111. *Properties of the Oxides of Nitrogen. Part VII. Flame Propagation in the System Dinitrogen Pentoxide–Ozone.*

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By spectrographic means it has been proved that the unstable dinitrogen hexoxide is present in a mixture of the pentoxide (nitric anhydride) and ozone undergoing slow decomposition and also in the flame-front in the explosive reaction of these gases. The kinetics of the slow reaction have been studied, and the mechanism shown to involve successively the unimolecular decomposition of the pentoxide, the reaction of ozone with the products, a bimolecular reaction of nitrogen trioxide formed in both the previous steps, and then the re-formation of dinitrogen pentoxide. The mechanism of the explosive reaction is exactly the same, the sequence of reactions proceeding at such a rate as to be adiabatic and self-propagating.

THE results of the detailed study of the explosive reaction between dinitrogen pentoxide and ozone (Part VI, J., 1937, 1461) showed that the flame is propagated by the diffusion of " hot " molecules from the flame-front into the unburnt gases, causing activation and further reaction.

The present paper deals with the actual reactions taking place in the flame-front, and by spectrographic means we have now proved that the unstable intermediate compound, nitrogen trioxide, is present both in the flame-front and in the mixture of nitric anhydride and ozone. A detailed study of the rate of the slow decomposition of the latter in the presence of the former has now shown it to be proportional to the two-thirds power of the concentration of each reactant. This, together with other results, supports the mechanism for the reaction suggested by Schumacher and Sprenger (*Z. angew. Chem.*, 1929, **42**, 627), in which the primary reaction is the decomposition of the pentoxide, the products combining with ozone to form nitrogen trioxide, which immediately decomposes bimolecularly. The dinitrogen pentoxide is continually re-formed, and the concentration remains constant.

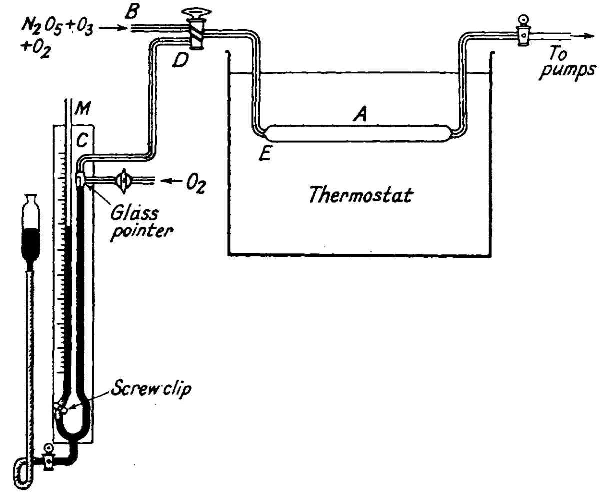
When the gas mixture is raised to a sufficiently high temperature it inflames, and the sequence of reactions, which is the same as in the slow process, becomes continuous, the energy liberated in the bimolecular decomposition of the trioxide causing further decomposition of dinitrogen pentoxide and resulting in a thermal energy chain mechanism. This conclusion differs slightly from that stated in our previous paper, in that the thermal energy required to propagate the reaction is drawn, not from the excess energy carried by the diffusing " hot " trioxide, but from the energy liberated in the exothermic bimolecular decomposition of nitrogen hexoxide.

EXPERIMENTAL.

The Slow Reaction between Dinitrogen Pentoxide and Ozone.—The apparatus is shown in Fig. 1, and for comparison with the results for the flame, the reaction vessel *A* was made from the same sample of soda glass and of the same shape as those used in the work on the flame.

The first tube used had an internal diameter of 13·6 mm. and a volume of 37·5 ± 0·5 c.c. Before use, the tube was washed with concentrated nitric acid, water, and then methylated spirit, and dried in a current of air. After being sealed on to the apparatus, the tube was washed out with dry oxygen and allowed to stand overnight full of oxygen. The apparatus was connected at *B* to the mixing bulb, and immediately after admission of the gases to the reaction vessel the latter was connected to the mercury manometer *M*. The space above the mercury from *C* to *D* was filled with oxygen, and the pressure at the beginning was so adjusted that, on connecting the reaction vessel and the manometer, oxygen was forced into the capillary *D* to *E*. The oxygen provided adequate protection for the mercury against the corrosive action of the gas mixture. The reaction results in the decomposition of ozone with consequent increase in pressure according to the equation : $2O_3 = 3O_2$. This increase of pressure was measured on the left-hand tube of the manometer, the mercury in the right-hand tube being kept at a fixed height, indicated by a glass pointer, by means of a screw clip on the rubber connection between the right- and the left-hand tube. The thermostat temperature was constant to 0·01°.

FIG. 1.



Variation of Rate of Decomposition of Ozone with Partial Pressure of Dinitrogen Pentoxide and Ozone.—Typical curves for the increase of pressure with time are shown in the lower part of Fig. 2. In the upper part of the figure the gradients of the pressure–time curves are plotted against time, and the exact initial rate of decomposition of ozone is obtained by extrapolation to zero time.

The rate of decomposition of ozone, expressed as the number of mm. decomposed per minute, is plotted against the partial pressure of the pentoxide in Fig. 3. The initial pressure of ozone in the mixing bulb was 50 mm., and the total pressure in the reaction vessel was 700 ± 2 mm. The curve in Fig. 3 is for the expression :

$$\text{Rate} = 0{\cdot}15p_{N_2O_5}{}^{2/3}$$

and the experimental values denoted by crosses follow this very closely; hence the rate is proportional to the two-thirds power of the partial pressure of dinitrogen pentoxide.

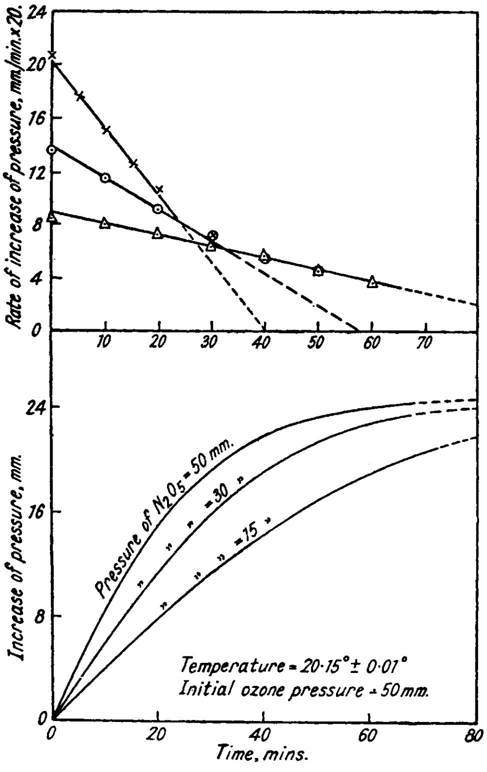
The logarithm of the rate of decomposition is related linearly to that of the partial pressure of ozone when the pentoxide pressure is constant. The gradients of these straight lines for several pressures of pentoxide are given in the following table. The average gradient is 0·63; therefore :

$$-\,d[O_3]/dt = K[O_3]^{0{\cdot}63}$$

N_2O_5 pressure, mm.	10	20	25	30	35	40	
Gradient	0·62	0·66	0·62	0·60	0·645	0·625	Mean 0·63

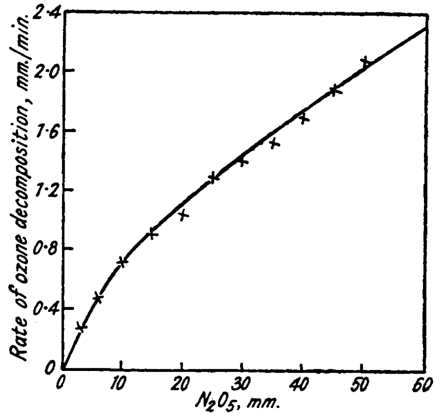
Variation of Rate of Decomposition with Temperature.—The initial rate was studied over the temperature range 20—45°. At higher temperatures the mixture inflamed when admitted to the reaction tube. From the results, the activation energy was calculated to be 19,720 cals., and the Arrhenius law is obeyed over the whole range of temperature. It was observed that at 40° and 45°, when all the ozone has been decomposed and the rate of decomposition of the pentoxide is appreciable, the pressure–time curves for the decomposition of ozone in the presence of the pentoxide do not become horizontal, but pass gradually into the straight-line curves for the decomposition of the latter alone. This suggests that the rate-controlling process in the decomposition of ozone is the unimolecular decomposition of the pentoxide, which is catalysed to a certain extent by the ozone, and the apparent decomposition of ozone is due to the combination of this with the decomposition products of the pentoxide. This view is supported by the results described above.

Fig. 2.



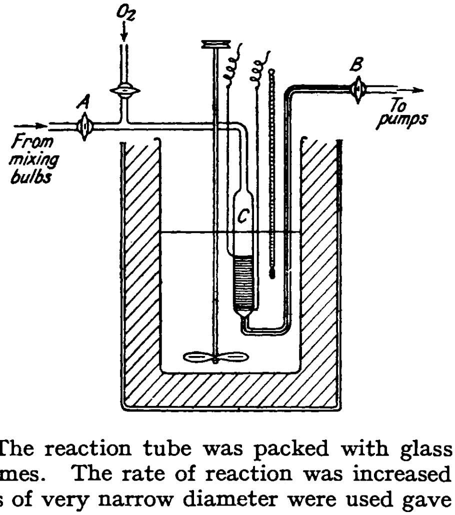
Rate of decomposition of ozone.

Fig. 3.



Rate of decomposition of ozone in presence of nitric anhydride.

Fig. 4.

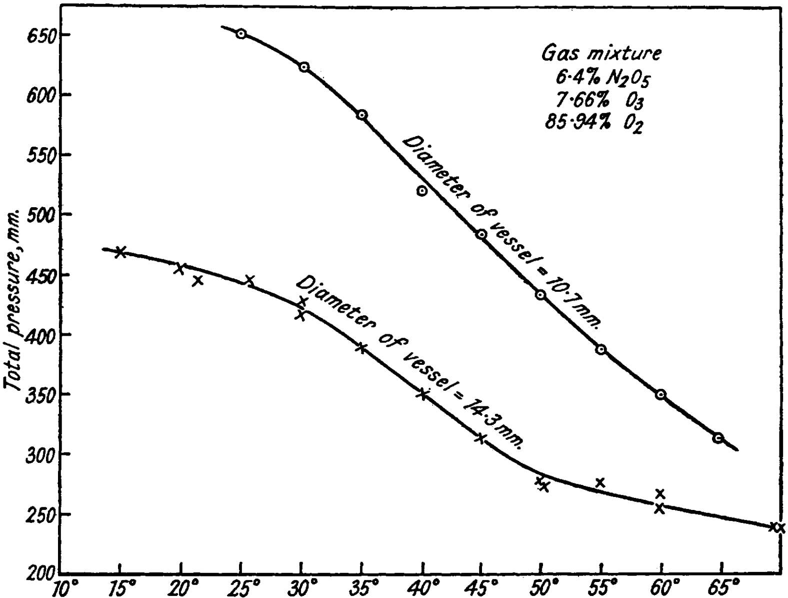


Effect of Increased Surface on the Initial Rate.—The reaction tube was packed with glass rods, the surface/volume ratio being increased 7·2 times. The rate of reaction was increased by only 2—3%. Other experiments in which vessels of very narrow diameter were used gave a similar result; *e.g.*, no difference in velocity could be detected in tubes of 5·4 and of 13·7 mm. diameter. The results show that the reaction between the pentoxide and ozone is almost entirely homogeneous, and that if it is a chain reaction the chain carriers are unaffected by diffusion to the walls of the containing vessel.

Variation of Ignition Temperature with Pressure.—The apparatus is shown in Fig. 4. A soda-glass tube, of 14·3 mm. diameter, was wound at its lower end with a nichrome heating coil. This was used for heating a constant-temperature bath of liquid paraffin. The bath was well stirred with a glass propeller, and its temperature could be kept constant to within 0·1° for several minutes. A big-bore stopcock *A* was used for admitting the gas mixture rapidly. The method was to get the bath to a suitable temperature, prepare a mixture containing 30 mm.

of dinitrogen pentoxide and 50 mm. of ozone, close stopcock *B*, and 10 mins. after the mixing of the gases had started, to admit them to *C* as rapidly as possible by opening *A*. If the conditions were suitable, the mixture inflamed at the bottom of the tube and the flame moved upwards. The reaction vessel *C* was evacuated, washed with oxygen, and another admission made 2 mins. after the first. This was continued at 2-min. intervals until two successive admissions gave no flame, *i.e.*, the critical pressure had been reached. This was repeated using higher temperatures and beginning with lower pressures of the mixture of same percentage composition. A reaction vessel of diameter 10·7 mm. was also used. The curves for the variation of ignition temperature with pressure are shown in Fig. 5.

FIG. 5.



Variation of ignition temperature with pressure.

The Stationary Flame.—In order to study the flame spectrographically, a stationary flame was obtained in a vertical tube of 5 mm. diameter by passing in a mixture of the pentoxide and ozonised oxygen at the bottom, and balancing the rate of admission against the rate of consumption of reactants at the flame-front. The flame could be held at any point for several minutes. It was observed that the tube became quite warm near the flame-front, but attempts to detect long-wave emission by means of infra-red and hypersensitive panchromatic plates were unsuccessful.

Absorption Spectrographs of the Flame and Gas Mixture.—An ordinary glass prism instrument with small dispersive power was used with hypersensitive panchromatic plates. A 25-watt, 220-volt lamp covered by four pieces of parchment was used as a source of light, and placed 3 feet away from the slit, which was 4 × 0·05 mm. The stationary flame-front was held in front of the slit, and short exposures of not more than 60 secs. made. The absorption spectrum appeared as a series of dark bands down the centre of each photograph, and the wave-lengths of the main bands were measured by comparison with a neon spectrum taken on the same plate. The photograph of the spectrum of the gas mixture was obtained by using a horizontal tube 82·5 cm. long, with a continuous stream of dinitrogen pentoxide and ozonised oxygen passing through it. The measurements for the flame and the gas mixture are recorded below. They compare favourably with measurements made by Warburg and Leithauser (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 229) on a mixture of the pentoxide and ozone.

Spectrum.	Wave-lengths of main bands, ± 4 A.	Spectrum.	Wave-lengths of main bands, ± 4 A.	Warburg and Leithauser's measurements.
Flame-front	6650—6593	Mixture of N_2O_5, O_3, and O_2	6650—6598	6640—6600
	6310—6209		6310—6208	6300—6220

The wave-lengths of the main bands for the flame-front and the gas mixture are identical. These bands are undoubtedly due to the presence of nitrogen trioxide; hence the blue flame-front and the reacting mixture contain this higher oxide of nitrogen. Warburg and Leithauser showed that dinitrogen hexoxide is only present to the extent of 1% in a mixture of 60 mm. of the pentoxide and 60 mm. of ozone. In the flame-front the concentration of hexoxide will be high, for probably the whole of the pentoxide has reacted with ozone.

DISCUSSION.

The spectrographic investigation of the flame-front and the gas mixture showed that nitrogen trioxide, NO_3, is present in each case, and no doubt is the intermediate product in the slow pentoxide-catalysed decomposition of ozone and in the explosive reaction between the last two reagents.

The results on the slow reaction show that the rate of decomposition of ozone is proportional to the two-thirds power of the concentration of each reactant; *i.e.*,

$$-\,\mathrm{d}[O_3]/\mathrm{d}t = k[N_2O_5]^{\frac{2}{3}}[O_3]^{\frac{2}{3}}.$$

This supports the mechanism for the reaction suggested by Schumacher and Sprenger (*loc. cit.*). The primary process is the simple decomposition of dinitrogen pentoxide, followed by two reactions which they assume to constitute a chain process, then the regeneration of the pentoxide from the products:

$$\begin{array}{llll} (1) & N_2O_5 = NO_2 + NO_3 \quad (k_1) & (3) & NO_3 + NO_3 = NO_2 + NO_2 + O_2 \quad (k_3) \\ (2) & NO_2 + O_3 = NO_3 + O_2 \quad (k_2) & (4) & NO_2 + NO_3 = N_2O_5 \quad (k_4) \end{array}$$

Here k_1, k_2, etc., are the rate constants for the forward reactions. On the basis of this assumed mechanism they derived the following theoretical expression for the rate of decomposition of ozone:

$$-\,\mathrm{d}[O_3]/\mathrm{d}t = k_3\sqrt[3]{(k_1k_2[O_3][N_2O_5]/k_3k_4)^2}$$

in agreement with our experimental result. The primary process, *i.e.*, the decomposition of dinitrogen pentoxide is well known to be a homogeneous reaction, which agrees with our observation that increase of surface does not affect the rate appreciably. Since the rate is slightly *increased* by packing the reaction tube or removing the inert gas (see Part VI, *loc. cit.*, p. 1466), the rate-controlling reaction must be unimolecular.

In 1884 van 't Hoff suggested that explosion in an exothermic reaction results from rapid acceleration in rate of reaction due to progressive self-heating. The idea has been further developed by Semenoff and a formula evolved for the relationship between critical explosion temperature and pressure, *viz.*, $\log_{10} P/T = A/T + B$, where $A = (E/2\boldsymbol{R})\log_{10}e$, and B depends on the composition of the gas mixture and the diameter of the vessel. From the results recorded in Fig. 5, linear relationships were obtained when $\log_{10} P/T$ was plotted against the reciprocal of absolute temperature, and A, the gradient of the straight lines, was found to be 1160 and 800. Calculated from the activation energy, A is 2170, *i.e.*, of the same order. The agreement with the theory is satisfactory in view of the complications involved in the method of measuring the ignition temperature. Semenoff showed that this relationship between pressure and temperature is obeyed whether the mechanism of explosion involves branching chains or is purely thermal. As will be shown later, we incline to the hypothesis of a purely thermal initiation in which "ignition depends upon heating a sufficient volume of gas to a sufficient temperature" (Taylor-Jones, "Induction Coil Theory and Applications").

The mechanism of the flame is the same as for the slow reaction, except that the processes involved are so rapid as to be adiabatic and self-propagating. The molecules of the unstable intermediate product, nitrogen trioxide, formed by the decomposition of dinitrogen pentoxide and by the combination of nitrogen dioxide and ozone, diffuse forward and combine to liberate thermal energy which serves to ignite the layer of gases in front. Nitrogen trioxide may also be decomposed by collision with a molecule of ozone. This is probable, for approximately 2 mols. of ozone are used up for 1 mol. of pentoxide to give a maximum flame speed (see Part VI, *loc. cit.*, p. 1465).

The complete mechanism of the flame is represented as follows :

(5) N_2O_5 + thermal energy $= NO_2 + NO_3$
(6) $NO_2 + O_3 = NO_3 + O_2$
(7) $NO_3 + NO_3 = NO_2 + NO_2 + O_2$ + thermal energy
(8) N_2O_5 + thermal energy $= NO_2 + NO_3$, etc.
also (9) $NO_3 + O_3 = NO_2 + 2O_2$.

The mechanism undoubtedly involves the initial formation of the unstable intermediate product, mononitrogen trioxide.

All the phenomena are typical of a flame and can be explained on the basis of a simple kinetic theory. Propagation of the flame is by diffusion of trioxide molecules from the flame-front into the unburnt gases, followed by a bimolecular reaction of those trioxide molecules in which sufficient thermal energy is liberated to ignite the layer of unburnt gases in front. The velocity of the flame is largely determined by the rate of diffusion of the trioxide molecules, as has been shown by the results of Part VI (*loc. cit.*).

The sequence of reactions taking place in the explosive and in the slow combination of dinitrogen pentoxide and ozone is essentially the same, but in the former the reactions proceed at such a rate as to be adiabatic and self-propagating.

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