

The Kinetics of the Oxidation of Sulphur Dioxide by Nitrous Oxide.

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Kinetic studies of oxidation by nitrous oxide are now extended to sulphur dioxide at temperatures between 650° and 736° and pressures of about half an atmosphere. Measurements of the initial rate at various concentrations of the reactants indicate an empirical rate equation of the form :

$$\text{Rate} = k'[\text{N}_2\text{O}]^{1.45} + k''[\text{N}_2\text{O}]^{0.58}[\text{SO}_2]$$

A reaction mechanism is proposed to account for the experimental results in terms of a splitting of activated nitrous oxide molecules into molecular nitrogen and atomic oxygen, followed by the oxidation of sulphur dioxide by the latter. The activation of the nitrous oxide molecules is predominantly by collision with their like; there is, however, some activation by collision with molecules of sulphur dioxide since in their presence the rate of decomposition of nitrous oxide is increased.

THIS communication describes the behaviour of nitrous oxide with sulphur dioxide which it oxidises smoothly and homogeneously. Reference to previous investigations which have dealt with the oxidation by nitrous acid of hydrogen (Melville, *Proc. Roy. Soc.*, 1933, *A*, 142, 524; 1934, *A*, 146, 737), carbon monoxide (Bawn, *Trans. Faraday Soc.*, 1935, 31, 461), methane (Robinson and Smith, *J.*, 1952, 8395), and the *n*-paraffins from propane to nonane (Smith, *J.*, 1953, 1271), shows that, except in the last, the experimental results can be readily ascribed to a reaction beginning, at about 600°, by fission of nitrous oxide into nitrogen molecules and oxygen atoms and continuing by chain reactions. With methane the chains include free alkyl radicals; but when such radicals are produced by pyrolysis of the hydrocarbon below 600°, as with propane, etc., then oxidation is initiated by their attack on the nitrous oxide, and takes place at a correspondingly lower temperature.

The reaction with sulphur dioxide was expected to be simpler, and, as no chains are involved, has proved so. Whittingham (*Nature*, 1947, 159, 232) noted that, in the presence of nitrous oxide, sulphur dioxide is oxidised at a measurable speed above 550°; this agrees with our finding oxidation barely detectable at 500°, slow at 600°, and convenient for measurement between 650° and 750°. As the amount of sulphur trioxide formed was small and oxygen absent from the products over the significant region, dissociation of the trioxide was clearly negligible and the observations relate only to the oxidation reaction. The rate depends mainly on the concentration of nitrous oxide and but slightly on that of sulphur dioxide. Broadly the picture is one of decomposition of nitrous oxide followed by oxidation of sulphur dioxide, as is made clear by the activation energy of the initial step approximating to that required for the splitting of nitrous oxide itself. But other factors, such as the different modes of activating and deactivating nitrous oxide molecules, and the reactions between oxygen atoms and nitrous oxide molecules, and between oxygen atoms themselves at a surface, must detract somewhat from the essential simplicity. Of these factors, the only one effective enough to demonstrate its presence in our rate measurements is the activation of nitrous oxide molecules by collision with sulphur dioxide molecules. The initial rates of reaction in mixtures of sulphur dioxide and nitrous oxide are appreciably greater than the rate of decomposition of nitrous oxide alone. Sulphur dioxide is of course by no means the only gas bringing about this activation (Volmer and Bogden, *Z. phys. Chem.*, 1933, *B*, 21, 257; Lewis and Hinshelwood, *Proc. Roy. Soc.*, 1938, *A*, 163, 441).

EXPERIMENTAL

Materials.—(i) Sulphur dioxide, the middle portion from a siphon of liquid, was dried (P_2O_5) and collected in a trap cooled in liquid nitrogen. After any non-condensable gas had been removed by pumping, the sample was fractionated between traps maintained at -72° and -196° , head and tail fractions being discarded.

(ii) Nitrous oxide, from a cylinder of anaesthesia-grade gas, was washed with concentrated pyrogallol solution, dried (P_2O_5), and frozen in a trap cooled in liquid nitrogen. Non-condensable gases were removed by pumping, and the material was further purified by fractionation between traps kept at -130° and -196° , the first and last portions being rejected.

The nitrous oxide and sulphur dioxide were separately stored in three-litre glass containers each of which was connected to its own one-litre sampling bulb.

Apparatus.—Two cylindrical, silica reaction vessels were used; an unpacked one, 19 cm. \times 4.5 cm., with a surface : volume ratio of 1.81 : 1, and another, 4 cm. \times 11 cm., packed with silica tubing, with a surface : volume ratio of 9.5 : 1. Each vessel had a thermocouple well and a capillary inlet which was fitted with a ground socket to connect it to the rest of the system. This was constructed of "Pyrex" glass, and was attached to a mercury-vapour pump backed by a rotary oil-pump.

In use, the reaction vessel was embedded in a well-lagged, tubular, electric furnace. The temperature was kept within $\pm 1^\circ$ by a "Sunvic" energy regulator and a hot-wire switch, and was measured by means of a "chromel-alumel" thermocouple in conjunction with a "Doran" potentiometer.

For charging the reaction vessel, a two-way tap enabled it to be connected in turn with the sulphur dioxide and nitrous oxide sampling bulbs. Between this tap and the reaction vessel was a manometer in the form of a U-tube of narrow bore. Dead space was kept to a minimum and maintained at 100° to prevent the condensation of sulphur trioxide.

The more readily condensable products were removed through a capillary tap to a series of traps where they were frozen by means of liquid nitrogen. What remained was absorbed on activated charcoal.

The analysis apparatus consisted essentially of a gas burette, capable of measuring volumes of from 0.01 ml. to 30 ml. with an accuracy of 0.1%. It could be used either as a Töpler pump or a McLeod gauge, and was connected to two adsorption bulbs in such a way that gas could be passed from the burette to the bulbs and back again for further measurement. Oxygen was removed by finely divided copper, precipitated on kieselguhr as described by Meyer and Ronge (*Angew. Chem.*, 1939, 52, 637), and sulphur dioxide by "Carbasorb."

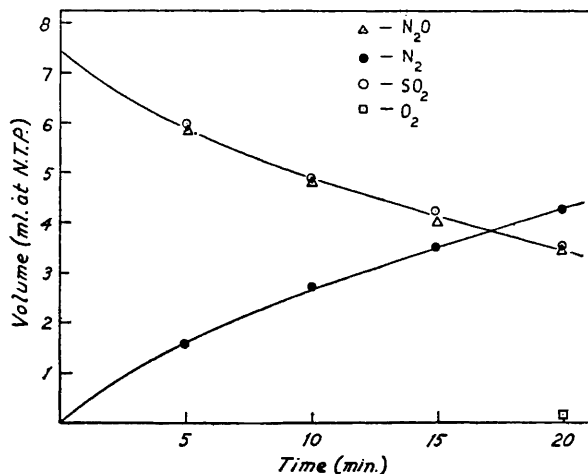
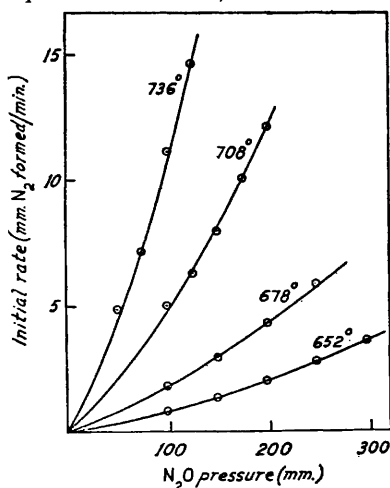
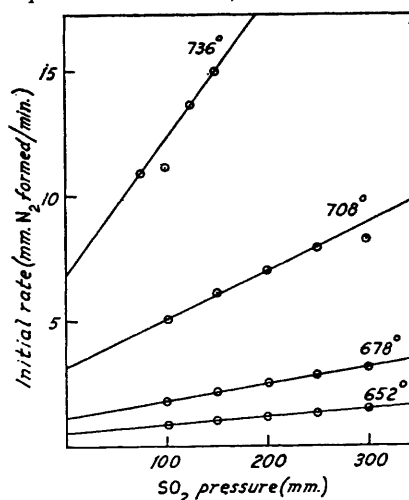
Operation.—Since the reaction between sulphur dioxide and nitrous oxide involves no pressure change, its progress was followed by analysing the mixtures obtained after various times of heating. The two gases were introduced into the reaction vessel in turn from the appropriate sampling bulb, the interval between the successive additions being within 5 sec. After a heating-time measured to ± 5 sec., the products were respectively frozen out or absorbed in the collecting traps. The condensable materials were first partially separated by fractionation between traps, the nitrous oxide and sulphur dioxide being taken off at -72° . The volume of this mixture was measured in the gas burette; the sulphur dioxide was then absorbed on "Carbasorb" and the decrease in volume measured. Oxygen was removed from the non-condensable portion by copper; the remaining gas was assumed to be nitrogen.

Analytical Results.—Complete analyses of the products formed after heating mixtures of nitrous oxide (100 mm.) and sulphur dioxide (100 mm.) at 697° for various times showed that the volume of nitrogen formed was equal to the volume of nitrous oxide and sulphur dioxide which had reacted, provided that not more than half the sulphur dioxide had been oxidised; within this limit no oxygen was found in the non-condensable products. A trace of oxygen was, however, detected when the reaction had proceeded beyond the half-way point. These results showed that the amount of nitrogen formed was an accurate measure of the extent of the reaction. Once this was established only nitrogen was determined. Composition-time curves, comprising all the components except sulphur trioxide, are given in Fig. 1.

Order of Reaction.—A series of experiments, in which the initial pressure of one reactant was fixed and that of the other varied, was made at four different temperatures. The amounts of nitrogen formed in the individual mixtures after various times of heating were measured and plotted against time. The graphs were smooth curves from which the initial rates of reaction were estimated. The effects on these rates of varying the concentrations of nitrous oxide and sulphur dioxide are shown in Figs. 2 and 3, respectively. From the graphs, it is seen that the order of reaction with respect to nitrous oxide is greater than unity, and that it is dependent on the first power of the concentration of sulphur dioxide. The curves are similar in form to those obtained by Robinson and Smith (*loc. cit.*) for the reaction between nitrous oxide and methane, and yield the following empirical equation for the rate of reaction :

$$\text{Rate} = k'[\text{N}_2\text{O}]^x + k''[\text{N}_2\text{O}]^y[\text{SO}_2]$$

Changes in the concentration of sulphur dioxide have markedly less effect on the initial rates of reaction than corresponding changes in the concentration of nitrous oxide; hence the contribution of the second term in the above equation to the overall rate of reaction must be small. When the contribution of the second term is neglected, logarithmic plots of initial rates against

FIG. 1. *Composition-time curve at 697° c.*FIG. 2. *Influence of pressure of nitrous oxide on initial rate (sulphur dioxide pressure = 100 mm.).*FIG. 3. *Influence of pressure of sulphur dioxide on initial rate (nitrous oxide pressure = 100 mm.).*

nitrous oxide concentrations give the following values for x at the temperatures specified: 1.47 (652°); 1.43 (678°); 1.46 (708°); 1.43 (736°); mean 1.45. To obtain y , plots were made of the initial rate against sulphur dioxide concentration for two different, fixed concentrations of nitrous oxide at 678°. The ratio of the slopes of these lines corresponds to $[\text{N}_2\text{O}]^y/[\text{N}_2\text{O}']^y$, $[\text{N}_2\text{O}']$ and $[\text{N}_2\text{O}']$ being the two nitrous oxide concentrations. From these data y proved to be 0.58, making the empirical rate equation:

$$\text{Rate} = k'[\text{N}_2\text{O}]^{1.45} + k''[\text{N}_2\text{O}]^{0.58}[\text{SO}_2]$$

Activation Energy.—The intercepts in Fig. 3 correspond to $k'[\text{N}_2\text{O}]^{1.45}$. Plotting the log of the intercept against $1/T$, and taking into account the variation of pressure with temperature gave the activation energy E' a value of 56 kcal.

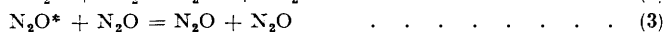
The slopes of the lines in Fig. 3 correspond to $k''[\text{N}_2\text{O}]^{0.58}$. From a plot of log of the slope (corrected for the variation of pressure with temperature) against $1/T$, the activation energy E'' , corresponding to k'' , was found to be 70 kcal.

Effect of Surface Area.—In a number of runs, a packed reaction vessel with a surface : volume ratio approximately five times that of the unpacked vessel was used. This change had no measurable effect on the rates of reaction.

DISCUSSION

The reaction between sulphur dioxide and nitrous oxide is similar to that between methane and nitrous oxide, and the empirical rate equations bear a close resemblance to one another. In each, the first term is almost identical with the empirical expression for the decomposition of nitrous oxide. At our experimental pressures and 652° , the rate of decomposition of nitrous oxide alone is proportional to $[\text{N}_2\text{O}]^{1.55}$ (Lewis and Hinshelwood, *Proc. Roy. Soc.*, 1938, *A*, **168**, 441), an order with respect to nitrous oxide slightly greater than that given by our experiments. The difference probably arises from the approximation made in calculating the value for x , namely the neglect of the contribution of the second term to the overall rate. Incidentally, the activation energy, E' , associated with the first term is significantly close to that for the thermal decomposition of nitrous oxide alone (for which Lewis and Hinshelwood obtained values of 55.3 and 57.1 kcal., from the decomposition at 100 mm. pressure). Thus there is good evidence that the first term concerns the decomposition of nitrous oxide itself.

The initial rate of the reaction, as Fig. 3 shows, increases linearly with the concentration of sulphur dioxide. The reasonable assumption being made that the oxidation, $\text{O} + \text{SO}_2 \rightarrow \text{SO}_3$, is fast, and independent of the concentration of sulphur dioxide (provided that there is an excess), it follows that the rate of formation of sulphur trioxide must depend solely upon the availability of oxygen atoms. These atoms are derived from the decomposition of active nitrous oxide molecules and we believe the observed increase in rate, following an increase in sulphur dioxide concentration, is attributable to the latter's participation in the activation of nitrous oxide. Increases in the rate of decomposition of nitrous oxide in the presence of a number of other gases have been ascribed to this cause. We therefore propose the following mechanism for the reaction :



(A rate constant carries the serial number of the equation to which it refers.)

Since the amount of molecular oxygen formed during the reaction is very small, and as no nitric oxide was detected at any time, reactions (7), (8), and (9) must be extremely slow compared with (6), and may safely be neglected. From the usual stationary state conditions we then have

$$\text{Rate} = \left\{ k_1[\text{N}_2\text{O}]^2 / \left(1 + \frac{k_3}{k_5}[\text{N}_2\text{O}] + \frac{k_4}{k_5}[\text{SO}_2] \right) \right\} +$$

$$\left\{ k_2[\text{N}_2\text{O}][\text{SO}_2] / \left(1 + \frac{k_3}{k_5}[\text{N}_2\text{O}] + \frac{k_4}{k_5}[\text{SO}_2] \right) \right\}$$

If k_4 were comparable in magnitude with k_3 , then the order of reaction with respect to sulphur dioxide would be expected to be less than unity. The straight-line plots in Fig. 3

show that this is not so, and hence k_4 must be appreciably less than k_3 . The above expression may therefore be simplified to :

$$\text{Rate} = k_1[\text{N}_2\text{O}]^2 / \left\{ 1 + \frac{k_3}{k_5} [\text{N}_2\text{O}] \right\} + k_2[\text{N}_2\text{O}][\text{SO}_2] \left\{ 1 + \frac{k_3}{k_5} [\text{N}_2\text{O}] \right\}$$

This equation approaches closely the form of the empirical rate equation. The first term is the same as that for the decomposition of nitrous oxide alone and corresponds to $k'[\text{N}_2\text{O}]^{1.45}$. The second term in the theoretical rate expression can thus be written in the form $k_2k'/k_1\{[\text{N}_2\text{O}]^{0.45}[\text{SO}_2]\}$. This predicts an order with respect to nitrous oxide in the second term near to that found experimentally. It is to be noted that, taking a value of 1.55 for the order with respect to nitrous oxide in the first term, we obtain a much closer agreement between the empirical and theoretical orders for nitrous oxide in the second term. The empirical rate constant k'' is identified with k_2k'/k_1 , and hence $E_2 - E_1 = 14$ kcal. Although small, the difference between the activation energies of the two reactions is not readily accounted for. It has been pointed out that the thermal decomposition of nitrous oxide is not a simple process, and that the complexity may be due to the occurrence of more than one quasi-unimolecular reaction, each involving a different mode of activation and a different transformation probability of the activated molecules (Hinshelwood, "Kinetics of Chemical Change," Oxford Univ. Press, 1940, p. 131). It is not unlikely that the two activation energies may owe their difference to the two types of molecular collision involved and the modes of activation resulting from them.

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