

XXVI.—CONTRIBUTIONS FROM THE LABORATORY OF
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XIX. *Compounds of the Oxides of Phosphorus with Sulphuric Anhydride.*

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1. R. WEBER (*Ber.*, **20**, 86) describes a solid compound of sulphuric and phosphoric anhydrides, $P_2O_5, 3SO_3$, which he prepared by distilling off in a sealed tube the excess of sulphur trioxide from a mixture of the two substances. It is decomposed at 30° .

2. As this appears to be the only compound of an oxide of phosphorus and sulphuric anhydride which has been described, I endeavoured to ascertain whether it might not be possible to prepare the compound $M_2O_3, 2SO_3$, which is so very stable in the case of nitrogen, and has a definite existence in the case of arsenic, whilst in the cases of antimony and bismuth the trisulphate, $M_2O_3, 3SO_3$, is formed.

The compounds of arsenic and antimony are directly obtained from the sesquioxide without oxidation, but in the case of nitrogen it is formed from nitric oxide, which, during the course of the reaction, becomes oxidised at the expense of the sulphur trioxide; consequently, I started with "acid phosphorous anhydrous," obtained from Messrs. Harrington Bros., Cork.

Quite recently, Thorpe and A. E. Tutton (*Trans.*, 1890, **57**, 545) have prepared pure phosphorous anhydride, which differs from the above in several respects, since the latter melts only at a considerably higher temperature than 30° , is not decomposed by light at any rapid rate, and is instantly soluble in water; the acid obtained from Messrs. Harrington contains 65.1 per cent. of P_2O_5 , and is, therefore, approximately H_3PO_3 , which contains 67.1 per cent. of P_2O_5 .

3. Anhydrous phosphorous acid dissolves quietly in concentrated sulphuric acid without forming an insoluble compound. The mixture when warmed gives off sulphur dioxide, and contains phosphoric acid only.

4. When anhydrous phosphorous acid was dropped into sulphur trioxide, there was a great development of heat, accompanied by the formation of sulphur dioxide and some sulphur. A blue, oily compound separated out in small quantity from the trioxide, which was itself coloured a fine indigo-blue. At the high temperature produced by the reaction, the phosphorous acid had reduced some of the trioxide

to sulphur, which dissolved in the trioxide to form blue sulphur sesquioxide.

In order to avoid the effect of the rise of temperature, the sulphur trioxide was distilled into a beaker to form a layer of about 2 mm. deep, which was then placed in a freezing mixture. The phosphorous acid was then carefully dropped, in small pieces, on the solid trioxide; as before, they united with violence, but formed no sulphur sesquioxide if the addition were gradual enough.

The compound remained liquid on the surface of the solid trioxide, and the contact and union of the phosphorous acid and the solid trioxide was seen to be accompanied by the liberation of a gas, which proved to be sulphur dioxide.

After the compound had remained in contact with the sulphur trioxide in the freezing mixture for some time, it was poured off and analysed. The results, which were fairly concordant, were as follows:—

	I.	II.	III.	IV.	V.	VI.
SO ₃	53·47	54·36	—	—	—	—
P ₂ O ₃	0·88	—	1·72	1·04	—	—
P ₂ O ₅	—	—	—	—	34·54	30·19
Calculated for						
	P ₂ O ₃ ,2SO ₃ .			P ₂ O ₅ ,2SO ₃ .		H ₃ PO ₄ ,3SO ₃ .
SO ₃	59·26			52·98		55·14
P ₂ O ₃	40·74			—		—
P ₂ O ₅	—			47·02		32·38

The phosphorous acid is almost completely oxidised, by the reduction of the trioxide in the cold, to sulphur dioxide, and, if warm, to sulphur dioxide and sulphur, forming the compound H₃PO₄,3SO₃.

5. The compound H₃PO₄,3SO₃ is a viscid liquid, generally coloured light-brown. It fumes in contact with the air, and dissolves in water with the development of heat, but without violence, forming sulphuric and orthophosphoric acids with only a trace of the pyro- and meta-acids. It is, on the whole, best represented as sulphonyl phosphate, (SO₃H)₃PO₄.

6. As phosphorous acid is so readily oxidised by sulphur trioxide, and as the lower oxides of phosphorus, with the exception of P₄O, are not well known, I next tried the action of phosphorus on sulphur trioxide.

When a piece of phosphorus is dropped into liquid sulphuric anhydride, it reduces the latter with violence to sulphur dioxide, and is itself oxidised, forming a white, flocculent solid floating in the liquid. When the pieces of phosphorus were large, the heat of com-

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bination raised the temperature of the phosphorus sufficiently high to ignite it.

It is difficult to free the solid from adhering trioxide, and at the same time to prevent its spontaneous ignition from the oxidation of finely divided globules of phosphorus disseminated throughout its mass. The trioxide requires to be near its boiling point for the reaction to take place, and this fuses the phosphorus.

The best way of obtaining a fairly pure product is to press out the phosphorus under water into a very thin plate, and then to drop pieces of this into the warmed trioxide. The reaction is violent, and frequently accompanied by a rain of sparks of burning phosphorus. When the reaction is complete, the trioxide is boiled, and the compound raked out on a warm, dry porous tile, which is placed in a desiccator over phosphoric anhydride in a warm place in the dark for two to three hours. The product can then be placed in a weighing bottle.

I have tried manipulating in an atmosphere of carbonic anhydride, but got no better results. Distilling the excess of trioxide from the compound is not a successful operation, as oxidation occurs just when the trioxide is gone. The solvents of phosphorus decompose the substance, and the method which seems to give the best results is to work at a low temperature in a dry atmosphere.

Heating phosphorus with sulphur trioxide in a sealed tube not only oxidises all the phosphorus, but converts it at once into phosphoric anhydride, which forms a clear solution in the trioxide.

The product prepared as above gave the following results on analysis :—

	I.	II.	III.	IV
P	35·03	32·33	—	—
SO ₃	—	33·85	30·83	—
P ₂ O ₃	—	—	—	35·93
	Calculated for			
	P ₂ O ₃ .SO ₃ .	P ₂ O ₄ .SO ₃ .	3P ₂ O ₄ .2SO ₃ .	
P	32·63	30·10	34·57	
SO ₃	42·10	38·82	29·75	
P ₂ O ₃	57·89	30·58	35·12	

The compound which must be represented as 3P₂O₄.2SO₃ decomposes on standing for 2—3 weeks over phosphoric anhydride in air into P₂O₅ and SO₂. The same change occurs when the substance is heated without sulphur trioxide to a temperature of about 55—60°; in this case the sulphur dioxide is given off in bubbles from the frothy mass. It is to be noted that P₂O₅.3SO₃ decomposes at 30°. It

is darkened very rapidly by light, which is rather more characteristic of P_2O_3 than of P_2O_4 . It is instantly decomposed by water, but the phosphorus-containing part dissolves only very slowly, which is also characteristic of P_2O_3 , and not of P_2O_4 , which dissolves immediately.

The group sulphate $P_2O_3, 2SO_3$, then, is not formed by this reaction, nor by any conditions attainable at present, its place being taken by the above compound, $3P_2O_4, 2SO_3$.

I have much pleasure in acknowledging the assistance of Mr. Pattison Muir, to whom I am indebted for the use of the laboratory of Gonville and Caius College during this work.
