CCXL.—*The Slow Oxidation of Phosphorus. Part I. The Inhibition of the Glow of Phosphorus by Phosphorous Oxide.*

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IN a recent publication (Miller, J., 1928, 1847), I showed that the glowing associated with the slow oxidation of phosphorous oxide prepared by Thorpe and Tutton's method (J., 1890, **57**, 545) is due to the presence of dissolved phosphorus. Phosphorous oxide freed from phosphorus by recrystallisation from carbon disulphide and exposure to light neither glows nor oxidises in oxygen and air at the ordinary temperature, and apparently exerts an inhibitory effect on the glow of phosphorus itself.

It is now shown that the trioxide may be freed from phosphorus without the use of solvents, which are themselves inhibitors of the glow. Additional evidence of the inhibitory effect of phosphorus trioxide on the glow of phosphorus is also given.

The Preparation of Pure Phosphorus Trioxide.—An attempt was previously made (Miller, *loc. cit.*) to remove phosphorus from phosphorus trioxide simply by exposing the oxide to light and then volatilising it from the red, amorphous phosphorus produced. As it was obvious that the failure at that time to obtain pure phosphorus trioxide by the light-exposure treatment alone was due to an insufficient number of exposures, the procedure was repeated with a few grams of oxide. The apparatus consisted of six glass bulbs, 3—4 cm. in diameter, joined together by short lengths of capillary tubing. At one end was a glass tap, and the other end was open so that phosphorus trioxide could be drawn into the first bulb. After introduction of phosphorus trioxide the end was sealed and the apparatus evacuated. The oxide in the first bulb was exposed to light, being frequently melted and resolidified until the surface of the bulb was so covered with red phosphorus that penetration of light was impossible. It was then transferred by distillation at 70° to the second bulb and the first bulb was sealed off. When all six bulbs had become impenetrable by light, six more were sealed on beyond the tap. Altogether, exposure to light in 12 bulbs was necessary to effect complete removal of phosphorus. Finally, the oxide was distilled through phosphoric oxide into a receiving bulb, where it was subsequently preserved in an atmosphere of carbon dioxide (see Miller, *loc. cit.*, p. 1856). As anticipated, the oxide had exactly the same appearance as that prepared by low-temperature recrystallisation from organic solvents and subsequent exposure to light, and it gave no glow when rubbed on the fingers. This definitely proved that the absence of glowing in the oxide formerly prepared was not due to inhibition of the glow by traces of solvents.

The Inhibition of the Glow of Phosphorus.

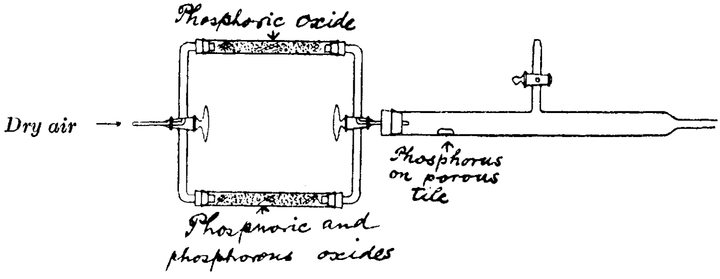
The following experiments, which, with the exception of Expt. 2, were performed at the ordinary temperature, show that phosphorus trioxide inhibits the glow of phosphorus, and that the inhibitory effect can be eliminated by moisture or ozone, both of which destroy the trioxide.

Experiment 1.—Over a drop of phosphorus trioxide solidified on a watch-glass was put 0·5 c.c. of a 1% solution of phosphorus in paraffin oil, and on another watch glass some of the paraffin solution alone. Both solutions glowed brightly. The watch glass with the trioxide was then placed on the hand in order to melt the oxide. A dark patch developed in the glowing disc and when the solution was shaken to effect mixing, darkness gradually spread over the whole disc till the glow was completely quenched.

Experiment 2.—To each of two 8-c.c. bulbs were added a little phosphoric oxide and 30 mg. of phosphorus which had been dried with filter paper. One bulb contained in addition a drop of phosphorus trioxide. Both were charged with oxygen to atmospheric pressure, sealed, and heated slowly in a beaker of water. In the bulb that contained no phosphorus trioxide the phosphorus glowed at 21° and ignited at 23°, but in the other, glowing did not appear round the phosphorus until the temperature reached 51°, and ignition took place only at 58°.

Experiment 3.—Into the boat of an apparatus similar to that previously described (Miller, *loc. cit.*, p. 1849) were put 5 c.c. of a solution of phosphorus in paraffin oil, and below it 8 c.c. of a 97% aqueous solution of phosphoric acid (aqueous tension, $<0{\cdot}2$ mm.). When oxygen was present at 50 mm. pressure the surface of the paraffin solution glowed brightly. 0·3 G. of phosphorus trioxide was then run into the boat and the apparatus was rocked up and down. Glowing entirely disappeared from the surface of the paraffin, but there was vivid glowing at the end of the tube beyond the boat (where phosphorus trioxide would be attacked by moisture), and a great deal of flashing according with the movement of the phosphoric acid. Brisk oxidation occurred. After ½ hour the glow was tending to move back to the paraffin solution, owing to exhaustion of the phosphorus trioxide. Admixture of more trioxide caused its departure.

FIG. 1.



Experiment 4.—An apparatus (Fig. 1) was arranged whereby dry air, either alone, or charged with phosphorus trioxide vapour, could be passed over a piece of porous tile impregnated with phosphorus. When air alone at the rate of 15 c.c./min. was passed over the tile it glowed distinctly and no other glow was visible. If, however, the air was then directed through the tube containing phosphorus trioxide, the glow on the phosphorus was extinguished in 5 secs., and after 90 secs. a luminous cloud appeared in the atmosphere beyond the end of the tube. The appearance of this cloud was attributed to the partial destruction of the inhibiting oxide by atmospheric moisture. On reversion to the phosphorus trioxide-free air current, the glow on the tile was restored in 30 secs. and a pulse of light travelled slowly along to the right until it was extinguished at a distance of 10 cm. from the phosphorus. The luminous cloud outside the tube disappeared in 100 secs.

Experiment 5.—The side tube shown in Fig. 1 was connected with a Siemens ozoniser so that ozonised oxygen could be passed into the long tube. Air containing phosphorus trioxide vapour was passed at the rate of 15 c.c./min. over the phosphorus, and a glow appeared at the far end of the tube. When the passage of dry ozonised oxygen (0·5—1% of ozone) was started at the same rate, a glow was immediately visible at the entry into the wider tube, and the glow at the end of the tube disappeared in 30 secs. Excess of ozone was escaping, which showed that all the phosphorus trioxide had been destroyed. When the stream of ozonised oxygen was suspended, the glow in the middle of the long tube moved slowly towards the right, becoming fainter, until, finally, the usual luminescence was established at the end of the tube. Similar effects were obtained when the rates of both gas streams were 3 c.c./min. If the rate of the air stream was then increased to 36 c.c./min. no glow was seen where ozone was entering the wide tube, and excess of phosphorus trioxide was escaping.

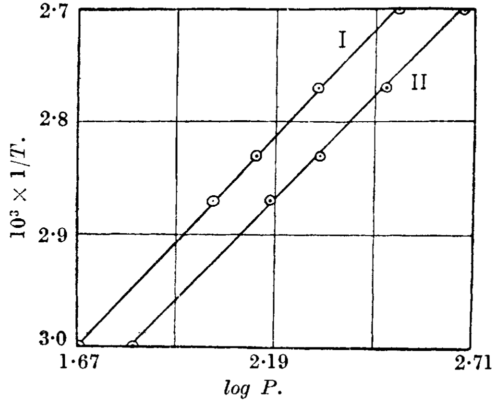
Experiment 6.—When phosphorus reacts with air in presence of moisture, ozone is formed. It was important to find if a stream of air passed over moist phosphorus would, in virtue of the ozone present, restore the glow to air charged with vapours of phosphorus trioxide and phosphorus. The arrangement was the same as in Expt. 5, except that the ozoniser was replaced by a tube containing phosphorus moistened with water. Between the tube and the usual apparatus was a drying bulb with phosphoric oxide to free the gas from moisture, which would itself have been capable of restoring the glow.

The same results were obtained as in Expt. 5, except that the effects were not quite so pronounced owing to the smaller amount of ozone available. When the moist phosphorus was replaced by dry phosphorus, no restoration of the glow occurred, which corroborates Russell's statement (J., 1903, **83**, 1263) that no ozone is liberated when dry phosphorus is oxidised.

From these experiments, it is evident that the glow of phosphorus is inhibited by phosphorus trioxide, and that the inhibitory effect can be removed by means of moisture or ozone, both of which destroy phosphorus trioxide. It is also obvious that the oxidation in presence of moisture of phosphorus trioxide containing dissolved phosphorus will be due as a rule to oxidation of both phosphorus and phosphorus trioxide, ozone produced in the oxidation of phosphorus, which has been at least partially freed by moisture from phosphorus trioxide, reacting with more of the oxide.

The Relative Inhibitory Effects of Phosphorus Trioxide and Ethylene.—The inhibitory effect of phosphorus trioxide was compared with that of the typical inhibitor, ethylene, by calculating for each inhibitor the ratio of its vapour pressure to that of phosphorus at the point where glowing was initiated. For ethylene the ratio was derived from Emeléus's graph (J., 1926, 1336) representing the effect of the concentration of the inhibitor on the temperature at which a glow occurred in ethylene–air mixtures at constant volume. An interesting fact came to light, namely, that the partial pressure of ethylene over the temperature range 60—97° was almost directly proportional to the vapour pressure of phosphorus. The ratio of the two pressures had the average value 145. This direct proportionality is very clearly shown in Fig. 2. Curve I is the usual straight line representing the relation between the logarithm of the vapour pressure (P) of phosphorus and the reciprocal of the absolute temperature (T). (The vapour pressure was multiplied by 100 for ease of comparison.) Curve II, which shows the corresponding relation for the partial pressure of ethylene at the glow point, is also a straight line very nearly parallel to the first.

FIG. 2.

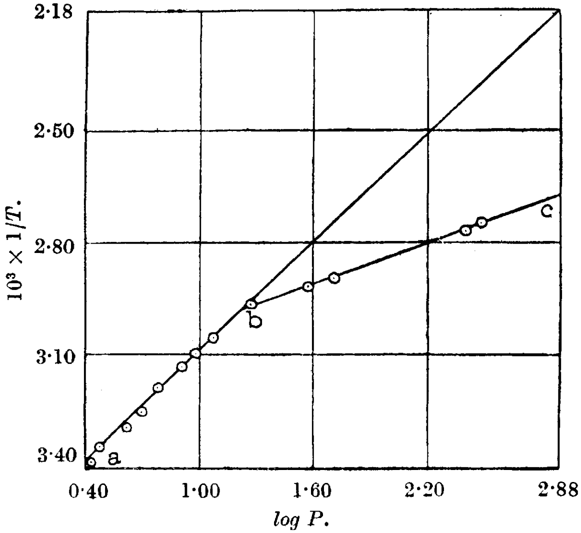


Curve I. *Phosphorus* (*values of log P increased by* 2·0).
Curve II. *Ethylene*.

The oxygen in the mixture apparently exerted very little effect, showing that if it was itself an inhibitor its action was weak compared with that of ethylene. No doubt its effect would have become more pronounced at lower temperatures, at which the ratio of the oxygen pressure to the vapour pressure of phosphorus would have been considerably increased.

The ratio of the vapour pressures of phosphorus trioxide and phosphorus at the glow point, 51° (see p. 1825), was calculated on the assumption that both these substances exerted their normal vapour pressures, *viz.*, 10·3 mm. (Schenck, Mihr, and Banthien, *Ber.*, 1906, **39**, 1506) and 0·284 mm. (MacRae and van Voorhis, *J. Amer. Chem. Soc.*, 1921, **43**, 547) respectively. The value of the ratio, *viz.*, 36, was probably not a satisfactory measure of the inhibitory power of the oxide owing to the preponderance of oxygen (760 mm.). As it was known, however, that phosphorus-saturated phosphorus trioxide did not glow in oxygen at low pressure at 25°, where the ratio of the vapour pressures of phosphorus trioxide and phosphorus was 56, it was assumed that the inhibitory power of phosphorus trioxide could be represented by a number between 40 and 50. Since the inhibitory power of ethylene was represented by the number 145, it followed that, molecule for molecule, phosphorus trioxide is about three times as powerful an inhibitor as ethylene.

FIG. 3.



The Vapour Pressure of Phosphorus Trioxide (*A Criticism*).—The vapour pressure of phosphorus trioxide has been determined by Schenck, Mihr, and Banthien (*loc. cit.*) over the temperature range 22—91°. I find that if the logarithm of the vapour pressure be plotted against the reciprocal of the absolute temperature, Fig. 3 is obtained. The first nine points lie on a straight line *ab* and the last five on another straight line *bc*, which intersects the first where $1/T = 0·00298$ (*i.e.*, $T = 336°$), and if extended in the other direction meets the line corresponding to log $p = 2·881$ ($p = 760$ mm.) where $1/T = 0·00267$. The boiling point of the liquid is therefore given by 1/0·00267 or 374° Abs.; Thorpe and Tutton (*loc. cit.*) found it to be 446° Abs. The boiling point derived from the graph by extending line *ab* is 458° ($1/T = 0{\cdot}002184$). It follows that Schenck, Mihr, and Banthien's estimations of vapour tension above 63° are defective, probably owing to interaction of phosphorus trioxide and moisture at that temperature with production of phosphine (compare Miller, *loc. cit.*, p. 1861).

Summary.

Phosphorus trioxide prepared by Thorpe and Tutton's method may be completely freed from phosphorus by repeated exposure to light, and subsequent volatilisation from the red amorphous phosphorus produced. Phosphorus trioxide inhibits the glow of phosphorus, being, molecule for molecule, about three times as powerful an inhibitor as the typical inhibitor, ethylene. The inhibitory effect of phosphorus trioxide is removable by moisture and ozone, both of which react with the trioxide. When phosphorus dissolved in phosphorus trioxide oxidises in presence of moisture, ozone liberated in the oxidation of the phosphorus reacts with surplus phosphorus trioxide, so that both phosphorus and phosphorus trioxide are oxidised.

Schenck, Mihr, and Banthien's determinations of the vapour tension of phosphorus trioxide are too high at temperatures above 63°, probably owing to the interaction of phosphorus trioxide and moisture at these temperatures, with production of phosphine.

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