305. *Properties of the Oxides of Nitrogen. Part V. Combustion in the System Nitric Anhydride–Ozone.**

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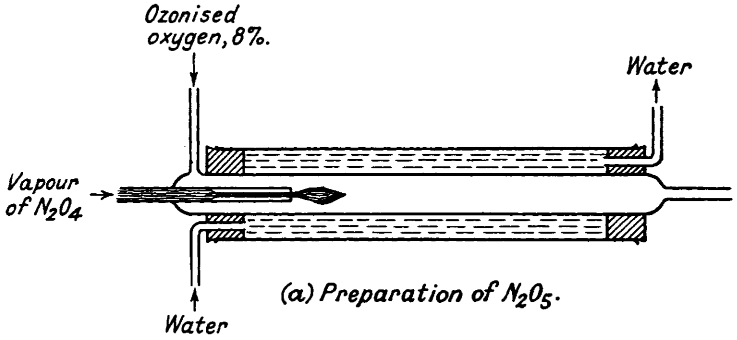
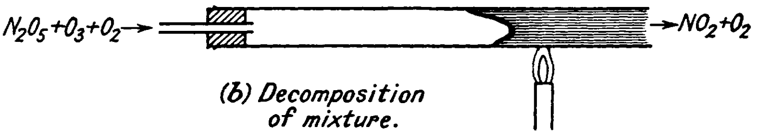
The purpose of the present paper is to give an account of a novel type of combustion in gaseous mixtures prepared by passing ozonised oxygen over solid nitric anhydride. The remarkable phenomena associated with this combustion are being studied in detail by Mr. R. V. Seddon, and final conclusions as regards the mechanism of the process must await the results of his experiments; but the observations made up to the present are compatible with the conclusion that the active materials are ozone and a " hyperoxide " of nitrogen, and that the combustion may perhaps be represented by the equation $NO_3 + O_3 = NO_2 + O_2 + O_2$. If this general conclusion is correct, the combustion is remarkable, not only for the unusual nature of the interacting components, but even more for the fact that two highly oxidised products actually burn *with liberation of oxygen.*



(a) Preparation of N_2O_5.



(b) Decomposition of mixture.

(c) "Flame" striking back.

(d) Stationary flame.

Observations of Blue Colour in the Preparation of Nitric Anhydride.—When nitric anhydride for use in experiments on the system N_2O_5–N_2O_4 (J., 1935, 692) was prepared by projecting nitrogen peroxide into ozonised oxygen from a capillary (Fig. *a*), the brown vapour was quickly decolorised, but on careful observation a distinct blue tinge could be seen along the lower edge of the brown jet. Similar phenomena were also observed in the converse process, when a fairly rapid stream of ozonised oxygen was passed over the surface of liquid nitrogen peroxide in a small " trap " cooled with iced water. With the slower stream of ozonised oxygen used in preparing nitric anhydride, the almost colourless gas in the upper part of the trap was seen to be faintly blue; but this colour disappeared when the supply of nitrogen peroxide was cut off by freezing, and could not therefore be attributed merely to the presence of ozone. A much more intense local blue colour was often seen in the trap when the gases were suddenly mixed, *e.g.*, by tapping the trap to promote evaporation of nitrogen peroxide and then cooling it in acetone and carbon dioxide snow. Much more striking was the appearance of a blue " flame " at the end of the inlet tube, where ozonised

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* A brief preliminary note appeared in *Nature*, 1935, **135**, 433.

oxygen came into contact with the vapour of nitrogen peroxide when the latter was caused to evaporate rapidly; sometimes, indeed, the gaseous contents of the trap became ignited and burnt with a blue " flame " which travelled through the faintly blue gas, leaving brown nitrogen peroxide behind it.

Observations of a Blue Flame in the System N_2O_5–O_3.—Much clearer evidence of combustion was obtained when attempts were made to determine the m. p. of nitric anhydride in presence of ozone (Lowry and Lemon, *loc. cit.*). The ozone in the escaping gases was then destroyed by passing them through a combustion tube heated by a small flame, and the oxides of nitrogen were absorbed by ferrous sulphate. Under normal conditions, with a tube of 1·2 cm. internal diameter and oxygen containing 8% of ozone, the faintly blue gas became brown when it approached within 2·5 cm. of the flame, but a deep blue colour was developed on a curved boundary of characteristic shape (Fig. *b*) between the faintly blue gas and the brown products of decomposition. When the concentrations were favourable, this boundary " struck back " along the combustion tube and travelled with a characteristic flame front (Fig. *c*) towards the point of entry of the gas. On reaching the point of entry, the flame was usually extinguished, but it sometimes continued to burn as a stationary flame (Fig. *d*), with a deep blue front, but without producing visible light or any marked development of heat. The size of the stationary flame could then be made greater by increasing the velocity of the gas.

When the concentrations were rather less favourable, the " flame " sometimes oscillated slowly over a range of 1—3 cm., and sometimes made a false start by travelling only a few cm. and then dying out. When the concentration of nitric anhydride became a little too low for the flame to strike back spontaneously, it could be caused to do so by turning off one of the taps and opening it again suddenly, so as to produce a rush of gas into the heated part of the tube. On further reduction of concentration, the boundary crept up to within 1·8 cm. of the Bunsen flame; it also became fainter and more greyish, until it was scarcely perceptible, whilst the heated gases became very pale brown in colour. The best conditions for demonstration were obtained by passing ozonised oxygen (8%) through a U-tube of nitric anhydride cooled in ice; it then has a vapour pressure of 50 mm., as compared with 120 mm. at 10°, 180 mm. at 15°, and 280 mm. at 20° (Daniels and Bright, *J. Amer. Chem. Soc.*, 1920, **42**, 1133).

In the absence of ozone, the colourless vapour of nitric anhydride became brown at about 2 cm. from the Bunsen flame (as compared with 2·5 cm. when the oxygen was ozonised) and the boundary was less sharp. No blue colour was developed, and the brown products of decomposition tended to spread backwards along the roof of the tube.

Velocity of Propagation.—The " flame " struck back very gently and with a velocity that became uniform after a slow initial propagation over a range of 5—10 cm. In a tube of 1·1—1·2 cm. diameter, through which the gas was passing at a speed of 2·5 cm./sec., the observed velocities over a range of 50 cm. were: Forward, 17 cm./sec.; backward, 10 cm./sec. The corrected velocities were: Forward, 14·5 cm./sec.; backward, 12·5 cm./sec. The true velocity of the flame was therefore 13·5 cm./sec., but it was carried forward with a velocity of about 1 cm./sec. by the expansion which accompanies the decomposition.

Conditions of Ignition.—(a) *Flame.* The combustion tube was too hot to hold at the point, 2·5 cm. from the small Bunsen flame, at which the blue boundary was developed, but the temperature of ignition appeared to be below 100°, since small drops of water did not boil unless placed within 1·5 cm. of the Bunsen flame. A thermometer at a distance of 2·5 cm. from the Bunsen flame registered 78—80° at the top of the tube and 65—67° at the side.

(b) *Steam.* The ignition temperature of the gas was proved to be below 100° by the observation that the blue flame could be started by means of a steam jet outside the glass tube. This experiment can be shown in the most spectacular way by allowing a long tube to fill with the mixture and then applying a steam jet to the middle. After about ½ minute, the mixture " takes fire " and the blue " flame " travels towards both ends of the tube, leaving it filled with brown nitrogen peroxide. Under favourable conditions, it could be seen that the heated gases, just beyond the steam jet, first became a more intense blue, and then suddenly turned brown, as ignition took place.

At concentrations of nitric anhydride which are too low for ignition, the steam jet produces no visible change of colour; but, in the absence of ozone, the nitric anhydride is decomposed to a small extent, and the gases which have been heated by the jet are of a faint yellowish brown.

(c) *Spark.* An induction coil, capable of producing 5-cm. sparks, was fitted to a spark-gap of 4—5 mm. in a tube through which the mixture was passing. Insufficient sparking, either with or without a condenser, produced a brown patch round the spark-gap, after which ignition was impossible. Sudden sparking of clean unburnt gas, however, sufficed to initiate the travelling flame. This might be a useful method for use in wide tubes where ignition with a flame is difficult. Platinum wires were used, since wires of "sealing alloy" (Fe, Cu, Ni) took fire and burned in the gas. In the absence of ozone, brown nitrogen peroxide was still produced, and continued to form in contact with the hot wires after the current had been switched off; but there was, of course, no ignition.

Decomposition at Atmospheric Temperatures.—A mixture of oxygen with 50 mm. of nitric anhydride and about 7% of ozone by weight had a faint blue colour, which was very obvious in a tube 93 cm. long and of 2·9 cm. external diameter. After 10—15 minutes the colour was fainter, and after an hour it had disappeared completely. After a further 1½ hours, when all the ozone had decomposed, the brown colour of nitrogen peroxide could be seen, and was increased to a maximum by fanning the tube with a flame. In the absence of nitric anhydride a blue colour could be seen in 8% ozonised oxygen, but it was thought to be not quite so strong as when nitric anhydride was present; the colour persisted for 8 or 10 days, but the smell of ozone could be detected after a fortnight.

In accordance with these observations, mixtures of nitric anhydride and ozonised oxygen could not be ignited after storing in Pyrex tubes for 12—20 minutes, since only a local cloud of brown nitrogen peroxide was produced where the tube was heated, without any blue flame or general decomposition of the mixture. The combustion can therefore be demonstrated only in freshly-prepared mixtures, on account of the rapidity with which ozone is decomposed in presence of oxides of nitrogen.

Origin of the Blue Flame.—Hautefeuille and Chappuis (*Compt. rend.*, 1881, **92**, 80; 1882, **94**, 1112, 1306; *Ann. École Norm. Sup.*, 1884, **3**, 103) showed that strong absorption bands in the red, and weak bands in the green, were produced by the action of a silent discharge on air. Since these bands were not given by ozone or by any known oxide of nitrogen, they were attributed to a new oxide of nitrogen, which the authors called "pernitric acid." A solid (apparently colourless) was frozen out by cooling to − 23°, and indirect analyses gave the empirical composition NO_3. Twenty-five years later, Warburg and Leithauser (*Ann. Physik*, 1906, **20**, 743; 1907, **23**, 209) observed the same spectrum in mixtures of nitric anhydride and ozone, and attributed it to a "substance Y" of less than 1% of the concentration of nitric anhydride in a mixture containing 60 mm. of the anhydride and 60 mm. of ozone. More recently, Schumacher and Sprenger (*Z. physikal. Chem.*, 1928, **136**, 49, 77; 1929, **140**, 281; 1929, *B*, **2**, 267; *Z. angew. Chem.*, 1929, **42**, 697) attributed the rapid decomposition of ozone in mixtures of the two gases (Tolman and White, *J. Amer. Chem. Soc.*, 1925, **47**, 1240) to an oxide of the formula NO_3 rather than N_2O_6, since its spectrum resembled that of NO_2 rather than N_2O_4. They could not confirm the suggestion of Trautz (*Z. anorg. Chem.*, 1914, **88**, 285; 1918, **102**, 49) that this oxide might be formed by direct combination of nitric oxide and oxygen, but Zenghélis and Evangelidès (*Compt. rend.*, 1934, **199**, 1418) obtained it by the action of a silent discharge on nitric oxide.

More recently, Schwarz and Achenbach (*Ber.*, 1935, **68**, 343) isolated a small quantity of nitrogen trioxide, NO_3, by the action of a glow discharge on ($NO_2 + 20O_2$) under a pressure of 1 mm. On cooling in liquid air, a volatile white solid was obtained, which decomposed slowly above − 142°, but was shown by gas analysis to have the composition NO_3. This white solid is presumably a colourless polymer of the blue gas with the characteristic absorption bands cited above. Since combustion in the system nitric anhydride–ozone is always associated with the development of a blue colour, which only appears when ozone and oxides of nitrogen are both present, it appears probable that the blue flame depends on the production and decomposition of the elusive trioxide, as represented by the equations $N_2O_5 + O_3 = 2NO_3 + O_2$, $NO_3 + O_3 = NO_2 + 2O_2$, and $NO_3 + NO_3 \longrightarrow 2NO_2 + O_2$. On the other hand, when once the combustion has been initiated, it is possible that nitric anhydride may also be " burned " directly, according to a scheme such as $N_2O_5 + O_3 = 2NO_2 + 2O_2$. The kinetics of the reaction, which suggest a chain mechanism, will be discussed in a subsequent paper.

The nitrogen peroxide was supplied in sealed glass tubes by Messrs. Imperial Chemical Industries, Ltd. (Explosives Group). The ozoniser has already been illustrated (J., **1935**, 695).

SUMMARY.

When ozonised oxygen is passed over nitric anhydride, a gas with a blue tint is produced, which probably contains nitrogen trioxide, NO_3. When the mixture is passed through a combustion tube, it can be ignited by the heat of a flame or by a steam jet playing on the outside of the tube. A blue flame front is then propagated forwards and backwards, with a velocity of the order of 12 cm. per sec. in a tube of 1 cm. diameter, leaving behind it the brown colour of nitrogen dioxide. The combustion may be attributed to the interaction of two highly oxidised gases, which burn *with liberation of oxygen,* according to an equation such as $NO_3 + O_3 = NO_2 + 2O_2$.

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