283. *The Thermal Decomposition of Nitrous Oxide. The Effect of Foreign Molecules.*

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The kinetics of the decomposition of nitrous oxide in the presence of carbon dioxide, carbon tetrafluoride, and the inert gases have been studied over the temperature range 650—750° and with pressures of nitrous oxide of 50—100 mm., and compared with results obtained with sulphur dioxide.[1] For these conditions the empirical rate equation is:

$$\text{Rate} = k'[N_2O]^{1{\cdot}55} + k''[N_2O]^{0{\cdot}55}[X]$$

Decomposition of the nitrous oxide molecule follows its activation by the two processes

$$N_2O + N_2O \longrightarrow N_2O^* + N_2O\ ;\quad N_2O + X \longrightarrow N_2O^* + X$$

The activation energy of the second of these is about 3 kcal. higher than that of the first. The efficiencies of the various foreign gases have been compared by determining the several ratios of the rate constants of the above reactions. From these results the relative efficiencies " collision per collision " have been calculated. The results indicate a behaviour of the inert gases different from that displayed by them in other unimolecular decompositions.

In studying the oxidation of sulphur dioxide by nitrous oxide [1] we found that the sulphur dioxide participates in the formation of activated nitrous oxide molecules which are produced by the reactions

$$N_2O + N_2O \underset{(1')}{\overset{(1)}{\rightleftharpoons}} N_2O^* + N_2O;\quad N_2O + SO_2 \underset{(2')}{\overset{(2)}{\rightleftharpoons}} N_2O^* + SO_2$$

Experiment indicates that reaction (2′) is less likely to occur than (1′) since there is no noticeable fall-off in the initial rate of reaction as the concentration of sulphur dioxide is increased, the graphs of initial rate against sulphur dioxide concentration being straight lines over the pressure range studied. We observed an energy difference, $E_2 - E_1$, of approximately 14 kcal.; this magnitude was difficult to understand, but, owing to the scatter of the points on one of the Arrhenius plots the figure was uncertain.

In order to test the reality of this energy difference we investigated the decomposition of nitrous oxide in the presence of carbon dioxide which accelerates the decomposition of nitrous oxide without undergoing chemical change.[2] Although the efficiency of reaction (2) compared with that of (1) for the nitrous oxide–carbon dioxide system had been estimated,[3] no data were available for comparing the activation energies of the two steps. This system has the advantage over the nitrous oxide–sulphur dioxide system that it can be followed by change of pressure with time, thus giving more accurate figures for initial rates. (The sulphur dioxide reaction, involving no change in pressure, must be followed by the tedious and less accurate method of gas analysis.) With carbon dioxide present we found that E_2 was greater than E_1 by approximately 3 kcal. An energy difference of the same order appeared when the added gas was carbon tetrafluoride.

Besides enabling us to compare the activation energies of reactions (1) and (2), the results afforded a method of comparing the efficiencies of the reactions. In the case of carbon dioxide, our relative efficiency figure differs appreciably from that of Volmer, Kummerow, and Nagasako,[2,3] whose results have been criticised on several grounds by Lindars and Hinshelwood.[4] Their experiments were not done at sufficiently high pressures

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[1] Bell, Robinson, and Trenwith, *J.*, 1955, 1440.

[2] Volmer and Kummerow, *Z. phys. Chem.*, 1930, **9**, *B*, 141.

[3] Nagasako, *ibid.*, 1931, **11**, *B*, 420; Volmer and Frohlich, *ibid.*, 1932, **19**, *B*, 85; Volmer and Bogdan, *ibid.*, 1933, **21**, *B*, 257.

[4] Lindars and Hinshelwood, *Proc. Roy. Soc.*, 1955, *A*, 231, 162.

to give an accurate value for k_∞, the limiting value of the first-order rate constant for the decomposition of nitrous oxide from which the relative efficiencies were calculated. The inaccuracies are apparent when their figures for k_∞ are compared with those calculated from the relation $k_\infty = 10^{11 \cdot 7} \exp(-61{,}000/\boldsymbol{R}T)$ derived by Hunter [5] from measurements at very high pressures.

Although carbon tetrafluoride accelerates the decomposition of nitrous oxide,[4] data on its relative efficiency were not available. We have found it to be the most effective of the foreign gases studied, being almost as efficient as nitrous oxide itself.

Published values of relative efficiencies of the inert gases in unimolecular reactions show them generally to increase with atomic weight. For the decomposition of nitrous oxide the only figures available are those of Volmer *et al.* which indicate that the relative efficiencies of the inert elements decrease in order of increasing atomic weight. To check this departure from the usual influence of the inert gases, their effect on the rate of decomposition of nitrous oxide has been studied, and their several relative efficiencies have been determined. Our figures for these, although different from those of Volmer *et al.*, show the same trend for the first four members, namely a decrease with increase in atomic weight. Xenon is singular in that its efficiency is approximately the same as that of argon.

EXPERIMENTAL

Materials.—(i) Nitrous oxide (anæsthesia grade) was dried (P_2O_5) and fractionated between $-130°$ and $-196°$, head and tail fractions being rejected. Before use it was repeatedly frozen and evaporated, occluded non-condensable gases being pumped off. The purified gas was stored in a 3 l. bulb. (ii) Carbon tetrafluoride from a cylinder (Imperial Chemical Industries) was dried (P_2O_5) and condensed in a trap cooled in liquid nitrogen; occluded non-condensable gases were pumped off, and the gas was distilled in a low-temperature Podbielniak-type column. A middle cut of the fraction boiling at $-129°$ was collected and stored in a 3 l. bulb. (iii) Carbon dioxide was obtained by allowing " Drikold " to evaporate in an evacuated bulb. The gas was condensed in a trap cooled in liquid nitrogen and then fractionated at $-130°$ into another trap cooled in liquid nitrogen, a middle cut being retained. After another similar fractionation the gas was deemed sufficiently pure. (iv) Helium, neon, argon, krypton, and xenon were transferred from the soda-glass containers in which they were supplied by the British Oxygen Company to a sampling bulb on the apparatus. Mass spectrometry showed the specimens to contain 99·99% of the gas in question with the exception of argon, which carried 0·2% of air, and xenon, which had 0·3% of krypton.

Apparatus.—A cylindrical reaction vessel, 15 cm. × 4·5 cm., of clear silica was used. It had a thermocouple well and capillary inlet and was connected to the rest of the system, which was of Pyrex glass, by a ground cone-and-socket joint sealed with Picein wax. The whole was evacuated by a mercury diffusion pump backed by a rotary oil pump. The reaction vessel was heated in a well-lagged tubular furnace the temperature of which was kept within $\pm 1°$ of that required by means of a " Sunvic " energy regulator and hot-wire switch. Temperatures were measured with a chromel–alumel thermocouple in conjunction with a " Doran " potentiometer. A constant volume manometer [6] was used to measure the pressure. The use of two cathetometers, one fixed and focused on the constant head and the other movable and focused on the moving limb of the manometer, gave improved accuracy. The reaction vessel was connected through a two-way tap to two sampling bulbs, dead space being kept to a minimum.

Operation.—The reactants were introduced separately into the reaction vessel, the time interval between successive additions being less than 5 sec. Pressure–time readings were taken during the first 10 to 15 min. at approximately half-minute intervals. Before every run the reaction vessel was kept under vacuum for 15 min.

RESULTS AND DISCUSSION

A series of estimations of initial rates of reaction were made for mixtures with the same initial nitrous oxide concentration and various amounts of carbon dioxide, and also with the same initial carbon dioxide concentration and various amounts of nitrous oxide.

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[5] Johnston, *J. Chem. Phys.*, 1951, **19**, 663.

[6] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, 122.

The plots of initial rate against the varied concentrations (Figs. 1 and 2) yield the following empirical rate equation for the decomposition of nitrous oxide in the presence of the added gas:

$$\text{Rate} = k'[N_2O]^x + k''[N_2O]^y[X]$$

where [X] is the concentration of the foreign gas. This equation corresponds to that given for the nitrous oxide–sulphur dioxide system, the initial rate curves being similar.[1]

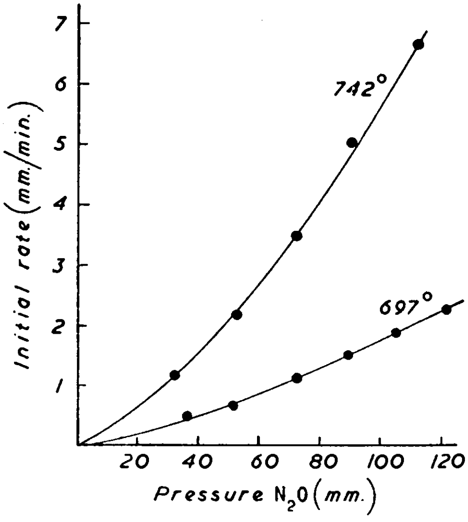

FIG. 1. *Variation of initial rate with pressure of nitrous oxide.*

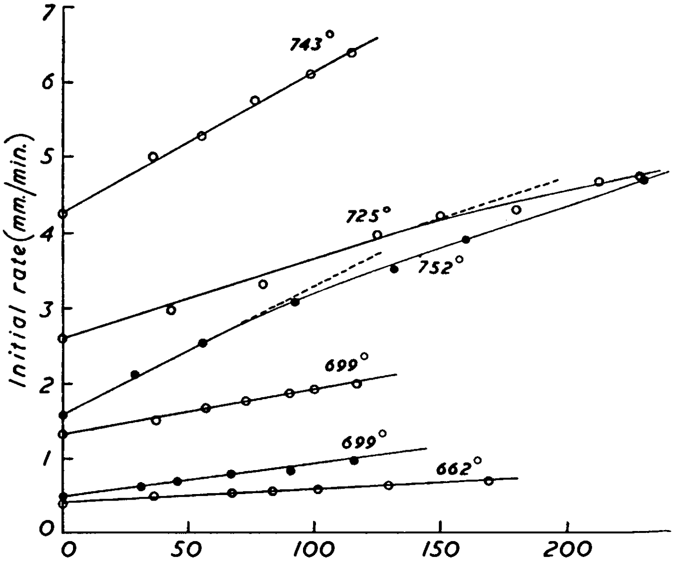

FIG. 2. *Variation of initial rate with pressure of carbon dioxide.*

● N_2O pressure = 50 mm.
○ N_2O pressure = 100 mm.

In general, the above equation holds only when [X] is less than [N_2O], for when the concentration of the added gas exceeds that of the nitrous oxide the points on the initial rate–[X] curve for constant nitrous oxide concentration deviate negatively from the straight line (Fig. 2).

Values of x were obtained from the plots of initial rate of reaction against [X] for the specific concentrations of 50 mm. and 100 mm. of nitrous oxide, measurements being made at 699° and 743°. x can be determined from the ratio of the intercepts at a particular temperature since these correspond to $k'[N_2O]^x$. The slopes of the graphs correspond to $k''[N_2O]^y$, so that y can be determined from their ratio. This assumed that x and y do not vary with pressure, which, though not strictly true, introduces a negligible error since the order of the nitrous oxide decomposition is known to change very little over our pressure range.

TABLE 1.

Added gas	Temp.	x	y	Added gas	Temp.	x	y
Carbon dioxide	699°	1·45	0·51	Carbon tetrafluoride ...	701°	1·60	0·62
,, ...	743	1·54	0·51	,, ...	730	1·61	0·57

Similar experiments with carbon tetrafluoride as the added gas were made at 701° and 730°. The values for x and y are summarised in Table 1, giving means of 1·55 and 0·55 respectively.

The empirical rate equation for pressures of nitrous oxide between 50 and 100 mm. is thus:

$$\text{Rate} = k'[N_2O]^{1\cdot55} + k''[N_2O]^{0\cdot55}[X].$$

In accounting for our results we have adopted the following simple mechanism for the decomposition of nitrous oxide in the presence of a foreign gas:

$$N_2O + N_2O \underset{(1')}{\overset{(1)}{\rightleftharpoons}} N_2O^* + N_2O \qquad O + N_2O \xrightarrow{(4)} O_2 + N_2$$

$$N_2O + X \underset{(2')}{\overset{(2)}{\rightleftharpoons}} N_2O^* + X \qquad O + N_2O \xrightarrow{(5)} 2NO$$

$$N_2O^* \xrightarrow{(3)} N_2 + O \qquad O \xrightarrow{(6)} \text{Walls}$$

Steps (4), (5), and (6) have recently been suggested by Kaufman, Gerri, and Bowman [7] as representing the most probable fates of atomic oxygen. They considered the reaction $O + O + M \longrightarrow O_2 + M$ improbable on the grounds that it involves triple collisions and that the presence of an inert gas is unlikely to increase this probability since such atoms are known to be remarkably inefficient third bodies.

Steps (1)—(6) lead to the theoretical rate equation

$$\text{Rate} = \frac{k_1[N_2O]^2 + k_2[N_2O][X]}{1 + k_{1'}[N_2O]/k_3 + k_{2'}[X]/k_3}\left\{\frac{2k_4[N_2O] + 2k_5[N_2O] + k_6}{k_4[N_2O] + k_5[N_2O] + k_6}\right\}$$

For small additions of the foreign gas the rate, as indicated by the straight lines in Fig. 2, depends on the first power of the concentration of the foreign gas. Thus the term $k_{2'}[X]/k_3$ must be small when [X] is small. Neglecting this term we have

$$\text{Rate} = \frac{k_1[N_2O]^2}{1 + k_{1'}[N_2O]/k_3}\left\{\frac{2k_4[N_2O] + 2k_5[N_2O] + k_6}{k_4[N_2O] + k_5[N_2O] + k_6}\right\} + \frac{k_2[N_2O][X]}{1 + k_{1'}[N_2O]/k_3}\left\{\frac{2k_4[N_2O] + 2k_5[N_2O] + k_6}{k_4[N_2O] + k_5[N_2O] + k_6}\right\}$$

The first term corresponds to that which would be obtained for the decomposition of nitrous oxide alone and can be identified with the first term of our empirical equation. The experimental order of 1·55 agrees with that calculated from the results of Lewis and Hinshelwood [8] for the pressure 50—100 mm. and 652°. As can be gathered from the theoretical rate equation, $x - y$ should equal unity, as is found experimentally. The mechanism postulated thus yields a theoretical equation similar in form to the empirical

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[7] Kaufman, Gerri, and Bowman, *J. Chem. Phys.*, 1956, **25**, 106.

[8] Lewis and Hinshelwood, *Proc. Roy. Soc.*, 1938, *A*, 168, 441.

equation. Hence the theoretical equation may be assumed to apply within the limited pressure range studied. We realise, however, that for a wider pressure range it would be necessary to invoke the more elaborate theoretical treatments of other authors.

In graphs such as those in Fig. 2, the expression Slope × $[N_2O]$/Intercept corresponds to k''/k', which equals k_2/k_1 in the theoretical rate equation. To determine this ratio a series of experiments were made at several temperatures with fixed initial concentrations of nitrous oxide. The results in Table 2 were derived from the slopes and intercepts of the plots of initial rate against pressure of the foreign gas. We judge the values of k_2/k_1 to have an accuracy of ±5%.

TABLE 2.

Carbon dioxide present						Carbon tetrafluoride present					
N_2O (mm.)	Temp.	k_2/k_1	N_2O (mm.)	Temp.	k_2/k_1	N_2O (mm.)	Temp.	k_2/k_1	N_2O (mm.)	Temp.	k_2/k_1
100	651°	0·42	100	725°	0·47	100	673°	0·80	50	730°	0·90
100	662	0·42	50	743	0·47	105	690	0·84	100	730	0·88
100	679	0·46	100	743	0·46	55	701	0·82	50	744	0·91
50	699	0·44	50	752	0·49	105	701	0·83			
100	699	0·46									

Plots of log (k_2/k_1) against $1/T$ gave for ΔE $(= E_2 - E_1)$ values of 2·3 and 3·6 kcal. with carbon dioxide and carbon tetrafluoride respectively. All the energy values quoted, except those for the sulphur dioxide reaction, have been derived from the Arrhenius plots by the method of least squares. In addition, values were obtained for $k' = \text{Intercept}/[N_2O]^{1\cdot55}$ and $k'' = \text{Slope}/[N_2O]^{0\cdot55}$. The Arrhenius plots for the individual rate constants gave with carbon dioxide: E', 53·6; E'', 55·9; $E'' - E'$, 2·3; and with carbon tetrafluoride 54·0, 57·6, and 3·6 kcal. respectively. As we found in the oxidation of sulphur dioxide, the values for E' are close to the accepted figure for the energy of activation of the decomposition of nitrous oxide itself. The agreement between ΔE and $E'' - E'$ provides a satisfactory check for the individual results.

To round off the work on the decomposition of nitrous oxide in the presence of sulphur dioxide, values for k_2/k_1 were calculated and $\log(k_2/k_1)$ plotted against $1/T$. The results are given in Table 3.

TABLE 3.

N_2O (mm.)	100	100	200	100	100
Temp.	652°	678°	678°	708°	736°
k_2/k_1	0·54	0·54	0·53	0·62	0·74

ΔE may be between 5 and 10 kcal.; it could not be precisely fixed from the Arrhenius plot owing to the scatter of the points.

The fraction k_2/k_1 is a measure of the relative efficiency of the foreign gas in activating the nitrous oxide, and from it can be derived the more useful quantity ρ, the relative efficiency " collision per collision," defined as the ratio of N_2O–N_2O collisions to N_2O–X collisions causing the same rate of formation of activated nitrous oxide molecules. According to the kinetic collision theory

$$\rho = \frac{k_2}{k_1}\left\{\frac{2\sigma(N_2O)}{\sigma(X) + \sigma(N_2O)}\right\}^2\left\{\frac{2M(X)}{M(N_2O) + M(X)}\right\}^{\frac{1}{2}}$$

where σ (Y) and M(Y) are the respective kinetic collision diameters and molecular weights of the species Y. Unfortunately there are no generally accepted values for collision diameters which can be used in calculating kinetic results. The published figures vary considerably, depending on their mode of calculation. We have used those given by Rowlinson,[9] who, for spherically symmetrical molecules such as carbon tetrafluoride

[9] Rowlinson, *Quart. Rev.*, 1954, **8**, 168.

and the inert gases, took σ as the mean of the values calculated from viscosity data and from the second virial coefficients, and for the remaining molecules calculated σ for the critical volumes. The collision diameters used here are as follows: He, 2·6; Ne, 2·8; A, 3·4; Kr, 3·6; Xe, 4·0; CF_4, 4·7; CO_2, 3·7; SO_2, 4·0; N_2O, 3·7 Å.

Calculations show that for both carbon dioxide and sulphur dioxide ρ is about equal to k_2/k_1 and for carbon tetrafluoride is $0{\cdot}8961k_2/k_1$. Thus ρ for carbon dioxide varies between 0·42 and 0·49 over our temperature range. This value was so different from that (1·3) of Volmer *et al.* as to lead us to determine by the same procedure the efficiency " collision per collision " of the inert gases.

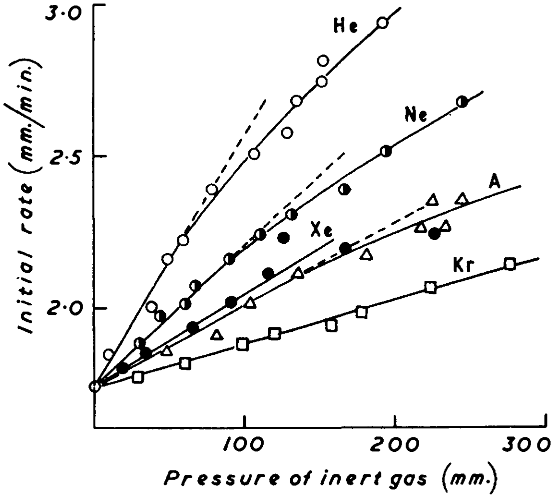

FIG. 3. *The influence of the inert gases on the initial rate of reaction.*

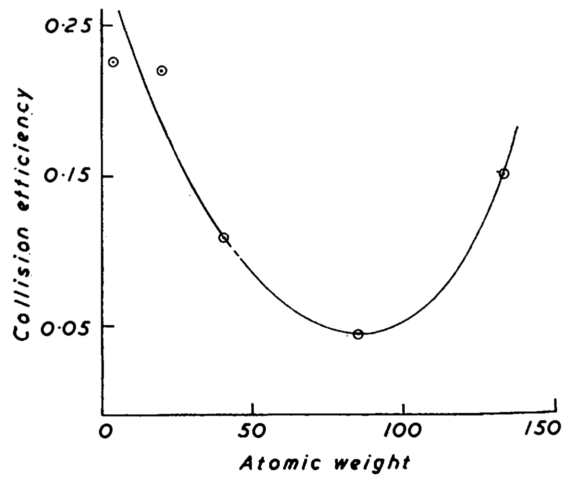

FIG. 4. *Variation of the collision efficiency of the inert gases with atomic weight.*

Initial rates were measured in the presence of different quantities of the several inert gases. Throughout the temperature was 708° and the pressure of nitrous oxide 98·8 mm. The graphs of initial rate against inert gas concentration, shown in Fig. 3, allowed values for k_2/k_1, which we believe to have an accuracy of $\pm 0{\cdot}004$, to be obtained from the intercepts and the slopes of the straight portions. The results for k_2/k_1, with the calculated collision efficiencies, are: He, 0·488 (0·275); Ne, 0·261 (0·268); A, 0·149 (0·158); Kr, 0·079 (0·094); Xe, 0·176 (0·199).

Fig. 4 shows the plot of ρ against the atomic weight of the inert gas.

The results indicate that the quantity ΔE is real, though of the order of only a few kcal. As the production of an activated nitrous oxide molecule, which will subsequently split according to reaction (3), does not appear to be a simple process, this small difference in activation energy seems reasonable. As a result of the difference, the collision efficiencies of the inert gases become temperature-dependent. Whether this phenomenon is general cannot yet be decided, as the reliable data on collision efficiencies in the literature refer to one temperature only.

Of particular interest are the values found for the relative efficiencies of the inert gases. Although the actual values differ appreciably from those of Volmer *et al.*[3] they show a similar decrease with increase in atomic weight as far as krypton, but xenon reverses the trend, being more efficient than either argon or krypton. The earlier workers found xenon to have a collision efficiency of 0·16 as compared with 0·18 for krypton and 0·20 for argon.

The trend of the relative efficiency figures in Table 5 bears no resemblance to those of the inert gases as displayed in other unimolecular decompositions where a fairly regular increase with atomic weight has been found.[10, 11, 12, 13] For example, Volpe and Johnston[13] showed that, in the decomposition of nitryl chloride, the relative efficiencies of the inert gases increase approximately linearly with their boiling points, and with the force of collision between the individual inert gas and the reactant molecule (the latter quantity being calculated from the Lennard-Jones potential). Using our results, we obtained curves of the form depicted in Fig. 4. We conclude, therefore, that the behaviour of the inert gases in the decomposition of nitrous oxide is exceptional since the differences to which we refer seem too large to be accounted for by either experimental error or the approximations of the simplified theoretical treatment. It is of interest that recent ultrasonic experiments[14] on mixtures of nitrous oxide and helium and of nitrous oxide and argon show that the number of N_2O–A collisions necessary to dissipate a vibrational quantum is approximately ten times the number of N_2O–He collisions required for the same purpose. The higher efficiency of helium in this process may bear some relation to its greater effect in promoting the decomposition of nitrous oxide.

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[10] Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563.
[11] *Idem, ibid.*, 1953, *A*, **218**, 416.
[12] Wilson and Johnston, *J. Amer. Chem. Soc.*, 1953, **75**, 5763.
[13] Volpe and Johnston, *ibid.*, 1956, **78**, 3903.
[14] Walker, Rossing, and Legvold, Natl. Advisory Comm. for Aeronautics, Technical Note 3210, 1954.