

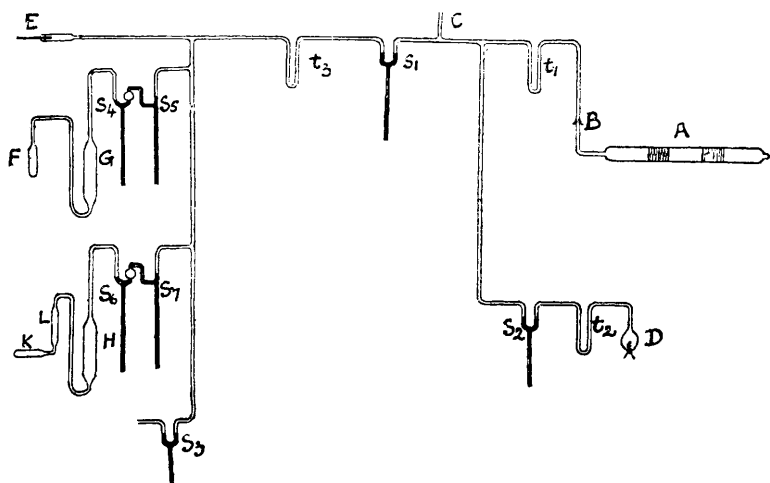
CLXXXI.—*The Direct Synthesis of Nitrous Oxide.*

By DAVID LEONARD CHAPMAN, RICHARD ALLEN GOODMAN, and
RODNEY THOMAS SHEPHERD.

HITHERTO it has not been found possible to effect a direct synthesis of nitrous oxide. We shall show that this compound is slowly formed when an electric discharge is passed through nitrogen at low

pressure in a quartz tube into the walls of which oxygen has previously been driven by means of the discharge, and can be isolated as it is formed by condensing it in a U-tube surrounded by liquid air. When completely decomposed by heating a platinum wire in it, the volume increases in the ratio 2 to 3, the proportion of nitrogen to oxygen in the decomposition products being 2 to 1.

The quartz tube, A (*vide* diagram), in which the discharge took place was approximately 1 m. in length and 1180 c.c. in volume. The rest of the apparatus was of glass, and was connected to the quartz tube by a ground glass joint, B, which was lubricated with glacial phosphoric acid and sealed by mercury. The long U-tube, t_1 , could be immersed in liquid air when desired, and served the



double purpose of keeping back mercury vapour and of condensing the nitrous oxide. A T-piece, C, led to the McLeod gauge used to measure the pressures. The discharge tube, with gauge and liquid-air trap, could be shut off from the rest of the apparatus by the mercury seals s_1 and s_2 . The seal, s_2 , served to put the quartz tube into communication with a U-tube, t_2 , and a bulb, D, which contained a spiral of fine platinum wire welded to thick platinum leads, which passed to the outside through a lead-glass seal. t_3 was another U-tube which could be surrounded by liquid air. Beyond the mercury seal, s_3 , was a mercury vapour pump and an auxiliary Sprengel pump. The remainder of the apparatus was for the purpose of generating and storing the gases required.

Hydrogen.—The hydrogen required for the analysis was admitted to the apparatus by diffusion through the walls of a platinum tube, E, sealed into the end of a glass tube. The platinum tube was heated

to redness in an atmosphere of hydrogen, prepared in the ordinary way in a small Kipp's apparatus from zinc and dilute sulphuric acid. The gas, after bubbling through a solution of caustic soda, was passed through a quartz tube which surrounded the platinum tube. To admit hydrogen to the apparatus the quartz tube was heated strongly.

Nitrogen.—The nitrogen was prepared by the decomposition of pure anhydrous barium azide contained in a vertical tube, F. This was connected to a reservoir, G, of capacity about 400 c.c., in which the gas was stored. One limb of the seal s_4 was blown out into a bulb, of volume about 4 c.c., the upper end being connected by millimetre capillary tubing to another seal, s_5 . This arrangement was employed to withdraw small amounts of gas from the reservoir, in which the pressure was about 1 cm., in the following way. The mercury in the seal s_4 was lowered, and when raised again, shut off a small amount of gas in the bulb. The seal s_5 was then lowered until the T-piece was just cleared. The mercury in s_4 was then raised, and the gas enclosed in the bulb driven past the seal s_5 into the apparatus. By subsequently lowering the mercury in the seal s_4 , the bulb could be again evacuated. The tube, F, containing the barium azide, was heated in a small bath of glycerol. The nitrogen was evolved at a convenient rate at 152° .

Oxygen.—The oxygen was prepared by the thermal decomposition of recrystallised potassium permanganate contained in the tube K. The gas passed up a tower, L, containing solid caustic potash to absorb any carbon dioxide. L was connected to a reservoir, H, and two seals, s_6 and s_7 , by means of which small quantities of gas could be removed as described above in the case of nitrogen.

The gases were not admitted to the discharge tube until they had remained in that portion of the apparatus between the seals s_1 , s_3 , s_5 , s_7 , for at least $\frac{1}{2}$ hour with liquid air surrounding the U-tube t_3 . The gases did not come into contact with any grease taps whatever.

The Discharge.—For the purpose of exciting the discharge, two pieces of aluminium foil about 6 cm. wide were fastened by copper wire round the tube at equal distances from each end and from each other. The aluminium electrodes were connected by means of copper wire with the secondary of a 10-inch induction coil, which was run from the 100-volt mains, a resistance keeping the primary current constant at about $2\frac{1}{4}$ amp. Interruption of the primary was effected by a mercury break of the simple dipper type. The dipper was oscillated by means of an eccentric coupled directly to the shaft of an electric motor. By this means constant interruption was obtained. There was an external spark-gap of 1 cm.

To conduct an experiment, the whole apparatus was first

thoroughly evacuated, all the tubing, including the McLeod gauge, being heated twice with a blow-pipe flame, in order to drive off gases retained by the surface of the glass. The quartz tube was thoroughly heated to redness, section by section, to expel any gas that might be absorbed. The required amount of oxygen was then withdrawn from the reservoir, and admitted to the quartz tube in the manner already described. The initial pressure of oxygen was about 0.08 mm. The pressures recorded below have been reduced to the temperature of 18°, allowance being made for the cooling effect of the liquid air on the small proportion of gas contained in the U-tube t_1 . After the discharge had been started, the progress of the absorption was followed by measuring the pressure at convenient intervals of time. The discharge was stopped when the pressure-time curve had become very flat. The liquid air was then removed, and the tube evacuated. Nitrogen was then admitted to a pressure of about 0.08 mm., the liquid air replaced round t_1 , and the discharge again started. From time to time the discharge was stopped, and the pressure measured both with and without liquid air surrounding the U-tube t_1 . The difference between these two pressures gave the amount of condensable gas formed. It was, of course, produced at a gradually decreasing rate. The results of four experiments are in Table I.

TABLE I.

Oxygen absorbed.	Nitrogen absorbed.	Condensable gas.	Duration.
0.01669 mm.	0.03777 mm.	0.01688 mm.	6½ hrs.
0.02168	0.04282	0.02321	9½
0.01576	0.04725	0.02999	11½
0.01479	0.04869	0.02185	17½

When a convenient amount of gas had been obtained, the tube was evacuated, the liquid air remaining round the U-tube. A small amount of the condensable gas was always lost during this operation, showing that the liquid had an appreciable vapour pressure at the temperature of liquid air. Some experiments were made with a view to determining the properties of the gas. It was quite stable, and could be kept for any length of time. It was very rapidly destroyed by the discharge, decomposition being complete in about 5 seconds. The observed expansion was dependent on the length of time during which the discharge passed, a maximum being reached in a few seconds. The contraction which followed the expansion was probably mainly due to combination of the oxygen produced in the decomposition with mercury vapour, in the presence of which this experiment had to be performed. The gas was not condensed when the U-tube was surrounded by solid carbon dioxide and ether. It did not react with oxygen when left to stand with this

gas, showing that it could not be nitric oxide. This conclusion was confirmed by the circumstance that the gas did not attack the mercury in the McLeod gauge either before or after it had been mixed with oxygen.

Analysis.—The gas was analysed in the following way. The mercury seal s_2 was opened, and the pressure of the gas in the whole of the apparatus to the right of the seal s_1 measured. Liquid air was then placed round the U-tube t_2 , and when all the gas had condensed, s_2 was closed. The liquid air was then removed, and replaced by solid carbon dioxide and ether, in order that the decomposition might be carried out in the presence of as little mercury vapour as possible. The platinum spiral was then heated to bright redness. After some hours the heating was stopped and the bulb allowed to cool. The flask containing the solid carbon dioxide and ether was removed, the seal s_2 opened, and the pressure measured both with and without liquid air surrounding the U-tube t_1 . The difference between these two measurements gave the amount of condensable gas undecomposed. The difference between this and the amount originally present represented the gas decomposed. The results are in Table II.

TABLE II.

	Mm.
Pressure after decomposition, with liquid air	0.03746
Pressure after decomposition, without liquid air	0.03948
Condensable gas undecomposed	0.00202
Initial amount of condensable gas	0.02661
Condensable gas decomposed	0.02459
Expansion on decomposition	0.01287

It will be seen that, within the limits of experimental error, the expansion is equal to half the amount of condensable gas decomposed.

The next analysis was made in such a way as to enable the amount of oxygen produced by the decomposition to be determined. When this was known, the relative proportions of oxygen and nitrogen in the condensable gas could be calculated.

The ratio of the volume of the quartz tube *plus* tubing up to the seals s_1 and s_2 , to the total volume when s_2 was opened, was first determined by measuring the pressure of the same amount of gas in the two volumes. The decomposition was then carried out in the same manner as before. While this was proceeding, hydrogen was admitted to the quartz tube, and its pressure measured. From the ratio of the volumes, the pressure this gas would produce in the total volume when s_2 was opened was calculated. After decomposition, the mercury in s_2 was lowered, and the pressure measured, as in the former case, with and without liquid air surrounding the

U-tube t_1 . The pressure of the products of decomposition was found by subtracting the pressure of the hydrogen from the total pressure measured after decomposition with liquid air surrounding the U-tube. t_2 was then immersed in liquid air, and the spiral heated for several hours until no further fall in pressure occurred. From the contraction due to the formation of water, the amount of oxygen present was deduced. The nitrogen was found by difference. The results are in Table III.

TABLE III.

(a) *Expansion on decomposition.*

	Mm.
Pressure after decomposition, with liquid air	0.05998
Pressure after decomposition, without liquid air	0.06064
Condensable gas undecomposed	0.00066
Initial amount of condensable gas	0.02156
Condensable gas decomposed	0.02090
Pressure of hydrogen admitted to quartz tube	0.03001
Ratio of volumes, quartz tube : total	0.9719
Pressure of hydrogen in total volume	0.02917
Pressure of nitrogen, hydrogen, and oxygen	0.05998
Pressure of products of decomposition	0.03081
Expansion produced by decomposition	0.00991

(b) *Estimation of oxygen.*

Initial pressure (hydrogen, nitrogen, and oxygen)	0.05998
Final pressure (excess hydrogen and nitrogen)	0.02891
Contraction	0.03107
Amount of oxygen required for this contraction	0.01036

(c) *Summary.*

Condensable gas decomposed	0.02090
Oxygen produced	0.01036
Nitrogen produced	0.02045

The expansion produced on decomposition is again seen to be half the amount of condensable gas destroyed, and the ratio of nitrogen to oxygen in the products is 2 to 1, leaving no doubt that the gas was nitrous oxide.

In experiments not described above, a small proportion of oxygen was added to nitrogen in the discharge tube. Even when the partial pressure of the oxygen was as small as one-tenth of that of the nitrogen, nitrogen peroxide was produced.