420. *Experiments on the Combination of Nitrogen Peroxide and Nitric Oxide in the Absence of Moisture.*

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Experiments have been made to determine whether the combination of nitric oxide with nitrogen peroxide to form dinitrogen trioxide is affected by prolonged drying. It was found that the carefully dried gases combined and condensed to a blue liquid as easily as the partly dried gases in a control tube.

EXPERIMENTS by H. B. Baker and Mrs. Baker (J., 1907, **91**, 1862; 1912, **101**, 2339) on dinitrogen trioxide appeared to demonstrate the catalytic effect of minute quantities of water vapour on its dissociation. The carefully desiccated liquid had a molecular weight (determined cryoscopically in benzene) of about 83, and determinations of the density of the vapour gave values varying from 38, corresponding to N_2O_3, to 62, a value which indicated a considerable proportion of N_4O_6. The vapour density given by one specimen of incompletely dry trioxide was about 28, in fair agreement with the results of earlier investigators. Further, the dried liquid showed a very marked rise in boiling point.

If, however, the reactions $N_4O_6 \longrightarrow 2N_2O_3$ and $N_2O_3 \longrightarrow NO_2 + NO$ are catalysed by water vapour, the converse reactions also should be catalysed, and we should expect to find that a dried mixture of equal volumes of nitrogen peroxide and nitric oxide would exhibit greater reluctance to combine and condense to a blue liquid than a moist mixture of the same composition. In order to investigate this the following experiments were carried out.

EXPERIMENTAL.

In some preliminary experiments in which the vapour of dinitrogen trioxide was sealed up in a tube with phosphoric oxide, it was observed that the brown colour of the gas gradually diminished in intensity, and that after a time the gas could not be condensed to a liquid by means of a freezing mixture of ice and salt; but on the cause of this effect being investigated, it was established that the phosphoric oxide absorbs the peroxide of nitrogen—gradually at the temperature of the laboratory, and rapidly at a higher temperature. Therefore, in all further experiments the phosphoric oxide was distilled into the experimental tube in the current of dinitrogen trioxide vapour, it being thereby ensured that the distillate would be saturated with nitrogen peroxide at the partial pressure of that gas in the mixture it was required to desiccate.

The trioxide was prepared by gently heating a mixture of arsenic trioxide and nitric acid. Most of the moisture was removed from the dissociated vapour by condensation in a reflux condenser, and the gas was dried by passing it through a long tube filled with phosphoric oxide. The dried vapour was condensed in a U-tube surrounded by a freezing mixture of ice and salt. The U-tube was connected with the Jena-glass tube, which it was required to fill with the dissociated trioxide, by means of a ground glass joint. The Jena-glass tube was constricted at a distance of about 15 cm. from the ground glass joint, and was bent at right angles at about 10 cm. from the constriction. It terminated in a capillary tube. A tube filled with fused calcium chloride was fitted on to the capillary end of the Jena tube to prevent the entrance of atmospheric moisture. Between the ground glass joint and the constriction of the Jena-glass tube several plugs of phosphoric oxide were introduced. Connections were made with ground glass joints lubricated with glacial phosphoric acid.

The filling of the tube was accomplished in the following manner. The freezing mixture surrounding the tube which contained the recently condensed trioxide was removed, and the temperature of the liquid trioxide was raised sufficiently to give a steady stream of gas. The phosphoric oxide in the Jena-glass tube was then heated with the naked flame, the constriction at the same time being kept at a moderately high temperature. The phosphoric oxide melted to a perfectly transparent liquid,* and easily distilled through the constriction into the front compartment of the tube between the constriction and the bend. Care was taken that its temperature should not rise too high during the distillation; this was to avoid contamination

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* Phosphoric oxide which is incompletely oxidised melts to a dark grey liquid. It was shown in separate experiments that the oxide which had been distilled in the oxides of nitrogen contained no lower oxides of phosphorus and was not contaminated with carbon.

of the distillate with metaphosphoric acid. After the phosphoric oxide had been distilled, the tube was allowed to cool with a slow current of the vapour passing through it, and it was then sealed before the blow-pipe at the constriction and at the terminal capillary tube. A similarly constructed control tube, which did not contain phosphoric oxide, was filled in the same manner from a corresponding middle fraction of the liquid and sealed in the same way.

The comparison of the properties of the dried vapour with those of the moist vapour was made in various ways. The tube containing the dried mixture and the control tube were placed symmetrically side by side in a freezing mixture so that the capillary tubes and the limbs of the wider tubes to which these were joined were surrounded by the freezing mixture, and the time required for condensation of a drop of the blue liquid was observed. It was the same in both cases and the colours of the liquids were identical. Also the maximum amounts of liquid condensed at the temperature of the freezing mixture were compared and found to be practically the same. When the tubes were removed from the freezing mixture, evaporation of the two specimens of liquid took place at the same rate, and the same changes in colour were observed in the liquids as they disappeared. The specimens of liquid obtained by immersing the tubes in a bath at 5° were green and of equal volume.

The comparison was made with mixtures which had been left in contact with phosphoric oxide for periods varying from 2 days to 2 years. Heating the tube which contained the dried gas and phosphoric oxide even to a temperature at which this oxide melted made no difference to the results obtained.

We can only conclude from these results that there is no difference between the properties of the very dry and the partly dried gas. It might be objected that the absorption of the gas by the phosphoric oxide reduces the efficiency of the latter as a drying agent, but we could detect no alteration in its appearance and hygroscopic character.

These experiments, therefore, as far as they go, fail to support the conclusions drawn from the Bakers' work on dinitrogen trioxide, and we think those results require further consideration. It should be noted that Baker himself observed that the colour of the vapour of the desiccated trioxide could not be distinguished from the colour of the mixed products of dissociation.

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