II.—*On the Oxidation of Phosphorus at a Low Temperature, and the Alleged Decomposition of Phosphorous Anhydride by Sunlight.*

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IN a paper read before the Southport meeting of the British Association, by the Rev. A. Irving, on the "Action of Sunlight on Phosphorous Anhydride," the author states that phosphorous anhydride, prepared by passing a slow stream of dry air over molten phosphorus,

decomposes when exposed to sunlight into amorphous phosphorus and phosphoric anhydride, and he mentions that this action has also been noticed in Wislicenus's edition of Strecker's Chemistry.

Wishing to verify these statements, we repeated the experiment described by Mr. Irving, and slowly passed well-dried air over molten phosphorus contained in the bend of a **V**-tube, one arm of which was of considerable length and drawn out at intervals of 6 inches, so as to form three small chambers. The air, dried by passing through two chloride of calcium tubes and a wash-bottle of sulphuric acid, was passed into the short arm of the **V**-tube and over the phosphorus, which was just kept above its melting point in a water-bath, the products of the action being deposited in the chambers of the long arm of the **V**.

The deposit close to the phosphorus was reddish-brown, and in the first chamber was slightly coloured, but in the two upper portions of the tube was perfectly white. These two portions were sealed off at the estrangulations, and one was placed in direct sunlight, whilst the other was kept in the dark. The tube exposed to sunlight soon lost its pure white colour, and after a few hours changed to light brown, whilst the tube which had been kept in the dark remained perfectly white; but on examining it through a lens, the surface of the glass above the deposit was seen to be spangled with minute and very brilliant crystals, and on opening the tube and shaking out the contents, the latter spontaneously inflamed.

The presence of the crystals in the tube at once suggested that the deposit was not pure phosphorous anhydride, but a mixture containing finely divided crystalline phosphorus, and as this would fully explain the phenomena described by Mr. Irving, we determined if possible to clear up this point.

The previous experiment was repeated, the temperature of the water-bath being from 52° to 56° C., and the air being passed at such a rate that the phosphorus just faintly glowed at the point with which the air first came in contact. The tubes containing the deposit were sealed off as before, and the centre tube of the three was taken for analysis.

The tube having been weighed had one end carefully cut off, and was immediately filled with distilled water, and the contents washed out upon a filter; the tube after careful rinsing being again dried and weighed.

The residue on the filter-paper, after careful washing, was readily shown to be phosphorus, as on drying the paper on a warm dish the small crystals caught fire and burnt away, charring the paper. The filtrate was then made up to 50 c.c., and the phosphorous anhydride was determined in 25 c.c. by its reducing action on mercuric chloride,

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the remaining 25 c.c. being evaporated to a syrup with strong nitric acid to convert any phosphites into phosphates, and the total phosphate was determined as magnesium pyrophosphate, all the usual precautions being observed. The numbers so obtained give the quantities of phosphorous and phosphoric anhydrides, and the amount of phosphorus is calculated from the difference between these and the weight of the contents of the tube.

Weight of deposit in tube .. 0.029

Consisting of—

Phosphoric anhydride	0.0206 or 71.0 per cent.
Phosphorous „	0.0028 „ 9.6 „
Phosphorus (by diff.)	0.0056 „ 19.3 „

showing that instead of being pure phosphorous anhydride, it was practically a mixture of phosphoric anhydride and phosphorus with a small quantity of phosphorous anhydride.

Another series of tubes was then prepared, the temperature of the water-bath heating the phosphorus being allowed to reach 62°, whilst the rate at which the air was allowed to pass continued about the same; and the contents of the centre tube were analysed as before, giving—

Phosphoric anhydride	0.0572 or 70.1 per cent.
Phosphorous „	0.0017 „ 3.2 „
Phosphorus (by diff.)	0.0141 „ 26.6 „

Weight of deposit..... 0.0530

In a third experiment the phosphorus was melted by a small naked Bunsen flame, as in Mr. Irving's original experiment, and the results obtained on analysis were:—

Phosphoric anhydride	0.0219 or 78.2 per cent.
Phosphorous „	0.0013 „ 4.7 „
Phosphorus (by diff.)	0.0048 „ 17.0 „

Weight of deposit..... 0.0280

Another experiment was then made in which the products of the action, after passing through one depositing tube, were made to pass through a small wash-bottle containing bisulphide of carbon, the escape of which was prevented by an upright Liebig's condenser connected with it.

After the products had passed through it for some time, the bisulphide of carbon was allowed to evaporate spontaneously on blotting-

paper, leaving enough phosphorus behind to give dense fumes, but not enough to ignite the paper.

From these experiments it is evident that Mr. Irving's so-called phosphorous anhydride is a mixture containing minute crystals of phosphorus, which are rendered amorphous when exposed to sunlight, and it seems highly probable that the spontaneous inflammability claimed for phosphorous anhydride is due to the same cause.