CCL.—*Besson's Supposed Phosphorus Suboxide*, P_2O.

By LESLIE JAMES CHALK and JAMES RIDDICK PARTINGTON.

BESSON describes (*Compt. rend.*, 1897, **124**, 763; 1897, **125**, 1032; 1901, **132**, 1556; compare *Bull. Soc. chim.*, 1900, **23**, 582) the preparation of an oxide, P_2O, (i) by heating phosphoryl chloride with phosphonium bromide, (ii) by the action of a slow stream of air on a solution of phosphorus in carbon tetrachloride, and (iii) by heating a concentrated solution of phosphorous acid with phosphorus trichloride. The identical products are stated to be yellowish-red and stable at 100°, but decomposed in a vacuum at 135° with the evolution of oxygen. Analysis gave about 79% of phosphorus (P_2O requires 79·49%). The substances obtained by Michaelis and Pitsch (*Ber.*, 1899, **32**, 337; *Annalen*, 1900, **310**, 45) by the action of hydrochloric acid on a solution of yellow phosphorus in aqueous-alcoholic potassium hydroxide, and by the action of acetic anhydride on a solution of hypophosphorous acid in glacial acetic acid, were considered by Besson to be largely P_2O contaminated by phosphorus and solid hydrogen phosphide.

Preparation of Besson's Oxide.—10 G. of Kahlbaum's phosphorous acid were dissolved in 8 g. of water in a flask under a reflux condenser and 50 g. of phosphorus trichloride were added. Hydrogen chloride was steadily evolved and crystals were formed. These consisted of phosphorous acid, and not phosphorus trioxide, as required by the equations given by Besson, *viz.*, $PCl_3 + H_3PO_3 = 3HCl + P_2O_3$, followed by $2P_2O_3 = P_2O + P_2O_5$. On heating for about 15 minutes on a water-bath with shaking, the crystals disappeared and a yellow solid began to separate. On further heating, red particles appeared. A viscous layer settled out which contained most of the deposit, the upper layer being unchanged phosphorus trichloride. Reaction is complete in 6 hours. Besson states that a substance with the appearance of phosphorus pentoxide is formed in the reaction, but this could not be confirmed, neither was a hissing noise observed on adding water to the residue, although heat was evolved by the action of water on unchanged trichloride—if the upper layer is poured off before the addition of water there is practically no evolution of heat.

The product was filtered, washed with cold water according to the directions of Besson, and dried in a vacuum over phosphorus pentoxide for 3 weeks. The filtrate contained phosphorous, phosphoric, and hydrochloric acids, most of the phosphorus being in the form of phosphorous acid. The dry powder was yellowish-red, but contained darker red particles, and was free from chlorine. The yield from 10 g. of phosphorous acid was 0·7 g. In this way, the preparations numbered I, II, III, and VII in the tables were obtained.

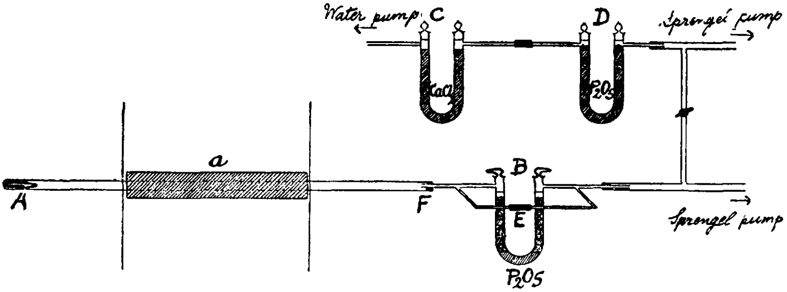
Action of Phosphorus Trichloride on Crystalline Phosphorous Acid.—Although the preceding experiment was performed exactly as specified by Besson, it was clear that it would be better to use crystalline phosphorous acid instead of the solution. 50 G. of phosphorus trichloride and 10 g. of solid phosphorous acid did not react until the mixture was warmed; the acid then dissolved completely and a yellow solid soon appeared. This turned redder on further heating for 5 or 6 hours, and the product was then isolated and dried as before. It was exactly similar in appearance to the previous product. The liquid poured off from the solid was mainly unchanged trichloride (43 g.). The yield of "oxide" was about the same as in the first method. The preparations numbered IV, V, VI, and VIII were obtained by this method. Preparation V, containing 86·7% of phosphorus, was not further examined.

The Action of Phosphorus Trichloride on Phosphorous Acid below 70°.—50 G. of phosphorus trichloride and 10 g. of phosphorous acid were heated so that the temperature never rose beyond 70°. The action was slow, but no further yield appeared after 20 hours. Only 0·15 g. of product resulted, which was pure yellow without any tinge of orange, and appeared homogeneous under the microscope. The washings contained phosphorous acid and a small amount of phosphoric acid, but no hypophosphorous acid. The upper layer yielded 33·5 g. of unchanged trichloride. The dry powder, specimen IX, had a stronger odour of phosphine than that prepared at 100°.

Analysis of the Products.—The preparations were analysed by the method described by Chapman and Lidbury (J., 1899, **75**, 973), except that phosphoric acid was estimated by the method described by Treadwell (" Quantitative Analysis," p. 437).

The water and hydrogen contents of the preparations were determined by a modification of the apparatus described by Burgess and Chapman (J., 1901, **79**, 1235), which is shown in Fig. 1. The aluminium foil used by these experimenters was omitted. The substance was weighed into a small tube, A, which was introduced into the Bohemian-glass tube, F, 9 mm. in diameter and 120 cm. long. The part inside the resistance furnace, *a*, contained a roll of bright copper gauze. The whole apparatus was first thoroughly cleaned and dried by prolonged heating in a vacuum. The junction with the phosphorus pentoxide absorption tube, B, was made with sealing wax, since this part remained quite cool, so that the tube B could be removed easily for weighing. A screw-clip on the pressure tubing, E, enabled the tube B to be evacuated independently of the tube AF. The substance in A darkened on heating and evolved gas, which was collected in the receiver of the Sprengel pump exhausting the apparatus. When no further gas collected and a vacuum was re-established, the apparatus was allowed to cool and disconnected, and the tubes A and B were weighed. The tube A contained a dark grey residue, sometimes containing white, opaque specks, which were not glassy. Practically the whole of the phosphorus content of this residue could be extracted by boiling water, but the undissolved residue was in every case analysed for phosphorus.

FIG. 1.



When the preparations were heated with water in a sealed tube for 8 hours at 100°, and the tube was opened under mercury, only a very small diminution in volume was noticed, and the solution was found to contain phosphorous, but not hypophosphorous, acid. Besson attributed the production of phosphorous acid in this experiment to oxidation of P_2O : $P_2O + O_2 + 3H_2O = 2H_3PO_3$, the absorption of oxygen being inferred from a diminution of pressure; he also noticed a smell of phosphine. We find no such diminution of pressure, and there can be no doubt from this and from the quantitative experiments described below that the phosphorous acid is present as such in the original preparations. On further heating the residue from this experiment with water, more phosphorous acid was obtained, but in diminished amount, and an adsorption phenomenon is indicated. The presence of uncombined water in the preparations is considered improbable, since a portion of preparation III, on being kept in a vacuum over phosphorus pentoxide for 2 months, gave practically the same results for water and hydrogen on distillation (0·1 g. gave 0·0142 g. of residue with 43% P, 2·2 c.c. of hydrogen and 0·0056 g. of H_2O) as the freshly dried preparation. The probable constituents of the preparations are therefore : free phosphorus, phosphorous acid, and solid hydrogen phosphides. The preparation made below 70° may be expected to contain more solid phosphides, since a slow reaction between phosphorus trichloride and phosphorous acid in the cold is said to give these substances, whilst at higher temperatures (170°) red phosphorus is said to be the only product.

We assume that the only primary constituents of the preparations are phosphorous acid and phosphorus, the amount of the former being directly estimated from the phosphoric acid in the residue left after distillation in a vacuum. The weight of water and the volume of hydrogen obtained on distillation in vacuum can then be compared with those calculated from the equation : $8H_3PO_3 = 3P_2O_5 + 9H_2O + 2P + 3H_2$. The phosphorus content of the residue was generally above 40%, whereas that of metaphosphoric acid is 38·8% and that of phosphorus pentoxide 43·7%. That the residue should consist mainly of phosphorus pentoxide rather than metaphosphoric acid might appear improbable, but the pentoxide may be produced by the prolonged heating in vacuum of free phosphorus and metaphosphoric acid : $10HPO_3 + 2P = 6P_2O_5 + 5H_2$. The results of the distillation experiments, as is seen from Table I, are in agreement with this hypothesis, except that the hydrogen obtained from the oxide prepared below 70° was greater than the calculated amount, a result which would be expected if solid hydrogen phosphides are present. In other cases, the hydrogen calculated is only slightly lower than the experimental value, which may indicate the presence of a little solid hydrogen phosphide (compare Burgess and Chapman, *loc. cit.*). The dark colour of the residue obtained on heating in a vacuum is probably due to a trace of free carbon derived from organic matter introduced from the cork of the flask in the preparation of the "oxide." This was estimated by difference on the assumption that the remainder of the residue was phosphorus pentoxide, and it was always very small.

In all cases the gas collected from 0·1 g. of preparation was 2—4 c.c. It was shown to be hydrogen by explosion with oxygen. No contraction was observed with the gas, before or after explosion, in contact with dilute acid or alkali. The contraction on explosion was slightly less than the calculated, although no gas except hydrogen could be detected by qualitative tests. The alleged evolution of oxygen on heating the substance was negatived by experiments in which the copper gauze was omitted. The gas collected in this case was phosphine; it suffered no contraction in contact with alkaline pyrogallol, and on explosion with oxygen gave white fumes of phosphoric acid. The phosphorus contents of the various preparations were as follows :

Preparation.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
% P.	85·1	86·0	86·8	81·1	86·7	86·2	88·8	88·2	87·6

These results definitely exclude the composition P_2O.

In Table I, column 2 gives the actual amount of oxide used in the analysis. The figures in the remaining columns, however, have been calculated to 0·1 g. of oxide for the purpose of comparison. This applies also to all the figures in Tables II and III.

TABLE I.

Effect of distillation of the preparations.

Prep. No.	Weight (g.).	Residue (g.).	H_2O (g.).	Gas (c.c.).	H_2 (c.c.).	H_2O (calc.) (g.).	H_2 (calc.) (c.c.).
I	0·0950	0·0160	0·0059	2·8	2·6	0·0054	2·2
II	0·1081	0·0155	0·0065	3·0	2·9	0·0057	2·4
III	0·1060	0·0135	0·0051	2·2	2·0	0·0050	2·1
IV	0·0987	0·0176	0·0074	3·5	3·2	0·0064	2·7
VI	0·0945	0·0149	0·0063	2·5	2·5	0·0054	2·3
VII	0·0993	0·0121	0·0050	1·7	1·5	0·0044	1·8
VIII	0·1058	0·0128	0·0055	2·1	1·9	0·0047	2·0
IX	0·0595	0·0116	0·0044	4·6	4·4	0·0034	1·4

Specimen IV still contained phosphorous acid which could be extracted by washing. Specimens VII and VIII were washed for a longer time than the others and the phosphorus content is higher, indicating a more complete removal of phosphorous acid. Only 0·0595 g. of Specimen IX was available for distillation.

Table II contains the analyses of the residues left after distillation. Except in the cases of Preparations I and IX, all the phosphorus (as phosphoric acid) was extracted by boiling water. In these two cases, the residues after extraction contained 0·0010 g. and 0·0008 g. of free phosphorus, respectively (compare Burgess and Chapman, *loc. cit.*). The fifth column gives the amount of phosphorous acid equivalent to the phosphorus contained in the residue as P_2O_5, the sixth the amounts of hydrogen and oxygen equivalent to this, *viz.*, $(H_3PO_3)\times(51/82)$. The last column contains the sum of the weights of phosphorus, hydrogen, carbon, and oxygen in 0·1 g. of preparation, *i.e.*, the sum of the figures in columns 4, 6, and 7, and is equal to 0·1 to within 2%. This supports the hypothesis that the supposed oxide P_2O contains free phosphorus and phosphorous acid only.

TABLE II.

Composition of residue after distillation.

Prep. No.	Weight g.	% P in residue.	C. (calc.).	H_3PO_3 equiv. to P extracted.	H and O as H_3PO_3.	P in 0·1 g. "oxide."	Total.
I	0·0160	38·4	0·0009	0·0217	0·0135	0·0851	0·0995
II	0·0155	42·0	0·0005	0·0230	0·0143	0·0860	0·1008
III	0·0135	42·2	0·0006	0·0201	0·0125	0·0868	0·0999
IV	0·0176	42·0	0·0007	0·0261	0·0162	0·0811	0·0980
VI	0·0149	42·2	0·0005	0·0222	0·0138	0·0862	0·1005
VII	0·0121	41·5	0·0006	0·0177	0·0110	0·0888	0·1004
VIII	0·0128	42·5	0·0004	0·0192	0·0119	0·0882	0·1005
IX	0·0116	37·2	0·0009	0·0139	0·0086	0·0876	0·0971

The percentage of phosphorus in Preparations VII and VIII corresponds very nearly with that in the supposed suboxide P_4O, but the behaviour on distillation in a vacuum is different. Burgess and Chapman (*loc. cit.*) found that 0·1 g. of the supposed P_4O gave on distillation about 10 c.c. of hydrogen and left practically no residue, whereas these preparations give only 1—3 c.c. of hydrogen and leave 12% of residue. Burgess and Chapman, however, decomposed the water vapour by heated aluminium.

From the experimentally determined values of phosphorus, oxygen, and hydrogen in the supposed oxide, a formula for the latter may be calculated. This is done in Table III, in which the total should be 0·1 g. This is seen to be the case within 2%. The oxygen is calculated on the assumption that the phosphorus extracted by hot water from the residue after distillation existed as pentoxide.

The properties of the supposed oxide are similar to those of scarlet amorphous phosphorus and of the supposed solid hydrogen phosphides. It is insoluble in water, alcohol, benzene, chloroform, or ether. Dilute nitric acid dissolves it at 40°, whilst concentrated nitric acid causes inflammation. Hydrogen peroxide and sodium

TABLE III.

Prep. No.	P (obs.).	H_2O (obs.).	O (calc.).	H (obs.).	C (obs.).	Total.	Formula.
I	0·0851	0·0059	0·0079	0·0002	0·0009	0·1000	$P_2O_{0·59}H_{0·65}$
II	0·0860	0·0065	0·0084	0·0003	0·0005	0·1017	$P_2O_{0·64}H_{0·70}$
III	0·0868	0·0051	0·0073	0·0002	0·0006	0·1000	$P_2O_{0·53}H_{0·53}$
IV	0·0811	0·0074	0·0095	0·0003	0·0007	0·0990	$P_2O_{0·77}H_{0·68}$
VI	0·0862	0·0063	0·0081	0·0002	0·0005	0·1013	$P_2O_{0·62}H_{0·67}$
VII	0·0888	0·0050	0·0065	0·0001	0·0006	0·1010	$P_2O_{0·48}H_{0·48}$
VIII	0·0882	0·0055	0·0070	0·0002	0·0004	0·1013	$P_2O_{0·52}H_{0·55}$
IX	0·0876	0·0044	0·0056	0·0004	0·0009	0·0989	$P_2O_{0·42}H_{0·63}$

hypochlorite solution oxidise it to colourless solutions containing phosphoric acid. Concentrated ammonia turns it slightly darker in colour, the original colour being restored by exposure to air or by the action of acids. Alcoholic potassium hydroxide forms a dark red solution with evolution of phosphine, the solution being similar to that formed by the supposed suboxide P_4O (as was found by trial).

The mechanism of the formation of Besson's substance (which is really of variable composition) is probably as follows. The phosphorous acid may be decomposed with evolution of phosphine. The latter is known to react with phosphorus trichloride giving, according to the conditions, solid hydrogen phosphide or phosphorus. When prepared at lower temperatures, the product may contain appreciable amounts of solid hydrogen phosphide. It is also possible that phosphorus trioxide may be formed by the action of the trichloride on phosphorous acid (Abegg, "Handbuch," III, iii, 420; the reference to Krafft and Neumann, *Ber.*, 1901, **34**, 566, there given does not appear to be relevant). The trioxide might then decompose, either alone or by interaction with phosphorus trichloride, to form phosphorus or solid hydrogen phosphides.

Summary.

The supposed oxide of phosphorus, P_2O, formed by the action of phosphorus trichloride on phosphorous acid under the conditions described by Besson has neither the composition nor properties attributed to it by that investigator. It is somewhat variable in composition and appears to be a mixture of finely divided amorphous phosphorus with strongly adsorbed phosphorous acid, although, especially when prepared at lower temperatures, solid hydrogen phosphides may be present. The amount of oxygen present is always much less than is required by the formula P_2O, and hydrogen also is always present, even after prolonged drying over phosphorus pentoxide.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

[*Received, May* 24*th*, 1927.]