277. *The Reaction of Phosphoric Anhydride with Nitrogen Dioxide and with Nitric Oxide.*

By E. M. STODDART.

It has been shown that phosphoric anhydride and nitrogen peroxide (dioxide) react at 250° to form a glassy *compound*, $P_2O_5,2NO$, with the liberation of oxygen. The compound P_2O_5,xNO_2, previously described by Smith and Hartung, does not appear to exist. The former compound is also formed by direct union of nitric oxide and phosphoric anhydride. The observations are of importance in considering the influence of " intensive drying " on the reaction between nitric oxide and oxygen.

SMITH (J., 1928, 1886) showed that nitrogen peroxide became colourless when heated for 6½ hours in contact with phosphoric anhydride at 250—300°. He accounted for this behaviour by assuming that the loss in colour was due to (i) reaction of the two reagents to form a compound, which had previously been prepared by Hartung and mentioned privately to Prof. Donnan, (ii) dissociation of the nitrogen peroxide, giving nitric oxide and oxygen, which did not recombine on cooling because the gases had then become intensively dried. The latter point seemed to be definitely proved when he showed that the dried gases, when collected in a tube which was opened under mercury, and moistened by addition of water, became brown owing to their reaction to form nitrogen peroxide. Smith points out that the water did not cause decomposition of the nitrogen peroxide–phosphoric anhydride compound, which was also believed to be present, because " no gas was seen to rise from the compound which was covered with mercury "; therefore the water merely caused the recombination of the dried gases.

Now, nitrogen peroxide is completely dissociated into nitric oxide and oxygen only at 600°, and Smith has shown that dried nitrogen peroxide is more stable than the ordinary gas; yet his observations, above, imply that complete dissociation occurs at 250—300°.

During a research into the conditions of reaction of nitric oxide (to be published later), the author considered that these contradictory results merited close investigation. As a prelude to the work, a clean dry Carius tube containing 2 c.c. of dry liquid nitrogen tetroxide was sealed; a similar tube containing in addition a little freshly sublimed phosphoric anhydride was also sealed. Both tubes were heated to 150°, and after a short time, the second tube exploded whereas the other did not. This was repeated many times to ensure that the explosions were in no way due to faulty sealing but to the development of high pressure. If Smith's conclusions were correct, no explosion would have been expected if the compound P_2O_5,xNO_2 was formed in large quantities. Therefore the high pressure must be generated (*a*) by the dinitrogen tetroxide dissociating completely into nitric oxide and oxygen with little formation of compound, which is unlikely at 150° (see above), or (*b*) by the dinitrogen tetroxide forming some compound with the phosphoric anhydride and liberating oxygen. The following experiments establish the existence of the *compound* $P_2O_5,2NO$.

EXPERIMENTAL.

Preparation of Materials.—Phosphoric anhydride was introduced into a long, dry Pyrex tube, and repeatedly sublimed along the tube in a current of oxygen. The final sublimation carried the anhydride into a wide-mouthed bottle, which was then stoppered.

The dinitrogen tetroxide was prepared by heating pure lead nitrate, first gently in a porcelain dish to expel moisture, and then strongly in a Pyrex tube, the evolved gases being passed into a vessel (Fig. 1) cooled in ice–salt. This vessel contained a small quantity of the pure phosphoric anhydride, which was easily introduced by removing one of the stoppers. The condensed dinitrogen tetroxide was thus dried. When 10 c.c. of the yellow liquid had been collected, it was repeatedly distilled in a current of oxygen into similar tubes containing a little phosphoric anhydride, the distillations ensuring that the material was very dry. The tetroxide was stored in one of these tubes over the anhydride.

It was essential to use pure dry materials, otherwise a product was obtained which contained a little moisture, probably in the form of phosphoric acid, which vitiated the determination of the formula of the compound.

Repetition of Smith's Observations.—A clean dry Carius tube was filled with dry nitrogen peroxide in contact with a little phosphoric anhydride, and heated to 250° for one hour. No explosion resulted, and the tube now contained a colourless gas; it was opened under dry mercury, and water admitted; no gas seemed to escape from the phosphoric anhydride compound, but nitrogen peroxide was formed in large quantities. These observations are in strict agreement with Smith's results, but further experiments showed that his interpretation was incorrect.

Investigation of the Products of Reaction.—The tube shown in Fig. 2 contained a little phosphoric anhydride, and was swept out with nitrogen peroxide gas, then sealed and heated for 3 hours at 250°, a colourless gas being thus produced. The bottom tip was then forced into a piece of pressure-tubing filled with mercury, attached to a pear reservoir, and the glass tip broken inside the rubber. The top of the tube was similarly attached to a Hempel gas burette containing mercury. The gas was swept out of the tube into the burette, and there treated with water. No darkening was observed. Hence the gases were not a mixture of nitric oxide and oxygen intensively dried and incapable of reaction. The gas was analysed and found to be 99% oxygen, the remainder being nitrogen.

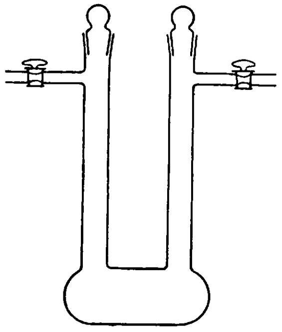

Fig. 1.

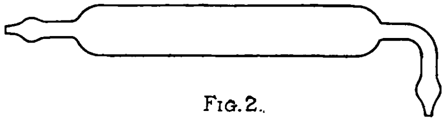

Fig. 2.

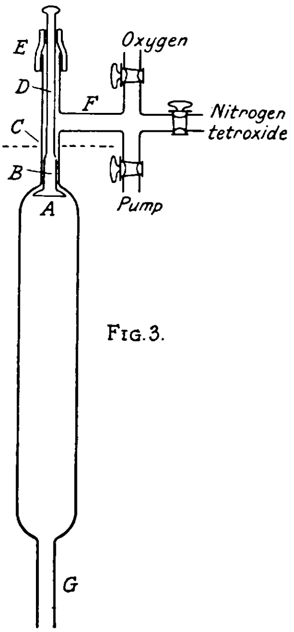

Fig. 3.

The Carius tube was then emptied of its mercury, and the solid scraped out. According to Smith, this solid should have contained the compound P_2O_5,xNO_2. A little of the solid was passed into a tube filled with mercury standing in a trough of mercury. A little water was added to the tube and a violent reaction occurred, a colourless gas being evolved. This gas was then transferred to another tube of mercury (free from the phosphoric acid which was present in the original tube) and a little ferrous sulphate solution added; the gas completely dissolved, and the solution became brown, indicating that the gas was pure nitric oxide. Therefore the products of the reaction are pure oxygen and a compound of nitric oxide with phosphoric anhydride.

Identification of the Compound as $P_2O_5,2NO$.—One difficulty in preparing a pure specimen of the compound is the fact that phosphoric anhydride is so easily sublimed at the temperature necessary for reaction. It is also essential that the initial materials be very dry (see above). The apparatus (Fig. 3) was constructed of Pyrex glass. The tube was 1½ in. wide and 18 in. long, and could be inserted into a tube furnace up to the broken line. The plunger *A* was ground into good contact with the inside surface of the tube; the stem *B* was also a good fit for the side arm *C*, whereas the stem *D* was of thin rod. This plunger worked through a piece of pressure-tubing *E*. This apparatus was cleaned and dried by heating to 250° under a vacuum obtained by a Hyvac pump. Oxygen, dried by passing through tubes of phosphoric anhydride, was passed through the tube *via* the side arm *F*, the plunger being pressed into the tube. Phosphoric anhydride (10 g.) was introduced at *G*, against the oxygen stream (which excluded atmospheric moisture), and *G* was sealed. The oxygen was pumped out of the tube *via F*, which was then filled with dry nitrogen peroxide. The plunger was now pulled firmly against the inside of the tube, which was then heated to 250° for 3 hours. Reaction took place, and the excess phosphoric anhydride was unable to escape from the tube owing to the good fit of the plunger. As reaction proceeded, more nitrogen peroxide was introduced by pressing the plunger, the oxygen being removed from time to time by pumping. The final *product* was a white glassy substance which was obtained by breaking the tube and scraping the product into a dry bottle. It was less deliquescent than the phosphoric anhydride, and quite easily handled.

Weighed quantities were dissolved in water and the phosphorus content.determined by the usual magnesium pyrophosphate method (Found: P, 30·6. P_2O_5,2NO requires P, 30·70%). The nitric oxide content was estimated by reaction with water, the volume of evolved gas being measured. The apparatus was a Lunge nitrometer attached to a small conical flask containing water. The amount of evolved gas agreed with the calculated amount within 1%.

Synthesis of the Compound.—Pure nitric oxide, prepared by heating a mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid, was stored over water. The gas was dried by passing over anhydrous calcium chloride, followed by phosphoric anhydride. The previous method of preparation was repeated, this gas being used in place of the nitrogen peroxide. The reaction took place more readily and the same product was obtained.

DISCUSSION.

The above work establishes the reaction between phosphoric anhydride and nitrogen peroxide as $N_2O_4 + P_2O_5 = P_2O_5,2NO + O_2$. No phosphoric anhydride–nitrogen peroxide compound is formed. Hence, Smith's explanation of his observations is incorrect. It is clear that when he treated his material with water, nitric oxide was evolved (but not noticed), $P_2O_5,2NO + H_2O = 2HPO_3 + 2NO$, and this gas reacted with the oxygen present to give the brown nitrogen peroxide.

The author repeated Smith's experiments as described, and when the tube was examined closely, the reaction of the compound with water was not detectable by the naked eye, but effervescence was detectable by using a powerful lens.

Some of Smith's experimental data merit consideration. He filled one of his tubes at 264 mm. of nitrogen peroxide. From the initial dissociation of the nitrogen peroxide, it is a simple matter to calculate what the final oxygen pressure should be: close agreement with his experimental observation (238 mm.) is obtained. Finally, it must be pointed out that Smith used his observations as evidence for showing that intensive drying could inhibit reaction between nitric oxide and oxygen, but it is clear that his work has no value in this respect. Baker's evidence (J., 1894, **65**, 611), therefore, is almost the only indication that drying can influence this reaction.

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