CCXLVI.—*The Influence of Intensive Drying on the System Nitrogen Peroxide–Nitric Oxide–Oxygen.*

By JOHN WILLIAM SMITH.

IT was observed by Baker (J., 1894, **65**, 611) that when carefully purified gaseous nitric oxide and oxygen, which had been dried separately over phosphoric oxide for 10 days, were mixed, no combination occurred, and on opening the container under dry mercury no contraction in volume was noted. When a trace of moisture was introduced, however, combination immediately took place. Hasche (*J. Amer. Chem. Soc.*, 1926, **48**, 2253) found that the velocity of reaction between carefully dried nitric oxide and oxygen was reduced by 20% if the walls of the reaction vessel were coated with paraffin wax. This he ascribed to a protective action, preventing the gases from coming into contact with the walls of the vessel, which would hold adsorbed water vapour. Briner (*J. Chim. physique*, 1926, **23**, 848) unsuccessfully attempted to repeat Baker's observations: although the duration of the drying in each case ranged from 3 months to a year, in no case did the gases remain colourless on mixing.

The thermal dissociation of nitrogen peroxide into nitric oxide and oxygen has been fairly fully worked out, notably by Richardson (J., 1887, **51**, 397), Bodenstein and Katayama (*Z. physikal. Chem.*, 1909, **69**, 44), and Bodenstein, Boes, Lindner, and Ramstetter (*ibid.*, 1922, **100**, 68). At pressures of the order of 1 atmosphere, considerable dissociation occurs at 500—600°. Hence it was thought that, if nitrogen peroxide were heated in the intensively dried state, interesting phenomena might be observed. Three possibilities presented themselves: (*a*) The nitrogen peroxide might not dissociate, *i.e.*, the colour of the gas would not diminish on strong heating. (*b*) Complete dissociation might occur into nitric oxide and oxygen, which might not recombine on cooling. (*c*) Some intermediate stage might be attained, and a definite shift in the chemical equilibrium might be observed, corresponding to a shift in the inner equilibrium in the case of dried liquids.

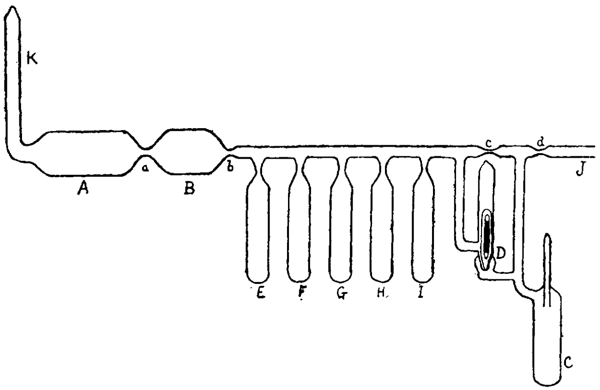
EXPERIMENTAL.

Apparatus No. 1.—The first apparatus employed was an adapted form of that used by Lewis and Rideal in their work on the synthesis of hydrogen bromide and the dissociation of hydrogen iodide (*J. Amer. Chem. Soc.*, 1926, **48**, 2554). The whole was constructed of " Durosil " glass which had been freed from capillaries by the method recommended by Smits and his co-workers (J., 1926, 2657). The apparatus (Fig. 1) consisted essentially of a horizontal tube carrying a series of reaction bulbs, *E*, *F*, *G*, *H*, *I*, each of which was connected to the horizontal tube through a capillary neck suitable for vacuum sealing. This tube connected at one end to two bulbs, *B* and *A*, for use when charging with phosphoric oxide, as described below, and at the other end to the vacuum pump system and to a bulb to serve as a nitrogen peroxide reservoir, connected as shown in the diagram.

After being cleaned with chromic acid, washed thoroughly, and dried roughly by heating to 300° in an electric oven, the apparatus was assembled and connected to a high-vacuum pump system through the tube *J*. After being tested for leakage, the whole apparatus was heated at 300° for 2 days, a high vacuum (10^{-6} mm.) being maintained in it during this period.

Dry air was then admitted, and pure resublimed phosphoric oxide introduced into *A* through *K*, which was immediately sealed off. The apparatus was again evacuated, all the tubes except bulb *A* being heated to 300°. It was then allowed to cool and bulb *A* was heated. In this way the pentoxide was sublimed in a vacuum from bulb *A* to bulb *B*. Bulb *A* was then removed by sealing off at the constriction *a*. The reaction bulbs were heated strongly again, and, after cooling, the pentoxide was sublimed into them by heating the bulb *B*. The bulb *I* was kept free from the pentoxide, so as to serve as a standard of comparison, and a free space was left in each of the other bulbs to admit of colour observation being made through the tube. Each had been drawn from a tube of uniform diameter, so that rough quantitative colour comparison could be carried out. The bulb *B* was then drawn off at the constriction *b*, and constriction *c* was also sealed. This disconnected the bulbs from the vacuum pump system and from the reservoir bulb *D*. Dry air was then admitted to *C*, followed by a little phosphoric oxide and a few c.c. of dry nitrogen tetroxide. The tetroxide was frozen in liquid air and the bulb was evacuated again. Occluded air was removed by allowing the tetroxide to re-melt in a vacuum, after which it was frozen again and the bulb re-evacuated. When a high vacuum was reached, the whole apparatus was sealed off at the constriction *d*.

FIG. 1.



After being left for a few days to allow the nitrogen peroxide to dry, the bulb *C* was cooled in ice, and the septum *D* broken. The gas was allowed to reach equilibrium with the liquid at 0°, and the separate bulbs were sealed off. Thus these bulbs were all sealed off at the same known pressure, *viz.*, the vapour pressure of nitrogen peroxide at 0°—264 mm. The bulbs were matched on a tintometer to a Lovibond scale.

After the gas had been allowed to dry in the bulbs for a further 3 days, one of the bulbs was heated at 250—300° for 1½ hours. On cooling, the colour of the gas had diminished to about one-half of its original intensity, and after a further 5 hours' heating it became practically colourless. At the same time the phosphoric oxide changed completely in appearance, passing from a finely crystalline, snow-like mass into colourless transparent plates of a type that had not been observed previously under any conditions. None of the other bulbs became so nearly colourless, but in each case a very marked diminution in the intensity was observed.

The fact that the gas became so nearly colourless was at first thought to be due to an almost complete shift of the equilibrium towards the dissociated side. At this stage, however, I was privileged to see a private communication from Dr. Hartung to Professor Donnan, in which it was noted that nitrogen tetroxide reacted with phosphoric oxide at temperatures above 200°, yielding an addition compound. The formation of this compound appeared to account for the great diminution in the colour of the bulbs, so, as other lines of attacking the problem were being commenced, this investigation was abandoned.

Some months later, however, a rough analysis of the residual gas was carried out by breaking the tip of a bulb under pure, dry, recently boiled mercury. In tube 1 the colour intensity was about one-quarter of the initial intensity. On opening, the volume of residual gas was 4·43 c.c. The mercury, however, rose steadily, and after 24 hours the volume was 2·26 c.c. An attempt was then made to introduce a small drop of water into the tube, but the mercury only was moistened. An immediate further contraction in volume was observed. This was complete in 5 minutes, a further 24 hours' standing causing no further change. The residual gas was then mainly nitric oxide, for on introduction of a drop of ferrous sulphate solution a brown colour was produced. A small bubble of other gas of unknown composition remained, however. The total volume of the tube was 13·04 c.c., so the pressure of the gas remaining after heating was 238 mm. The bulb had been filled at a pressure of 264 mm., so it was concluded that some combination must have taken place with the phosphoric oxide, but that the pressure change was small compared with the colour change. Hence it was concluded that the colour change was not due entirely to a simple absorption of the gas by the pentoxide.

This was confirmed by tube 2, in which the colour was too faint to match on the tintometer. The tip of this bulb was opened under mercury which had been carefully purified and dried over phosphoric oxide for a year. On the introduction of moisture, the residual gas immediately turned dark brown and contracted in volume from 3·02 c.c. to 1·30 c.c. The peroxide formed gradually acted on the mercury, leaving a bubble of nitric oxide at the top of the tube. The residual gas pressure (130 mm.) was here again large compared with that to be expected from the colour change.

Hence it seems quite clear that the tubes contained nitric oxide and oxygen, and that the moisture introduced caused recombination. The actual temperature of drying is here unknown—it may have been carried out before the tube was heated, or at the higher temperature when the gas was somewhat dissociated. At first sight, this result seems to be in conflict with that obtained later with apparatus No. 3, but it may be accounted for if the drying were effected while the gas was slightly dissociated. However, the residual gas appears to have been much more dissociated than normal nitrogen peroxide would be on heating to the same temperature under the same pressure, so a definite shift in the equilibrium seems to be indicated. These experiments seem to confirm Baker's observation of the co-existence of nitric oxide and oxygen gases in the intensively dried state.

Apparatus No. 2.—It was thought desirable to be able to test the residual gas in the absence of the nitrogen peroxide–phosphoric oxide compound, since it might be alleged that admission of moisture to the tubes liberated the peroxide from this compound, thereby causing the dark brown coloration. Such an explanation was regarded as very improbable, for the moisture was introduced only on the surface of the mercury and no gas was seen to rise from the compound, which was covered with mercury. This explanation, also, did not account for the rapid volume change. In this apparatus the bulbs were prepared with a constriction in the middle. Phosphoric oxide was sublimed into one section of this only, so that the compound could be removed before testing. The bulbs were sealed off at the same pressure as before.

Tube No. 6 was heated at 300° for 18 hours, the gas being then quite colourless. After cooling, the tube was divided, and the section free from the phosphoric oxide was opened under dry mercury. A considerable volume of gas remained. On the introduction of moisture, very little effect was noticed, however, and the residual gas proved to be 2·81 c.c. of oxygen and 1·41 c.c. of nitrogen. No nitrous oxide could be found. The ratio of oxygen to nitrogen (2 : 1) is here so exact that it must be supposed that the peroxide had completely dissociated into its elements, although it does not normally do so at any appreciable rate at this temperature. The volume of the bulb was 22·17 c.c. The loss was presumably due to the compound formation. The bulb containing the compound was treated in exactly the same way, but no coloration was observed on introducing a little moisture, and no volume contraction occurred. Hence the results obtained with tubes 1 and 2 were shown not to be due to the decomposition of this compound. The introduction of excess of moisture caused only comparatively slow decomposition.

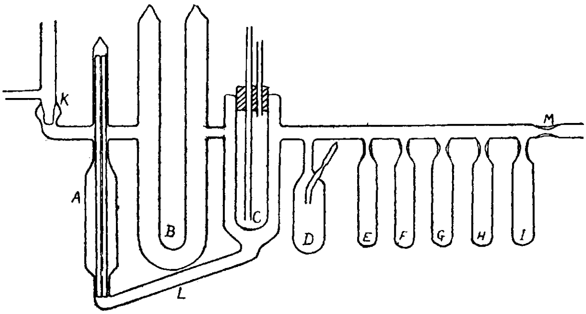
Tube 7 was heated at 300° for 6 hours. It was then cooled, divided, and opened under mercury as in the previous case. The mercury was not so dry as that used before, and the residual gas gradually contracted in volume and became deeper reddish-brown in colour. Rather more moisture than was desired was then added, and a definite aqueous film was produced. This caused a sharp contraction in volume which was complete in a very short time, further standing producing only a minute further contraction. The residual gas was again nitrogen and oxygen, but in about equal parts. The fact that the proportion of oxygen to nitrogen was lower in this case may be attributed to the interaction of some of the nitrogen peroxide with mercury, yielding nitric oxide, which absorbed more oxygen, and so on. This appears to confirm the observations made with tubes 1, 2, and 6.

The decomposition of the nitric oxide into its elements may be catalysed by the large surface of the phosphoric oxide, which was very finely divided indeed. It has been found that the elements are not formed to any great extent on heating the nitrogen peroxide–phosphoric oxide addition compound, and also that they are not formed to any extent if the tubes are heated in the initial stages to temperatures of about 350°, at which the phosphoric oxide passes into the glass-like form. The evidence of these experiments shows that a temperature of about 300° and prolonged heating favour the decomposition of the nitrogen oxides into their elements, a reaction which is almost entirely absent at slightly lower temperatures.

The Effect of Intensive Drying at the Ordinary Temperature on the Thermal Dissociation of Nitrogen Peroxide into Nitric Oxide and Oxygen.—The apparatus employed (Fig. 2) embodied the circulation principle used by Smits, de Liefde, Swart, and Claassen (J., 1926, 2659). The liquid evaporated from the bulb *A*, passed through the phosphoric oxide in the wide U-tube *B*, and was condensed in *C*, which was cooled by a stream of water passing through the inner tube, as shown. From here it ran back along the tube *L* into *A*. The apparatus was connected to a bulb, *D*, in which the liquid could be frozen out, and to a series of bulbs, *E*, *F*, *G*, etc., in which small amounts of the gas could be sealed off for testing purposes. The apparatus at this side ended in a connexion to a high-vacuum pump system through the constriction *M*. The constrictions joining the bulbs to the horizontal tube were not made very narrow, but the walls at these points were made very thick so that the bulbs could still be readily sealed off in a vacuum. This avoided the usual restriction on the diffusion of gases, and hence also of moisture, from the bulbs—a very serious drawback to capillaries in drying apparatus.

The whole apparatus was constructed of capillary-freed " Pyrex " glass. It was heated under a high vacuum for a week, after which phosphoric oxide was sublimed into the U-tube *B*. The nitrogen peroxide was introduced into *D*, where it was frozen out, the apparatus was evacuated, and the constriction *M* sealed off. The apparatus was kept in an air thermostat at about 30° while a stream of cold water was passed through the inner vessel, *C*. In this way a steady circulation was maintained, the average amount condensing being about 10 drops a minute.

FIG. 2.



After 3 months, the liquid was all condensed in bulb *D*. This was then placed in a bath at 0°, and when equilibrium was reached a bulb of the gas was sealed off. The colour of the gas in this bulb, when matched on a tintometer, was not appreciably different from that of a blank undried specimen. The bulbs were slowly heated together in an electric furnace. The colours deepened similarly up to about 400° ; on raising the temperature further, however, the colour of the undried gas appreciably lightened owing to dissociation into nitric oxide and oxygen, but that of the dried gas remained constant, so far as could be judged visually. The colour difference was quite perceptible at 500°, and at 600° it was very marked. It being thought possible that the rate of dissociation was very much retarded by the intensive drying, the bulbs were maintained at 550° for 24 hours. Even after this period, the nitrogen peroxide did not appear to have dissociated to any appreciable extent. On slow cooling, the colour of the moist bulb became about the same as that of the dry bulb at about 400°. On further rather rapid cooling to room temperature, the dry bulb remained somewhat darker than the undried one. About 3 hours were required before the colour of the former returned to that of the moist bulb. This was evidently due to the slow rate of polymerisation of the NO_2 molecules.

From this simple experiment the following deductions may be drawn. (*a*) Intensively dried gaseous nitrogen peroxide does not dissociate very considerably into nitric oxide and oxygen, even on heating at 550° for 24 hours. (*b*) The rate of polymerisation of the coloured NO_2 molecules to form the colourless N_2O_4 molecules is retarded by the intensive drying.

After drying for 6 months, another bulb was sealed off from the same apparatus. The complication had now arisen that the vapour pressure at 0° had so far increased that the colour of the gas in equilibrium with the liquid at 0° was much darker than in the specimen " wet " tube. Accordingly, the liquid was cooled in a freezing mixture until the colours were as nearly matched as possible. The bulb was then sealed off. It was observed later that this bulb was a little lighter in colour than the standard tube. On heating to 600°, however, it was appreciably darker. The tubes were maintained at about 620° for 24 hours, this temperature being as near to the softening point of the glass as it was thought safe to heat the bulb. The bulbs were then of equal colour intensity, and on cooling and re-heating all abnormality seemed to have disappeared from the bulb. This was probably due to the fact that at such high temperatures the " Pyrex " glass tends to decompose superficially, evolving a small quantity of water.

Summary.

When nitrogen peroxide is heated with phosphoric oxide, at least three reactions take place : (*a*) The pentoxide combines with the nitrogen peroxide, yielding the compound described by Hartung (private communication). (*b*) The nitrogen peroxide is dissociated into nitric oxide and oxygen to a greater extent than in the moist gas, and these products do not recombine on cooling. (*c*) The nitric oxide decomposes into its elements at a greater rate than normally. This reaction may be catalysed by the large surface of the phosphoric oxide.

A temperature of about 300° and prolonged heating favour reaction (*c*).

Nitrogen peroxide which had been intensively dried at the ordinary temperature did not dissociate very considerably into nitric oxide and oxygen, even on heating at 550° for 24 hours, but on heating at about 620° for the same period, it seemed to revert completely to the normal form, probably owing to a superficial decomposition of the glass.

In the dried gas the rate of polymerisation of the coloured NO_2 molecules to form the colourless N_2O_4 molecules is retarded.

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