According to this model the length in Å. of the stretched chain is 2.5 n and its diameter is *ca.* 3 Å. Thus the well-known equation[7] for the rotary diffusion constant of a prolate ellipsoid in terms of its major, a, and minor, b, semi-axes can be treated as shown below (assuming η = 1.0 centipoise)

$$\theta = \frac{3kT}{16\pi\eta a^3}\left[-1 + 2\ln\frac{2a}{b}\right] \approx \frac{1.32 \times 10^{11}}{\bar{n}^3}\,[-1 + 4.61 \log 1.64\bar{n}] \quad (3)$$

This relationship between θ and n is plotted in Fig. 2 where it is compared with the experimental points. These experimental points were obtained by empirically extrapolating the data of Tables II through IV to infinite rate of shear on plots of log θ *vs.* $1/\sigma$ and further extrapolating these values of $\theta_{\sigma = \infty}$ to zero concentration. Thus the points in Fig. 2 represent rough, average values of θ under conditions where the anions are not interfering with each other. The correspondence between the theoretical curve and the experimental points again indicates that the observed birefringence is of the right order of magnitude to be attributable to the fully stretched molecule-ions themselves. The lack of exact agreement between the curve and the points is attributable to inaccuracies and uncertainties in the physical model, the data and the extrapolation of θ to infinite rate of shear.

Since the rotary diffusion constant measured at a given concentration of a polyphosphate is considerably larger in the presence of added salts of low molecular weight than in pure solution, it can be inferred that the polyphosphate anion must assume a relaxed or curled position in the presence of the added salt. This inference is based on the assumption that the charges on an anion have no effect *per se* on birefringence measurements but only show up through the geometrical effects of their interaction.

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ANNISTON, ALABAMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. III. Effect of Foreign Gases

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The decomposition of nitrogen pentoxide in the presence of nitric oxide has been studied in a 22-liter flask at 50.5° with added argon, nitrogen, carbon dioxide or sulfur hexafluoride. Reactant pressures were each about 0.08 mm. and foreign gas pressures varied from about 0.02 to 10 mm. By means of the general Lindemann mechanism for unimolecular reactions, it is shown that these data give the second-order activational rate constants for each reactant and for each foreign gas. The relative values of the limiting low-concentration rate constants are: A, 0.14; N_2, 0.23; NO, 0.30; SF_6, 0.32; CO_2, 0.40; N_2O_5, 1.00. From the data for each foreign gas an estimate is made of the mean-life with respect to decomposition of normally distributed activated reactant molecules; these estimates agree within experimental error. The application of this type of data to the problem of the form of the deactivational rate function is discussed.

Introduction

The initial rate of reaction of nitrogen pentoxide with nitric oxide is the rate of the elementary unimolecular reaction[1,2,3] $N_2O_5 \rightarrow NO_2 + NO_3$. With a slight excess of nitric oxide the initial rate continues unchanged for about three or four half-lives, and thus with this system it is easy to get a good measure of the rate constant of an elementary reaction. It is of great interest to study the effect of inert gases on the rates of unimolecular reactions, since this type of study gives the relative efficiency of various gases in activating the reactant molecule and some information about the form of the deactivational rate functions.

Experimental

The apparatus was the same as that described previously.[4] It consisted of a 22-liter Pyrex bulb in a stirred air thermostat. Two pipets of 0.001 volume of the flask and two pipets of 0.01 volume of the flask were connected by a three-way stopcock which permitted two gas samples to be passed simultaneously into the evacuated bulb. The reaction was followed by light absorption of nitrogen dioxide. An effort was made to improve the precision of results obtained from the apparatus. The light source was an AH-4 General Electric mercury arc stabilized by a Cenco constant voltage auxiliary. The IP 28 photo-multiplier tube was placed outside of the air thermostat to reduce dark current, since most runs were made at 50.5°. Many of the stopcocks were replaced by Corning high vacuum type and Greiner three-way high vacuum type. A McLeod gage was added, and the 22-liter bulb was evacuated to 10^{-4} mm. or lower before each run.

Nitrogen pentoxide and nitric oxide were prepared and purified as described before.[2] The foreign gases were Linde nitrogen, Stuart carbon dioxide and Matheson argon and sulfur hexafluoride. Nitrogen was passed directly from the tank through a liquid nitrogen trap into its storage bulb. Argon, carbon dioxide and sulfur hexafluoride were condensed by liquid nitrogen and fractionated into the storage bulb.

The carrying out of runs and the computation of rate constants were done as follows: The two large pipets were filled with a foreign gas to a known pressure. The two pipets were shut off from each other. One small pipet was filled to a known pressure with nitric oxide, and this was mixed with the foreign gas in one of its pipets. The second small pipet was filled with nitrogen pentoxide to a known pressure (as found by a null Bourdon gage), and this was mixed with the foreign gas in the other pipet. To start the reaction a three-way stopcock was turned so that it simultaneously passed into the 22-liter flask the nitric oxide plus foreign gas and the nitrogen pentoxide plus foreign gas. It has been established[4] that mixing was complete and temperature equilibrium was attained within three seconds. Before the run started the initial light intensity I_0 was obtained. Readings were made of light intensity every 3, 5 or 10 seconds depending on the rate of reaction. If the half-life was 6

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[1] J. H. Smith and F. Daniels, THIS JOURNAL, **69**, 1735 (1947).

[2] R. L. Mills and H. S. Johnston, *ibid.*, **73**, 938 (1951).

[3] H. S. Johnston, *ibid.*, **73**, 4542 (1951).

[4] H. S. Johnston and R. L. Perrine, *ibid.*, **73**, 4782 (1951).

seconds or longer, this method could be used satisfactorily. The reaction was followed for at least 10 half-lives. For each reading the optical density $D = \log I_0/I$ could be computed. The final reading D_∞ was taken, and $D_\infty - D$ was computed for each point. The term $D_\infty - D$ is proportional to unreacted nitrogen pentoxide (if nitric oxide is in excess). On semi-logarithmic paper a plot was made of log $(D_\infty - D)$ against time. It was noticed that the points lay on a straight line for at least three or four half-lives. To be conservative, points were retained for only the first two half-lives. To calculate a first-order rate constant the slope of the line was found by the method of least squares for all observed points from the first after the stopcock was turned until about two half-lives had passed. When nitrogen pentoxide was in excess, the rate constants were based on two half-lives of nitric oxide. Under all conditions it was established that nitrogen tetroxide was negligible; otherwise the simple computation using $D_\infty - D$ could not be used.

In all 206 successful runs were made with reactants alone or with added argon, nitrogen, carbon dioxide or sulfur hexafluoride. Most reactions were carried out at 50.5°, but a small number were made with nitrogen at 27°. These detailed rate constants, Tables I–V, are available on microfilm.[5]

Mechanism

The mechanism of this reaction in the presence of various species M has been analyzed previously.[3] It is a, b, c, d, f in the previous nomenclature, and the rate expression is given by eq. 8.[6] When $B(M)[NO_2] \ll f[NO]$, the expression reduces to that for an elementary unimolecular reaction, for which the first order rate constant is

$$k = \sum_i \frac{c_i \sum_M a_{Mi}[M_M]}{\sum_M b_{Mi}[M_M] + c_i} \qquad (1)$$

From microscopic reversibility one gets $a_{Mi} = b_{Mi}P_i$, where P_i is the equilibrium fraction of reactant molecules in the excited state i, and P_i is the same for all species of [M]. When this relation is used the rate-constant expression is

$$k = \sum_i \frac{c_i P_i \sum_M b_{Mi}[M_M]}{\sum_M b_{Mi}[M_M] + c_i} \qquad (2)$$

A statistical interpretation has been given to the functions a_i, b_i, and c_i,[7] but these interpretations do not change in any way the form of the rate expressions previously used in the studies of this reaction.[2,3,4]

In this article eq. 1 is used to analyze the data at the low-concentration limit, and eq. 2 is used to compare the effect of the different foreign gases on rate constants just above the low-concentration second-order region.

Low-concentration Limit for Each Foreign Gas.— It is only at the low-concentration limit that the relative values of rate constants for different foreign gases give the relative values of the activating efficiencies of these gases. It can be seen from eq. 1 that at higher concentrations, the concentration of M appears in such a non-linear manner that the ratio of rate constants for different gases has no simple interpretation. The ideal way to test relative efficiencies of inert gases is to have the foreign gas in great excess over reactants, and to let the foreign gas pressure approach zero. Since the observable quantities are reactants or products, the ideal experiment cannot be carried out in this case; it calls for immeasurably small concentrations of reactants. However, it can be shown that by analyzing eq. 1 one can get for each in a mixture of gases the separate second-order rate constant for activation by a simple graphical method.

At the low-concentration limit

$$\sum_M b_{Mi}[M_M] << c_i \text{ for all } i \qquad (3)$$

and eq. 1 reduces to

$$k^0 = [M_1]\sum_i a_{1i} + [M_2]\sum_i a_{2i} + \cdots + [M_M]\sum_i a_{Mi} \qquad (4)$$

$$= k_1^0[M_1] + k_2^0[M_2] + \ldots + k_M^0[M_M] \qquad (5)$$

Here k^0 is the observed first-order constant when conditions of eq. 3 are met; k_1^0 is the second-order rate constant for activation of reactant by foreign gas M_1, etc. For this particular reaction there are necessarily two species of M present: nitrogen pentoxide, M_1; nitric oxide, M_2. The first problem is to get the separate values of k_1^0 and k_2^0 and still be sure that eq. 3 is obeyed. One holds $[M_1]$ constant at some very low value and varies $[M_2]$. A plot of observed first-order rate constant will have a finite intercept $k_1^0[M_1]$ as $[M_2]$ approaches zero, and there will be a straight line of slope k_2^0, so long as eq. 3 is obeyed. When conditions of eq. 3 are no longer met, higher order terms must be added to eq. 5, and the plot of k *vs.* $[M_2]$ will curve downward. Thus by graphical inspection, one picks the range of $[M_2]$ over which to fit a least-squares straight line to

$$k^0 = (k_1^0[M_1])_{\text{const}} + k_2^0[M_2] \qquad (6)$$

A series of runs was made at 50.5° in which nitrogen pentoxide was held constant at 0.077 mm., and nitric oxide was varied. The results were plotted as observed first-order rate constant k against nitric oxide concentration. The linear portion of this plot and the least-squares straight line are given in Fig. 1. The intercept divided by nitrogen pentoxide concentration gives 22.5×10^5 cc. mole^{-1} sec.$^{-1}$ as the low-concentration limiting rate constant for activation by nitrogen pentoxide. The slope 6.75×10^5 cc. mole^{-1} sec.$^{-1}$ is the low-concentration limit for pure nitric oxide. These values and the standard error of estimate are listed in Table VI.

When a third gas is added, one holds both nitric oxide and nitrogen pentoxide constant and varies the concentration of inert gas $[M_M]$. So long as eq. 3 is obeyed, there will be a straight line of slope k_M^0 and intercept $k_1^0[M_1] + k_2^0[M_2]$

$$k^0 = (k_1^0[M_1] + k_2^0[M_2])_{\text{const}} + k_M^0[M_M] \qquad (7)$$

Nitrogen pentoxide and nitric oxide were held constant at about 0.077 and 0.085 mm., respectively, and a series of runs was made with various amounts

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[5] Order Document 3711 from American Documentation Institute, % Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

[6] Note a misprint in eq. 8 of ref. 3, where (M) in the denominator should be replaced by B(M).

[7] H. S. Johnston, *J. Chem. Phys.*, **20**, 1103 (1952).

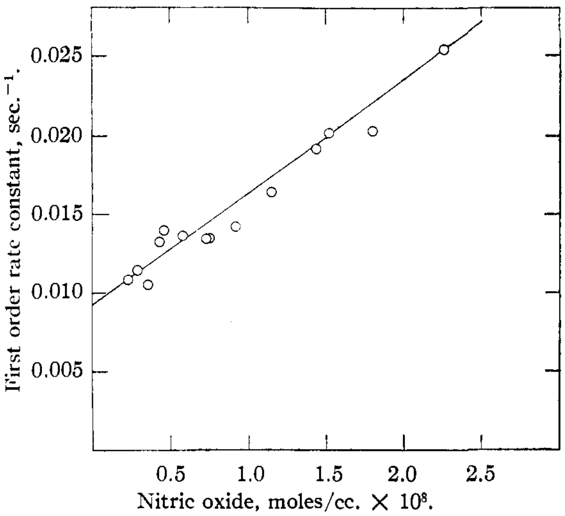

Fig. 1.—Low concentration limit for nitric oxide and nitrogen pentoxide separately; $[N_2O_5]$ is constant, 50.5°.

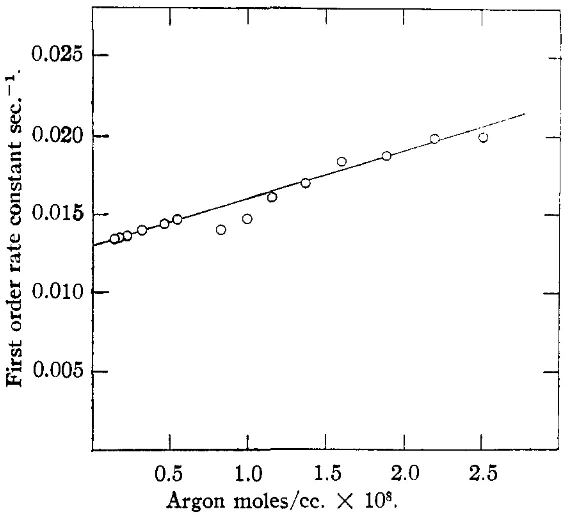

Fig. 2.—Low concentration limit with argon as foreign gas. [NO] and $[NO_2O_5]$ are constant, 50.5°.

of argon. By inspection it was decided over what region the curve was linear, and points inside this region were fitted with a straight line by least squares, Fig. 2. The intercept, slope and standard error of estimate are listed in Table VI. The data for nitric oxide and argon had better precision than those for the other gases. For the other gases it was assumed that eq. 7 would apply out to the same value of k as it did for argon and nitric oxide. In this way the low-concentration second-order rate constants were found for nitrogen, carbon dioxide and sulfur hexafluoride. The slopes, intercepts and errors are listed in Table VI.

TABLE VI

LOW-CONCENTRATION SECOND-ORDER RATE CONSTANTS FOR THE DIFFERENT GASES AT 50.5°

M gas	No. of points	Intercept sec.⁻¹	Low-concentration rate constant, cc.m ⁻¹sec.⁻¹ × 10⁻⁵ Value	Standard error	Ratio to pure N_2O_5
N_2O_5			22.5		1.00
A	15	0.0130	3.04	0.24	0.135
N_2	12	.0116	5.27	.72	.234
NO	14	.00922	6.75	.42	.300
CO_2	11	.0122	8.9	1.8	.40
SF_6	14	.0137	7.2	1.2	.32

Mean Life of Activated Reactant Molecules.—If it is assumed, temporarily, that one species of foreign gas M_M is in great excess and if the condition of the low-concentration region is met

$$b_{Mi}[M_M] < c_i \text{ for all } i \qquad (8)$$

then expansion of Eq. 2 of two terms gives

$$k/[M_M] = \sum_i b_{Mi}P_i - \sum_i (b_{Mi}^2/c_i)P_i[M_M] + \ldots \qquad (9)$$

$$= \overline{(b_M)P} - \overline{(b^2_M/c)}P[M_M] + \ldots \qquad (10)$$

$$= k_M{}^0 - n_M[M_M] + \ldots \qquad (11)$$

where $P = \sum_i P_i$; $k_M{}^0$ and n_M are the observed intercept and slope of a plot of $k/[M_M]$ against $[M_M]$ in the region where the plot is still linear; and the bar indicates average value over the distribution function P_i. If one follows Kassel,[8] etc., and assumes

$$\overline{(b_M)} = b_{Mi} = b_M \qquad (12)$$

where b_M is the kinetic collision constant, one can evaluate $\overline{(1/c)}$, the mean life of activated reactants with respect to decomposition if they had their equilibrium distribution

$$\overline{(1/c)} = n_M/b_Mk_M{}^0 \qquad (13)$$

The quantity $\overline{(1/c)}$ is a property only of the reactant molecule, and thus one should get the same value in the presence of each foreign gas. An interesting, though incomplete, test of the theory up to this point is to evaluate $\overline{(1/c)}$ for a series of different foreign gases which have widely different values of $k_M{}^0$ and to see if one gets the same number for $\overline{(1/c)}$ in each case. The implications of this test are analyzed in the Discussion section.

In eq. 9, 10, 11, it is assumed that one foreign gas is present in large excess, but for these data it was necessary to retain non-negligible amounts of reactants. However by use of the approximation[9] of eq. 12 and the values of $k_M{}^0$, one can reduce the effect of a mixture of foreign gases to the equivalent effect of a single foreign gas. A new variable $[\mathbf{M}]$, the equivalent concentration of nitrogen pentoxide, is defined as

$$[\mathbf{M}] = [M_1] + [M_2]k_2{}^0/k_1{}^0 + [M_M]k_M{}^0/k_1{}^0 \qquad (14)$$

As in the preceding section M_1 represents nitrogen pentoxide, M_2 nitric oxide, and M_M stands for the foreign gas. The summation $\sum_M b_{Mi}[M_M]$ in eq. 2 is replaced by $b_{1i}[\mathbf{M}]$ to give

$$k = \sum_i \frac{c_iP_ib_{1i}[\mathbf{M}]}{b_{1i}[\mathbf{M}] + c_i} \qquad (15)$$

Expansion of eq. 15 in the low-concentration region to two terms gives expressions like eq. 9, 10, 11, 13.

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(8) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1932.

(9) Actually the assumption here is not as severe as that of eq. 12. It is sufficient merely to assume that $b_{Mi} = b_Mf_i$, where b_M is a different constant for each gas and f_i is any function, the same for all foreign gases.

Thus one can evaluate $\overline{(1/c)}$ for each foreign gas without neglecting the small but definite contribution of the reactants.

For runs made with pure reactants, the equivalent concentration of nitrogen pentoxide was calculated as $[N_2O_5] + 0.30[NO]$. For each point k was divided by $[\mathbf{M}]$, the values of $[\mathbf{M}]$ and $k/[\mathbf{M}]$ are included in Table I. The plot of $k/[\mathbf{M}]$ *vs.* $[\mathbf{M}]$ had a finite intercept at zero concentration, a straight line of negative slope up to 5×10^{-8} m. cc.$^{-1}$ and the points curved upward for higher values of $[\mathbf{M}]$. The points between zero and 1×10^{-8} m. cc.$^{-1}$ have already been used to evaluate k_1^0 and k_2^0. To get an independent measure of k_1^0 from this plot, the points used in Fig. 1 were omitted, and those points of Table IB below 5×10^{-8} m. cc.$^{-1}$ were used. The least-squares slope and intercept are given in Table VII.

TABLE VII

ESTIMATES OF MEAN LIFE OF EXCITED NITROGEN PENTOXIDE MOLECULES

Foreign gas from 1 to 5×10^{-8} mole cc.$^{-1}$., nitrogen pentoxide and nitric oxide each 0.4×10^{-8} mole cc.$^{-1}$.

M gas	N. of points	Intercept, cc.m.$^{-1}$ sec.$^{-1}$	Slope cc.^{2} m.$^{-2}$ sec.$^{-1}$ $\times 10^{-13}$ Value	Standard error	$\overline{(1/c)}$ sec. $\times 10^7$
A	17	26.0	2.37	0.33	0.97
N_2	20	23.5	1.85	.31	.84
N_2[a]	19	26.6	2.02	.26	.81
CO_2	19	23.9	2.30	.32	1.02
SF_6	18	24.4	2.02	.52	0.88
$NO + N_2O_5$[b]	10	23.8	2.04	.43	0.91

[a] Reactants were each 0.6×10^{-8} m. cc.$^{-1}$ for this series.
[b] Reactants were equal and varied from 0.5 to 3.5×10^{-8} m. cc.$^{-1}$ for each reactant.

By means of eq. 14 and by use of the rate constants in Table VI, the equivalent concentration of nitrogen pentoxide was calculated for all runs with foreign gases. The values of $[\mathbf{M}]$ and $k/[\mathbf{M}]$ are included in Tables II–V, which are available on microfilm.[5] For each gas, plots were found to be linear up to about 5.2×10^{-8} m. cc.$^{-1}$. Points below 1×10^{-8} m. cc.$^{-1}$ were not retained for several reasons: the data have been used once (Table VI), and if they are not used, the intercept provides an independent check on k_1^0, above 1×10^{-8} m. cc.$^{-1}$ the foreign gas was definitely in excess so that it makes the greatest contribution to $[\mathbf{M}]$. For the plots of $k/[\mathbf{M}]$ against $[\mathbf{M}]$, the least-squares intercepts, slopes and errors are listed in Table VII. The mean life of activated reactants was calculated from the data for each foreign gas, the value chosen for b_1 at 50.5° was 0.94×10^{14} cc. m.$^{-1}$ sec.$^{-1}$. All foreign gases give the same value for $\overline{(1/c)}$ within experimental error, even though the low-concentration rate constants differ by a factor of eight between nitrogen pentoxide and argon.

Discussion

The maximum value for the deactivational rate is the rate of collision. If deactivation does not occur on every collision, the collision rate should be multiplied by an efficiency factor which, in general, might be a function of every state i and a different function for each foreign gas M. This general efficiency function will be written f_{Mi}. Thus one may factor out the kinetic collision constant b_M from the deactivational function b_{Mi}

$$b_{Mi} = b_M f_{Mi} \qquad (16)$$

If f_{Mi} depends strongly on the nature of M, one expects $\overline{(1/c)}$ as computed by eq. 13 to vary from one gas to another. If f_{Mi} is a strong function of i but the same f_i for each species of M, then $\overline{(1/c)}$ as computed from eq. 13 will be the same number for each gas M, but this number is not literally the mean value of $1/c_i$, rather it is the mean value of f_i^2/c_i divided by the mean value of f_i. Furthermore, if $b_{Mi} = b_M f_i$, then from high to low limits k will be everywhere a unique function of $[\mathbf{M}]$, defined by eq. 14, regardless of the identity or proportions of the various gases which make up the value of $[\mathbf{M}]$. With slight qualifications, this can also be shown to be the necessary condition for k being everywhere a unique function of $[\mathbf{M}]$. Thus studies of unimolecular reactions as a function of the identity of foreign gas M_M are capable of giving some information about the form of the deactivational efficiency function f_{Mi}, that is, whether it indeed depends on the identity of M_M. The present study gives only an incomplete answer to this question: no strong dependency of f_{Mi} on M_M has been found, but the range of $[\mathbf{M}]$ covered is so narrow and experimental error so large, that this study cannot be regarded as a very sensitive test.

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