set free by the conversion of the oxide into phosphorous acid. As the phosphorus trioxide might contain 1% of phosphorus, as judged by results of analysis, its rate of oxidation was compared with that of a 1% solution of phosphorus in paraffin oil. With the latter the pressure of oxygen fell 100 mm. in 3—4 minutes. This rapid rate of oxidation therefore bore no resemblance to the rates found for phosphorus trioxide. Glowing appeared only at the surface of the paraffin solution.

The rate of oxygen absorption by phosphorus trioxide, with low water-vapour pressure, was examined at constant pressure and volume. The boat tube was connected as shown in Fig. 1 with a 45—55 c.c. oxygen reservoir, to which were attached a mercury manometer, reading up to 800 mm. pressure, and a flask in which oxygen was generated by heating potassium permanganate, and dried by passage through a short column of phosphoric oxide.

The boat apparatus was provided with a manometer, registering up to 600 mm. pressure, which on account of its weight was attached at *c* by means of rubber tubing to the reaction bulb. The latter was moved up and down as before. The boat apparatus and as much as possible of the reservoir were put in a thermostat at 25°. The volumes of the reaction vessel and of the reservoir between *b* and *e* were known for all pressures.

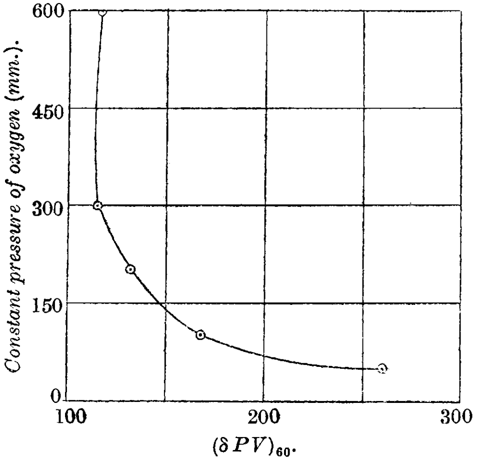
In an experiment, the reservoir was charged with oxygen at a pressure about 300 mm. above the constant pressure required; 8 c.c. of a 97% solution of phosphoric acid and 0·5 g. of phosphorus trioxide were run into the reaction bulb and the apparatus was quickly evacuated between *a* and *d*. Tap *f* was closed and oxygen admitted to the evacuated bulb through tap *b* until the pressure was just below that required. The rate of inflow was controlled by means of the narrow capillary, *g*. When the apparatus had been 10 minutes in the thermostat, the pressure in the reaction vessel was carefully adjusted to the constant-pressure mark by admitting oxygen from the reservoir. Immediately after closing tap *b*, the time was noted and the pressure in the reservoir read off. Pressure in the reaction bulb was next allowed to fall not more than 5 mm. and then raised by admission of oxygen to about 5 mm. above the constant-pressure mark. The pressure fell again from this point, and the times of reaching the constant-pressure mark and the pressure of the reservoir were noted. Readings were made at intervals for 1½ hours or until the phosphorus trioxide was exhausted. From the change in PV, the product of the pressure and the volume of the reservoir, the amount of oxygen absorbed in a given time could be determined. For an experiment performed at 25° and at constant pressure (100 ± 4 mm.) the following results were obtained:

t (mins.).	P (cm.).	V (c.c.).	PV.	$(PV)_0 - (PV)_t = (\delta PV)_t$.
0	31·35	50·5	1583	0
7·5	31·0	50·5	1566	17
25	30·15	50·4	1520	63
29·5	29·9	50·4	1507	76
36	29·55	50·35	1487	96
42	29·2	50·3	1469	114
49	28·85	50·3	1451	132
57	28·35	50·25	1425	158
67	27·8	50·2	1395	188
75	27·4	50·15	1374	209
82·5	26·9	50·1	1348	235
90·5	26·4	50·1	1323	260

The change in PV in the time t, $(\delta PV)_t$, was equivalent to the volume of oxygen absorbed (in c.c. at 25° and 1 cm. pressure). Except for a slight initial retardation, the rate of absorption was practically constant. Experiments performed with the pressure of oxygen constant at 600, 300, 200, and 50 mm. gave results of the same type, but showing different rates of absorption of oxygen. In order to compare the rates, the amount of oxygen absorbed in 60 minutes, $(\delta PV)_{60}$, was determined for each and the corresponding curve constructed (Fig. 3). It was unnecessary to correct for the change in volume of the reaction vessel with pressure, for the reaction only took place in the bulb part, which was the same for all.

An experiment at 25 mm. pressure was unsatisfactory, as the rate of oxidation on two occasions suddenly increased considerably. Fig. 3 indicates that the rate of oxygen absorption may become very great at pressures below 50 mm., an indication, probably, of ignition.

FIG. 3.



The results, which were all obtained with one specimen of phosphorus trioxide, showed that the rate of absorption of oxygen between 600 and 300 mm. pressure was practically constant but increased regularly as the pressure fell below 300 mm. This bore a resemblance to the rate of oxidation of phosphorus in moderately dried oxygen (see Russell, J., 1903, **83**, 1263).

In all experiments the position of the luminescence was striking. Bright flashing occurred principally below the boat, just above the acid surface, or at the end of the tube beyond the boat, *i.e.*, away from the source of phosphorus trioxide and near the water-vapour source. Attention has already been directed to the appearance of luminescence at sources of moisture at considerable distances from the oxide (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 239). Owing to the ease with which phosphorus trioxide took up water vapour in a partially evacuated apparatus, it was difficult to imagine that in every instance phosphorus trioxide existed where luminescence appeared. Could the luminescence have been due to dissolved phosphorus? And if so, why did not luminescence appear at the surface of the liquid oxide as in the case of phosphorus dissolved in paraffin oil? The only explanation seemed to be that phosphorus trioxide prevented the luminescence of phosphorus. Phosphorus trioxide vapour containing phosphorus would therefore only luminesce if something were present to destroy the phosphorus trioxide. Water vapour, which is essential for the luminescence at the ordinary temperature, has this effect. One would then expect phosphorus trioxide to destroy the glow of slowly oxidising phosphorus. The following experiment was performed. Below the boat of the apparatus in Fig. 1, 5 c.c. of a solution of phosphorus in paraffin oil were introduced. Oxygen was present initially at 50 mm. pressure, and the solution glowed quite brightly at the surface. The pressure fell 29 mm. in 28 minutes. The experiment was started afresh, and after a minute 0·5 g. of phosphorus trioxide was run into the boat. The glow was immediately extinguished, and the pressure afterwards fell only 16 mm. in 170 minutes. This was not further studied, but the observation favoured the foregoing explanation that the glowing of phosphorus trioxide might be due to dissolved phosphorus.

Owing to its mode of preparation, the crude phosphorus trioxide contained phosphorus, which was no doubt partly removed by distillation. When the distillation proceeded too far, small globules of phosphorus accompanied the liquid phosphorus trioxide into the receiver and appeared not to dissolve to any extent. The phosphorus trioxide ordinarily used was therefore probably a saturated solution of phosphorus in phosphorus trioxide. Distillation over copper was not specially effective in removing phosphorus. Analysis, as previously mentioned, suggested the presence in the oxide of 1% of phosphorus. The well-known reddening of phosphorus trioxide in light has also been attributed to dissolved phosphorus. It is significant that the actual extent of decomposition is slight; for instance, Thorpe and Tutton (J., 1891, **59**, 1019) found only 1% of red phosphorus in a sample of oxide exposed for 7 months to light.

In order to determine the part, if any, played by phosphorus in the luminous oxidation of phosphorus trioxide, it was obvious that the preparation of a phosphorus-free oxide was desirable. An unsuccessful attempt was made to dehydrate pure phosphorous acid. In another attempt phosphorus trioxide was exposed to light in an evacuated bulb, and the oxide was volatilised from the red solid at 25° into a second bulb where it was again exposed. Reddening occurred as before and the process was once more repeated. The reddening effect was purely a superficial one. The light seemed to affect the white, opaque phosphorus trioxide, not the transparent crystals which sometimes formed. If the latter were melted and resolidified, they gave a white opaque solid which was affected by light. As there was apparently no diminution in the amount of reddening in the third bulb, this attempt to separate phosphorus was abandoned.

The next method adopted was the recrystallisation of freshly distilled phosphorus trioxide from a suitable solvent. Carbon disulphide is by far the best solvent for phosphorus but phosphorus trioxide also dissolves readily. A preliminary trial showed, however, that it could be employed if the temperature of recrystallisation was about −18° and the amount used was small. The sulphide was dried and distilled over mercury before use. Carbon sulphide is known to be a strong inhibitor of the glow of phosphorus, but it was found that there was no diminution of the glowing of a specimen of phosphorus trioxide after it had been dissolved in carbon disulphide and the solvent removed by evaporation, finally with the aid of a pump.

The Recrystallisation of Phosphorus Trioxide.—As a trial a small quantity of freshly distilled phosphorus trioxide was recrystallised four times from carbon disulphide in an atmosphere of carbon dioxide. The solvent was then expelled by a fairly rapid stream of carbon dioxide, and the purified oxide, about 25% of the original bulk, transferred to a boat apparatus (Fig. 1) and oxidised at 25° in presence of a 97% solution of phosphoric acid and oxygen at a constant pressure of 100 mm. (compare p. 1851). At first no glowing was seen, but after a time there were occasional bright flashes without pressure change in 50 minutes. It was suspected that a trace of carbon disulphide was responsible for the lack of oxidation. The apparatus was therefore re-evacuated and fresh oxygen passed in. Slight glowing occurred and the pressure fall corresponded to $(\delta PV)_{40} = 5{\cdot}2$. After a further evacuation and addition of oxygen the pressure fall was practically the same. The rate of oxidation of ordinary distilled phosphorus trioxide was previously found to be represented by $(\delta PV)_{40} = 108$ (see table, p. 1852), therefore the rate of oxidation of the purified oxide was reduced to one-twentieth of the original, probably corresponding to a similar reduction in the amount of dissolved phosphorus. The phosphorus trioxide obtained from the mother-liquor was found to oxidise at the normal rate.

These results showed that greater care had to be taken in eliminating solvent from the purified oxide. The apparatus shown in Fig. 4 was designed for recrystallisation experiments. It consisted of a flat-bottomed tube provided with a side tube through which the mother-liquor from the crystals could be poured. It was further provided with a rubber stopper holding a small tap-funnel, and with a glass rod to which was attached by platinum at the lower end a perforated porcelain disc of nearly the same diameter as the tube. The disc could be moved up and down the tube like a piston. Dry carbon dioxide was passed into the apparatus as shown. Freshly distilled phosphorus trioxide and carbon disulphide were mixed by stirring in the tube and cooled to −18°, the perforated disc being moved up and down to prevent formation of crystals on the walls. The crystals were then allowed to settle and the disc was pressed down to force out the liquor. The latter was quickly poured off into the side bulb and thence removed. The recrystallisation was repeated and the crystals were finally washed with cooled carbon disulphide. The purified oxide was melted, transferred to a small tube, and solvent removed by evacuation with an oil pump, the oxide meanwhile being many times melted and resolidified. The yield of oxide was slightly higher than before. The specimen glowed when rubbed on the fingers, and in ozonised oxygen, but did not ignite on cotton wool. When oxidised according to the usual method the amount of oxygen absorbed was $(\delta PV)_{40} = 9$, slightly more than before, and there was quite bright flashing at intervals.

FIG. 4.

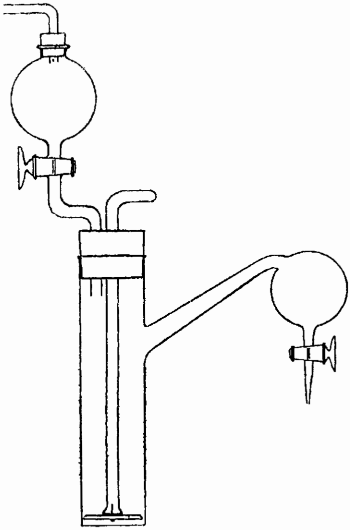
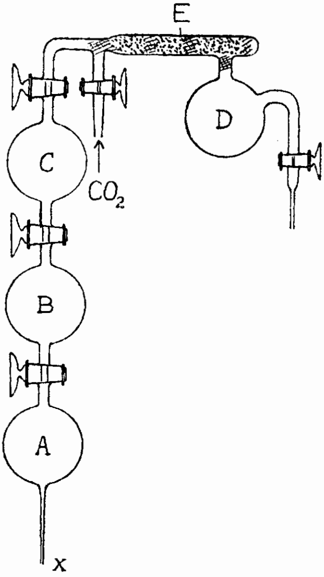


FIG. 5.



The maximum amount of oxygen absorbed by this oxide corresponded to little more than 0·1% of dissolved phosphorus.

Light petroleum (b. p. 40—60°) was tried in case the preceding results were due to carbon disulphide. Recrystallisation was effected five times and the solvent removed as before. The amount of oxygen absorbed by a portion of the oxide was equivalent to $(\delta PV)_{40} = 27$, three times the value found above. If the oxidation was due to phosphorus alone, this result indicated that there was three times as much phosphorus left in the oxide as in the preceding experiment and one-quarter of the amount present in the ordinary distilled oxide for which $(\delta PV)_{40}$ was 108. One might expect to obtain identical results for the rate of absorption of oxygen by the three specimens of phosphorus trioxide obtained by saturating the two purified oxides and the unpurified oxide (if not already saturated) with phosphorus at 25°. For the first two the values of $(\delta PV)_{40}$ were found to be 92 and 90, and for the last, 100. The two lower values were attributed to the fact that only minimum quantities of the solutions were prepared and phosphorus separated slightly while the oxides were being measured out. This did not happen with the third specimen. The value 100 was lower than that previously obtained for phosphorus trioxide, *viz.*, 108. The latter value was due to the use of oxide melted at 30—40°, which contained sufficient phosphorus to saturate it at a temperature above 25° and more than enough to saturate it at 25°.

The recrystallisation of a much larger quantity of phosphorus trioxide was attempted. Light petroleum was apparently not so effective as carbon disulphide in removing phosphorus, but it had the advantage that larger quantities could be used. A combination of methods was therefore adopted, the recrystallisation being effected with carbon disulphide and the crystals washed with light petroleum. 40 C.c. of freshly distilled phosphorus trioxide were mixed with one-third of the volume of pure carbon disulphide and recrystallised at $-18°$. The crystals were pressed as free as possible of liquor and washed with 15 c.c. of cooled light petroleum. The process was twice repeated with diminishing quantities of the solvents, and followed by two final washings with light petroleum (5 c.c. and 10 c.c.). The crystals were melted and filtered through glass-wool into a bottle from which air was displaced by dry carbon dioxide. The yield was about one-third of the original bulk.

The oxide in the mother-liquors was recovered, excess of phosphorus removed, and the oxide distilled and recrystallised as before. In all, three products were obtained and put in one bottle from which the remaining solvent was carefully removed as before. The phosphorus trioxide in the last mother-liquor was recovered from solution in the usual manner and distilled in a vacuum to give a clear phosphorus-saturated solution of phosphorus trioxide.

A little of the purified oxide was oxidised in presence of 4 mm. of water vapour. The total amount of oxygen absorbed corresponded to about 0·02% of dissolved phosphorus. Bright flashing occurred under the boat during the first ½ hour; after 3 hours no glowing was seen and the pressure remained steady. This experiment indicated further removal of phosphorus from the oxide. A drop of this purified material when rubbed on the fingers gave a bright but momentary glow, whereas a drop of the ordinary oxide gave a glow sufficiently bright and lasting to illuminate the whole hand. It was supposed that the purified oxide glowed and absorbed a minute quantity of oxygen because of the retention of a trace of phosphorus. Elimination of this trace by further recrystallisation was impracticable, but it was thought that it might be eradicated by exposure of the oxide to sunlight, a process in which there was no further introduction of substances with an inhibitory effect on the glow. According to expectations the oxide reddened in sunlight, but not to the extent shown by the unpurified oxide. The apparatus shown in Fig. 5 was designed. Initially only that part was used which consisted of the three glass bulbs joined together as indicated. Phosphorus trioxide was drawn into bulb *A* and *x* was sealed off. The three bulbs were then thoroughly evacuated and the taps closed. As large a surface as possible of the phosphorus trioxide was exposed to light for a few hours and considerable reddening took place. The apparatus was re-evacuated and the phosphorus trioxide in bulb *A* volatilised into bulb *B* by heating *A* to 40° and cooling *B*. The oxide was again exposed to light, whereupon further reddening occurred, and then transferred to bulb *C* for a third exposure. In bulbs *B* and *C* the reddening was not so extensive as in bulb *A*. The second part of the apparatus, which had not been contaminated with phosphorus trioxide vapour containing phosphorus, was now sealed on to the three bulbs, and the tube *E* charged with phosphoric oxide. The whole apparatus was evacuated and the phosphorus trioxide in bulb *C* volatilised through the phosphoric oxide into the receiving bulb *D*. The drying tube and the bulb *D* were then filled with pure, dry carbon dioxide to atmospheric pressure, and portions of the oxide removed as required.

The Properties of Purified Phosphorus Trioxide.—1. At the ordinary temperature the oxide was a transparent, crystalline solid, lacking the opaque, waxy appearance of the unpurified product, caused probably by the separation of phosphorus from solution, on solidification.

2. A clear, colourless sample of purified phosphorus trioxide

contained in an evacuated bulb was exposed to light for 10 weeks in a well-lit laboratory, but, although it was several times melted and resolidified, it remained colourless and transparent. Crude phosphorus trioxide similarly treated was readily affected by light (see p. 1854). A second sample of purified oxide, which was kept in an atmosphere of carbon dioxide and used for the following experiments, was also exposed to light. The colourless crystalline mass assumed, during the first few hours' exposure, a faint pink tinge which did not deepen on further exposure for 6 weeks. The colour was due to the separation of a very small quantity of red substance.

3. When rubbed on the fingers the purified oxide gave no glow, and for a short time there was a pungent acid smell resembling that of hydrochloric acid. The phosphorus smell so readily detected with ordinary phosphorus trioxide was entirely absent. The pure oxide when spread on cloth did not ignite as does the ordinary product, but when mixed with a small proportion of the crude oxide, or with phosphorus, glowing and ignition were restored.

4. The m. p.'s of the purified and unpurified oxides were determined in a vacuum in small melting-point tubes, the oxide in each case having been initially volatilised through phosphoric oxide. The values found were: Purified oxide, 23·8°; unpurified oxide, 22·4°.

5. In order to obtain an indication of the amount of phosphorus dissolved in the unpurified oxide, the depression constant of the pure oxide was found by determining by Rast's method (*Ber.*, 1922, **55**, 1051) the lowering of freezing point produced by naphthalene as solute. With solutions containing 1·98 and 2·67% of naphthalene the lowerings were 1·85° and 2·4° respectively, giving for the depression constant the values 11,700 and 11,200. For the lowering of freezing point produced by phosphorus, *viz.*, 1·4°, a depression constant of 11,000 gives 1·6 g. as the amount of phosphorus (as P_4) dissolved in 100 g. of trioxide.

6. The pure oxide and the oxide saturated with phosphorus at 25° were analysed quantitatively: 0·15—0·25 g. was melted under water in a small flask and heated at 40—50° till converted into phosphorous acid. The pure oxide left no residue, whereas the unpurified oxide left a residue of phosphorus. An excess of liquid bromine was added and then 3—4 c.c. of 4*N*-sodium hydroxide, since hypobromite is known to oxidise phosphorous acid. Phosphorus was also completely oxidised. After a short time 5 c.c. of concentrated nitric acid were added and the solution was boiled to free it from bromine. The phosphoric acid was precipitated twice as magnesium ammonium phosphate, which was converted into pyrophosphate

(Found, for purified oxide: 100·04, 100·05; for unpurified oxide: 101·37, 101·47%). On the assumption that the purified oxide was entirely free from phosphorus, the last two results correspond respectively to 1·74 g. and 1·87 g. of free phosphorus in 100 g. of trioxide.

7. The solubility of phosphorus in the purified oxide at 25° was determined by shaking a weighed excess of purified phosphorus with about 1 g. of phosphorus trioxide in a small stoppered tube, in an atmosphere of carbon dioxide. The tube was first heated sufficiently to melt the phosphorus and then allowed to stand at 25°. The excess of phosphorus collected into a globule which was easily removed, washed, and weighed. The weight of phosphorus dissolved corresponded to 1·71 g. per 100 g. of trioxide. Experiments 5, 6, and 7 therefore showed satisfactory agreement.

8. The behaviour of the purified oxide in oxygen was studied. At 25° and in presence of 4 mm. of water vapour, the oxide neither glowed nor absorbed oxygen at 100 mm. or 18 mm. pressure, in contradistinction to the absorption of oxygen, accompanied by luminescence, exhibited by impure phosphorus trioxide (see Expt. 3, p. 1859). In presence of concentrated sulphuric acid it gave no deposition of oxides at 25° in oxygen at 600 mm. pressure, whereas unpurified phosphorus trioxide, under similar conditions, deposited phosphorus tetroxide (see Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 239). At higher temperatures, the following phenomena were noticed. 0·2—0·3 G. of oxide was mixed with phosphoric oxide and volatilised into a 6 c.c. bulb into which pure dry oxygen was passed to a pressure of 300 mm. The bulb was sealed and heated gradually, but no glowing or fuming was seen below 200°. At about 220°, fuming was observed, accompanied by a very faint glow. The action was not brisk, for after ¼ hour's heating at this temperature oxygen was still present. With undried phosphorus trioxide and moist oxygen the result was much the same, but in a second similar experiment oxidation appeared at 130°. Unpurified phosphorus trioxide gave an entirely different result, igniting at 40° in dry oxygen at 300 mm. pressure and using up all the oxygen. When ozonised oxygen containing 1% of ozone was passed at a slow rate over the pure phosphorus trioxide at 25°, oxidation occurred without luminescence. Under similar conditions, ordinary phosphorus trioxide glowed brightly and difficulty was experienced in preventing ignition.

9. When the purified oxide was melted under excess of water and heated gradually, it was simply converted into phosphorous acid, until a temperature of 75—80° was reached. At this point decomposition set in, bubbles of gas passed up through the water

from the oxide, and yellow and red solid products were formed. The gas fumed at the surface of the water and gave bright flashes. Unpurified phosphorus trioxide exhibited the same phenomena at a somewhat lower temperature.

When purified phosphorus trioxide in excess was sealed in an evacuated bulb with a small quantity of water, a clear yellow syrup formed, which after several days became opaque. The bulb was opened under water, but no gas was present. The amount of yellow solid was so small that accurate analysis was impossible—it is possibly a suboxide.

10. When the purified oxide was heated in a vacuum at 300°, red, yellow, and white decomposition products were formed, phosphorus tetroxide being amongst them. The thermal decomposition of ordinary phosphorus trioxide gives a similar result.

11. A portion of the pure trioxide was saturated with purified phosphorus at 25°. The oxide so obtained assumed on solidification the white, opaque appearance of unpurified phosphorus trioxide, glowed in air, ignited on cloth, and reddened in light.

Summary.

A study of the rate of absorption of oxygen by phosphorus trioxide in presence of water vapour at various pressures led to the conclusion that the luminescence of the oxide was essentially connected with the presence of dissolved phosphorus.

Phosphorus trioxide, as prepared by Thorpe and Tutton's method, invariably contained phosphorus, the bulk of which could be removed by several low-temperature recrystallisations from carbon disulphide. The remainder was removable by exposure of the oxide to light and subsequent volatilisation from the red product.

The pure oxide so obtained melted at 23·8°, *i.e.*, 1·4° higher than the unpurified product, and lacked many of the properties formerly attributed to phosphorus trioxide. For instance, it neither glowed nor oxidised in moist or dry oxygen at the ordinary temperature and was unaffected by sunlight. When it was heated in a sealed bulb with dry oxygen at 300 mm. pressure, fuming and very faint glowing were observed at about 200°. By addition of pure phosphorus to the pure oxide the properties previously regarded as characteristic of phosphorus trioxide were restored.

The trioxide was found to dissolve 1·7 g. of phosphorus per 100 g. when saturated at 25°.

It is not yet known if the absorption of oxygen by the impure oxide is due to phosphorus alone or to phosphorus and phosphorus trioxide together, but this point is being investigated.

A study of the oxidation products of phosphorus in oxygen and

of phosphorus trioxide in oxygen and ozonised oxygen is being continued.

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