XC.—*Phosphorous Oxide.* Part II.

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Action of Light.—In our first communication on this subject (Trans., 1890, 553), we stated that phosphorous oxide was acted upon by light. Even diffused daylight turned it yellow, and in strong sunshine it rapidly became dark-red. On melting the residual oxide and decanting it from the red product, and redistilling it, the clear, colourless substance, on exposure to sunshine, quickly became red as before.

Further observation, however, has rendered it doubtful whether *pure* phosphorous oxide is affected by light. We have been able, as a matter of fact, to prepare a sample of crystallised phosphorous oxide which, after a year's continuous exposure to light, has not suffered the slightest change in colour. A few grams of the freshly-distilled and apparently pure oxide were sealed up in a tube previously filled with dry carbon dioxide. It was then placed in the direct rays of the sun, when it rapidly became red. After nearly three months' exposure to light, the dark-red substance was warmed to the melting point of the oxide, passed through glass-wool to remove the suspended red powder, and the oxide again distilled into a fresh tube, in which it solidified in large, transparent, colourless crystals. On again exposing the crystals to light, they ultimately became as deeply-red as before. The operations of melting, filtering, and distilling were repeated a third time, but the result was the same. Finally, the oxide was simply melted at the lowest possible temperature, filtered through glass-wool, and again exposed to sunshine. It was no longer acted upon by light, but has remained perfectly clear and colourless after nearly 12 months' exposure.

The red substance is the so-called amorphous modification of phosphorus. Although the distilled oxide, when exposed to light, eventually becomes dark-red, the actual extent of decomposition is not very considerable. We have determined the weight of red phosphorus formed in one case after four months, and in another after seven months' exposure. In the first instance it was 0·8 per cent. of the total weight of oxide; in the other case it was 1·0 per cent.

We have made many attempts to obtain preparations of the oxide which should be unaffected by light, by distillation, at the ordinary temperature, in a vacuum; but however many times the same specimen was redistilled in a Sprengel vacuum, it invariably became red on exposure to light. Frequently, however, large, isolated crystals of the oxide of perfect form were obtained by slow spontaneous sublimation in a vacuum, which retained their clear, transparent appearance for days. If, however, the crystals were melted by the warmth of the hand, the liquid drops, on solidification in the wax-like form, rapidly became red. Indeed, it seems not improbable that the permanency of the crystallised oxide is in some way connected with its crystalline character.

It is of course important to determine the bearing of these observations on the question of the phosphorescence of phosphorous oxide. We have repeated our original experiments with samples of oxide which have been several times exposed to light and afterwards distilled in a vacuum, but in no case did the phosphorescence show any diminution in intensity.

Action of Bromine.—Liquid bromine acts violently upon phosphorous oxide, and the mass generally inflames. To study the nature of the change, a known quantity of the recently distilled oxide was placed in a closed glass apparatus so arranged that it could be continuously acted upon at the ordinary temperature by bromine vapour. Small, lemon-yellow, and perfectly homogeneous crystals quickly made their appearance above the oxide. These continued to grow until they were about 2 mm. in diameter; they consisted of short prisms, terminated at both ends by pyramids. It was impossible to determine their crystallographic characters with greater precision, as they deliquesced immediately when in contact with the air. Quantitative analysis showed that they consisted of pure phosphorus pentabromide. The numbers obtained were as follows:—

0·4350 gram of crystals gave 7·57 per cent. phosphorus and 93·32 per cent. bromine.

PBr_5 contains 7·19 per cent. phosphorus and 92·81 per cent. bromine.

The oxide in the flask quickly became covered with a white, amorphous powder, resembling phosphorus pentoxide. After a time both it and the crystals became dissolved in the excess of bromine which condensed upon them. When the reaction was apparently complete, the contents of the flask were distilled. A small quantity of bromine first appeared, after which the thermometer suddenly rose to 190°, and a quantity of phosphoryl bromide passed over and solidified in the receiver. It boiled constantly at 195° (corr.), and melted at 45°. The residue in the flask consisted of a dark, resinous mass, resembling the so-called "metaphosphoryl chloride" of Gustavson (compare G. N. Huntley, this vol., p. 202); it probably consisted of the bromine analogue of that compound. The first action of bromine upon phosphorous oxide appears, therefore, to result in the formation of phosphorus pentabromide and phosphoric oxide.

$$5P_4O_6 + 20Br_2 = 8PBr_5 + 6P_2O_5.$$

The pentabromide crystals are afterwards washed down upon the pentoxide by the excess of bromine, and the two substances then react, forming the oxybromide and "metaphosphoryl bromide." Hence the ultimate action of bromine upon phosphorous oxide appears to be similar to that of the action of chlorine. The reaction may thus be represented:—

$$P_4O_6 + 4Br_2 = 2POBr_3 + 2PO_2Br.$$

The yield of phosphoryl bromide actually obtained was very nearly that required by this equation.

Action of Iodine.—Iodine reacts very slowly with phosphorous oxide, forming an orange-red solid. Even when the substances are heated together in a sealed tube at 150°, the reaction is far from complete.

When the two substances are heated, under pressure, with a quantity of carbon bisulphide, phosphoric oxide is formed, and orange-red prisms of P_2I_4 separate out from the concentrated solution. No formation of the tri-iodide could be detected. The main reaction is probably in accordance with the equation

$$5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5.$$

Action of Hydrogen Chloride.—This gas is rapidly absorbed by phosphorous oxide with the formation of a viscous mass and a clear, mobile liquid. The semi-solid substance is at first quite white, but as the reaction proceeds it changes to yellow and orange. The clear liquid consists of phosphorus trichloride, boiling at 76°; the semi-solid residue is, for the most part, soluble in water, and the solution contains phosphorous and phosphoric acids. The yellow solid was identified as free phosphorus. With a view of obtaining a quantitative determination of the nature of the change, a weighed quantity of phosphorous oxide, contained in a small distilling flask, was connected with a graduated gas eprouvette standing over mercury, and which could be replenished from time to time with dry hydrogen chloride as the absorption proceeded. By noting the volume of gas absorbed, and checking the amount by occasionally weighing the flask, the amount of the reacting hydrogen chloride could be ascertained. The main action may be represented by the equation

$$P_4O_6 + 6HCl = 2PCl_3 + 2H_3PO_3.$$

Geuther (*J. pr. Chem.* [2], **8**, 359) has pointed out that phosphorus trichloride reacts with phosphorous acid to form yellow phosphorus and orthophosphoric acid, and our own observation confirms the statement. The reaction is probably

$$PCl_3 + 4H_3PO_3 = 3H_3PO_4 + P_2 + 3HCl.$$

In an actual experiment carried out by the above method, but in which the reaction was not quite complete even after a week's duration, we obtained from 5 grams of phosphorous oxide a little over 4 grams of phosphorus trichloride, 1·5 grams of orthophosphoric acid, 0·4 gram of phosphorus and 2·7 grams of phosphorous acid.

Action of Sulphur.—When phosphorous oxide and sulphur are heated together in an atmosphere of carbon dioxide or nitrogen, the two substances at first melt and form separate layers of liquid. At about 160°, however, a violent reaction occurs, and the mixture becomes solid. No gas is produced. The solid substance is an addition product, having, as we shall show, the formula $P_4O_6S_4$. Direct experiments have proved that it is formed quantitatively in accordance with the equation

$$P_4O_6 + 4S = P_4O_6S_4.$$

It may be obtained in well-formed crystals by sublimation in a vacuum, or by crystallisation from carbon bisulphide. We propose to call it *phosphorus sulphoxide*.

Phosphorus sulphoxide may be readily prepared in the following manner:—From 3 to 5 grams of recently-distilled phosphorous oxide are transferred to the bottom of a strong glass tube, closed at one end, and previously filled with dry carbon dioxide or nitrogen. The requisite amount of sulphur, preferably in the form of small crystals, calculated for the above reaction is then added, and the tube sealed at the blowpipe, and immersed for the lower half of its length in a bath of glycerin, the temperature of which is gradually raised. No reaction is apparent up to 155°, the sulphur merely melting at 115°, and forming a layer below the phosphorous oxide. At a temperature varying in different experiments from 154° to 168°, the lower layer of sulphur is suddenly projected into the phosphorous oxide, and the whole mass is violently thrown up to the top of the tube, with a distinct rushing sound.* In two or three seconds, during which time the contents of the tube are in rapid motion, the reaction is complete, and the internal walls of the tube are seen to be covered in the cooler portion with feathery, colourless crystals, together with compact masses of a yellowish-grey, crystalline solid, which fuses to a viscous liquid in the more strongly heated portion of the tube. The heating may, of course, be carried out in an air-bath, but in that case it is impossible to observe the curious phenomena accompanying the reaction. The product is next transferred to a similar tube, which is then exhausted by the Sprengel pump and sealed. On heating the lower half of the vacuous tube, the sulphoxide sublimes in perfectly colourless, strongly-refractive crystals. The sublimation begins at about 90°, but the most favourable temperature is about 140—150°. A portion of the sublimate at first condenses as a viscous liquid which subsequently solidifies to a colourless, vitreous or crystalline mass; a large proportion, however, always condenses in the form of feathery aggregations, or long needles extending across the tube, or isolated rectangular crystals. Analysis has shown that these various forms of the sublimate possess the same composition.

Phosphorus sulphoxide melts at about 102°, and boils constantly at 295° (corr.). The melting point is not very sharp, as the substance seems to become somewhat viscous before it actually liquefies. The distilled sulphoxide is pale-yellow, and almost wholly sublimes

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* It is important that the quantities taken should not exceed the amounts specified, for if more than 5 grams of phosphorous oxide and its equivalent of sulphur are employed, the reaction is so violent that it usually results in a loud explosion, the tube being shattered into fragments. The explosion is accompanied by the production of an intensely bright flame.

in a vacuum in the form of the colourless crystals above described. Three distinct preparations, analysed by oxidation with bromine-water and determination of the phosphorus by magnesia mixture and the sulphuric acid by barium chloride, yielded the following results:—

	I.	II.	III.	Calculated for $P_4O_6S_4$.
Phosphorus ...	35·81	35·71	35·94	35·63
Sulphur	36·08	36·88	36·36	36·78

It was at first surmised that the substance might be a mixed anhydride, that is, phosphoric anhydride in which a portion of the oxygen had been replaced by an equivalent amount of sulphur, or $P_2O_3S_2$; but that it actually has the composition $P_4O_6S_4$, or, in other words, is an additive compound of phosphorous oxide and sulphur, is established by the determinations of its vapour density. These were made by Victor Meyer's method, in an atmosphere of nitrogen, and at a temperature of 350—400°, using a bath of molten lead. No decomposition was evident at this temperature; on cooling, the unaltered substance was found crystallised on the walls of the cylindrical tube. The following results were obtained:—

	I.	II.	III.	Calculated for $P_4O_6S_4$.
Wt. of substance..	0·2853	0·3558	0·2700	—
Density, H = 1...	180·4	171·9	170·8	174
„ air = 1 ...	12·5	11·9	11·8	12·1

Determinations II and III were made with crystals obtained by subliming the distilled sulphoxide in a vacuum.

Phosphorus sulphoxide deliquesces rapidly in air, and hence smells of sulphuretted hydrogen. It is quickly dissolved by water, forming sulphuretted hydrogen and, at first, metaphosphoric acid:

$$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S.$$

The metaphosphoric acid passes, eventually, rapidly if the solution is evaporated upon a water-bath, into orthophosphoric acid. Phosphorus sulphoxide is readily soluble in twice its volume of carbon bisulphide, from which it crystallises unchanged. It is also soluble in benzene, upon which, however, it reacts, as the liquid becomes dark and sulphuretted products are formed.

The isolated colourless crystals of phosphorus sulphoxide obtained by sublimation in a vacuum consist of rectangular prisms, frequently attaining a length of 2 to 3 mm., and a thickness of from 1 to 2 mm. A large number of crystals have been examined goniometrically and measured, in spite of their rapid deliquescence. This result has been obtained by employing the ingenious little arrangement supplied by

Fuess, of Berlin, with the large horizontal-circle goniometer. The essential part of the arrangement consists of a small closed glass chamber, so shaped as to carry in its lower portion a desiccating substance, such as calcium chloride or phosphoric anhydride, and fitting on the adjusting table instead of the ordinary crystal holder. The crystal is enclosed in this dry chamber during the measurement, and the signal passes from the collimator to the crystal, and from the crystal face to the telescope through two adjacent plate-glass sides.

In the case of every crystal examined, no faces were observed besides those of the rectangular prism and basal plane, all the numerous angles measured being almost and in some cases exactly 90°. On examining the crystals, under the microscope, in parallel polarised light, looking through one of the three pairs of faces, the crystals are always found to be isotropic, while the other faces extinguish parallel to the prism edges. In convergent light, the uniaxial circular rings and dark cross are seen through the isotropic face, provided the crystal is at least 2 mm. thick in this direction; if thinner, only the cross is seen, owing to the feeble double refraction. On rotating the crystal, the cross appears stationary, and does not, unless badly adjusted, break up into hyperbolæ. The crystals, therefore, appear to be uniaxial, or, if biaxial, the angle between the optic axes must be exceedingly small. Hence they are probably tetragonal prisms, terminated by the basal plane.

Although several distinct preparations were made, no other faces were ever observed, the whole of the crystals being homogeneous and exhibiting nothing but pinacoidal faces and basal plane. In order to obtain, if possible, crystals showing further forms, so as to enable the axial ratios to be determined, a considerable quantity of the sulphoxide obtained by sublimation in a vacuum was dissolved in carbon bisulphide, and the latter slowly evaporated in a vacuum from one limb of a V-tube to the other by cooling the second limb with ice. Large, well-formed crystals were again obtained, but they consisted, like those formed by sublimation, of tetragonal prisms terminated by the basal plane and exhibited no other faces whatever.

As previously mentioned, the sulphoxide is sometimes deposited, generally in that part of the tube nearest the surface of the glycerin of the bath, as a colourless, viscous liquid. On cooling, this solidifies to a transparent glass, which sooner or later devitrifies into crystals of the same form as the isolated ones. Generally, the formation of crystals occurs an hour or so after cooling, but in one case devitrification suddenly set in several days after preparation, with production of fantastic feathery aggregations of the rectangular crystals. The fact that the isolated crystals, the vitreous modification, and the feathery and acicular forms are composed of the same substance was proved by direct analysis. The feathery forms are merely aggregations of small, tetragonal prisms, and the needles, similar prisms largely developed in the direction of the vertical axis.

Action of Selenium.—Selenium appears to form a crystalline compound with phosphorous oxide, similar to the sulphoxide, but owing to the fact that the phosphorous oxide is largely decomposed at the temperature of the reaction, the sublimed substance is mixed with the products of the decomposition.

Action of Sulphur Trioxide.—When the vapours of sulphur trioxide and phosphorous oxide are allowed to act on one another in a closed apparatus at the ordinary temperature, white flocks of phosphoric anhydride are deposited upon the walls of the apparatus, and sulphur dioxide is liberated. When the two oxides are separately placed at the two ends of a closed tube fitted with a side tube connected with a gas cylinder standing over mercury, and the phosphorous oxide is slowly melted down upon the sulphur trioxide, a somewhat violent reaction occurs with evolution of heat, formation of phosphoric anhydride, and liberation of sulphur dioxide. Even when the reaction is moderated by cooling with ice, no compound of the two oxides appears to be formed, but merely an oxidation of the phosphorous oxide at the expense of the sulphur trioxide.

Action of Sulphuric Acid.—Concentrated sulphuric acid dropped upon phosphorous oxide occasions a great rise of temperature. Sulphur dioxide is liberated and the phosphorous oxide becomes oxidised to phosphoric acid. When quantities of a gram and upwards are employed, the reaction is so violent that the mass generally ignites.

Action of Sulphur Chloride.—Sulphur chloride, S_2Cl_2, acts with great violence on phosphorous oxide, forming phosphoryl and thiophosphoryl chlorides, free sulphur, and sulphur dioxide:

$$P_4O_6 + 6S_2Cl_2 = 2POCl_3 + 2PSCl_3 + 2SO_2 + 8S.$$

Action of Ammonia.—Ammonia slowly reacts in the cold with phosphorous oxide. A small quantity of phosphorous oxide placed in a tube over mercury in an atmosphere of ammonia absorbed a quantity of ammonia corresponding to between 7 and 8 mols. of ammonia per mol. of phosphorous oxide. When ammonia is led over phosphorous oxide melted by the warmth of the hand, in an apparatus previously filled with nitrogen, a somewhat violent reaction occurs with production of a white cloud; the mass ignites, and a considerable quantity of amorphous phosphorus or the red suboxide is formed. The violence of the reaction may, however, be controlled by surrounding the flask with iced water. On removing the cold bath and again melting by the hand, the same sudden combination with production of flame occurs.

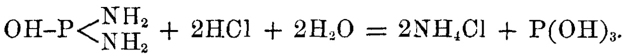
The reaction between ammonia and phosphorous oxide is more easily regulated when the phosphorous oxide is dissolved in benzene or ether. When benzene was used as the solvent, the reaction was accompanied by a rise of temperature to about 50°, necessitating occasional cooling by a cold-water bath. The formation of a white solid begins with the passage of the first bubbles of ammonia, and it is necessary to shake the flask continually so as to prevent the formation of a solid layer upon the surface of the liquid. When no more heating is noticeable upon removing the cold bath, the reaction is at an end, and the benzene may then be evaporated away in a vacuum. If the benzene is distilled off over a water-bath, considerable decomposition occurs. In two experiments performed in an apparatus previously filled with nitrogen, the amount of ammonia taken up corresponded to a little over $6NH_3$ and $7NH_3$ respectively. The reaction is most readily carried out when ether is used as a solvent of the phosphorous oxide, there being but little heating effect even when large quantities are used. 15·63 grams of phosphorous oxide took up 8·46 grams of ammonia, corresponding to a little over $7NH_3$. The same white product is obtained as in the case of phosphorous oxide dissolved in benzene, together with smaller quantities of a yellowish, viscous or deliquesced substance. The ether may readily be removed by gently warming in a current of nitrogen. An analysis of 0·843 gram of the solid white substance, separated as completely from the viscous substance as possible, showed the presence of 37·8 per cent. of phosphorus. This corresponds approximately with the hitherto unknown diamide of phosphorous acid, $OH{\cdot}P{<}^{NH_2}_{NH_2}$, which contains 38·7 per cent. of phosphorus. A complete separation of the diamide from the viscous substance is impossible, owing to the highly inflammable nature of the product of the reaction, which takes fire at once in contact with the air.

It appears probable that phosphorous oxide reacts with 8 mols. of ammonia with the formation of 4 mols. of phosphorous diamide and 2 mols. of water, which may further react with production of a molecule of the corresponding di-ammonium salt. The appearance of deliquescence or formation of small quantities of a viscous substance is probably due to the action of the water produced:

$$P_4O_6 + 8NH_3 = 4OH{-}P{<}^{NH_2}_{NH_2} + 2H_2O;\ 2H_2O + OH{-}P{<}^{NH_2}_{NH_2} = OH{-}P{<}^{ONH_4}_{ONH_4}.$$

$$\text{Or}\qquad P_4O_6 + 8NH_3 = 3OH{-}P{<}^{NH_2}_{NH_2} + OH{-}P{<}^{ONH_4}_{ONH_4}.$$

Phosphorous diamide is a white powder which dissolves instantly in water with sufficient rise of temperature to induce incandescence. When heated in a dry test-tube, ammonia is evolved, then fusion and a partial sublimation occur. Treated with moderately dilute hydrochloric acid, a violent reaction occurs with liberation of non-spontaneously inflammable phosphoretted hydrogen, separation of free phosphorus, and formation of a solution of ammonium chloride and phosphorous and phosphoric acids. The fact that the gas evolved was phosphoretted hydrogen was established by a determination of its vapour density by the method described by Thorpe and Rodger in their paper on "Thiophosphoryl Fluoride" (Trans., 1889, **55**, 306). The density obtained was 17·4, that of pure phosphoretted hydrogen being 17·0. In this reaction, the effect of the hydrochloric acid appears to be first to form ammonium chloride and phosphorous acid, but the heat of the reaction is so great that the latter compound is partially converted into phosphoretted hydrogen, phosphoric acid, and free phosphorus:



$$OH{-}P{<}\genfrac{}{}{0pt}{}{NH_2}{NH_2} + 2HCl + 2H_2O = 2NH_4Cl + P(OH)_3.$$

Substituted ammonias behave similarly with phosphorous oxide dissolved in ether, forming the corresponding substituted diamides of phosphorous acid, as white and somewhat viscous solids, which evolve phosphoretted hydrogen on the addition of hydrochloric acid, with separation of yellow phosphorus.

Action of Nitrogen Peroxide.—A few grams of phosphorous oxide were placed in one V of a W-tube, and a corresponding quantity of liquid nitrogen peroxide in the other, and the open ends of the apparatus sealed. After some days, it was found that the phosphorous oxide had become converted into a voluminous mass of what was afterwards proved by analysis to be phosphoric anhydride. The red liquid nitrogen peroxide had simultaneously become green. On softening one end of the apparatus in a flame, comparatively little gas escaped. Hence it appears probable that the phosphorous oxide had become oxidised to phosphoric anhydride and the nitrogen peroxide reduced to nitrogen trioxide or nitric oxide, which changed the original colour of the nitrogen peroxide to green. No compound of phosphorous oxide and nitrogen peroxide appeared to be formed, for on dissolving the bulky white substance in water violent hissing occurred, but no red fumes escaped, and the solution gave no reaction with ferrous sulphate.

Action of Phosphorus Pentachloride.—Phosphorus pentachloride reacts somewhat violently with phosphorous oxide, with considerable evolution of heat. The product is a liquid which is raised to its temperature of ebullition, unless the containing vessel is cooled by ice.

The reaction is complete when the proportion of 6 mols. of phosphorus pentachloride to 1 mol. of phosphorous oxide is employed. When the liquid has cooled to the ordinary temperature, and no further rise of temperature occurs on shaking, it may safely be distilled, when it is found to be a mixture of phosphorus trichloride and phosphoryl trichloride :

$$P_4O_6 + 6PCl_5 = 6POCl_3 + 4PCl_3.$$

Action of Phosphorus Trichloride.—Phosphorus trichloride and liquid phosphorous oxide are miscible without action at ordinary temperatures, and practically the whole of the phosphorus trichloride may be distilled off unchanged. When heated together in a sealed tube at 180° for some hours, however, provided the phosphorus trichloride is not present in more than the proportion of 4 mols. to 1 mol. of phosphorous oxide, the whole is converted into solid products. As the temperature is rising towards 180°, a white solid commences to be deposited, which rapidly turns yellow and then red. The formation of the solid continues until the whole mixture is solid. The red solid is found to consist of a mixture of phosphorus pentachloride, phosphorus pentoxide, and amorphous phosphorus. The phosphorus pentachloride may be readily extracted by carbon bisulphide. Phosphorus trichloride, therefore, appears to react with phosphorous oxide only at a temperature approaching the boiling point of the latter, and in a closed apparatus under these circumstances does not form phosphoryl trichloride, but a mixture of pentachloride and pentoxide of phosphorus together with amorphous phosphorus.

Hydrogen, phosphoretted hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen, nitric oxide, cyanogen, and ethylene have apparently no action upon either cold or warm phosphorous oxide.