

Kinetics of the Rapid Gas Phase Reaction between NO, NO₂, and H₂O

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Using the absorption of light by nitrogen dioxide as a measure of its concentration, the rate of the gas phase reaction $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_2$ was measured over a fivefold range of water vapor and nitrogen dioxide concentrations, with nitric oxide greatly in excess. Changes in light intensity were detected by means of an electron-multiplier photo-tube and recorded by photographing the screen of a cathode-ray oscilloscope. Half-times as short as 0.014 sec were observed. The reaction rate was found to depend more strongly upon the concentration of water vapor than upon that of nitrogen dioxide and to be kinetically consistent with a mechanism involving termolecular collisions.

The equilibrium constant of the reaction has been calculated and its order of magnitude experimentally confirmed, and a lower limit has been fixed for the rate of dissociation of nitrogen sesquioxide.

INTRODUCTION

FOLLOWING the successful application by Johnston and Yost¹ of the combination of multiplier photo-tube, cathode-ray oscilloscope, and camera to the study of the kinetics of the very rapid reaction between nitrogen dioxide and ozone, it appeared desirable to study by this technique other reactions whose rates are so great as to be unmeasurable by the common methods. The reaction between nitric oxide, nitrogen dioxide and water vapor is of interest because of its possible importance in connection with theories of rainfall. It was reported by Wulf,² who studied the equilibrium spectroscopically, to be practically instantaneous. The system was therefore selected for study.

Instances in the literature of the quantitative study of kinetics of homogeneous reactions involving water vapor as a primary reactant are rather rare, and most of these concern pyrolysis of hydrocarbons or other high temperature studies in which the effect of chain reactions is predominant. The reaction between water vapor and sulfur trioxide in the gas phase was studied³ at room temperature by the Polanyi streaming method; in this case the product, sulfuric acid, appeared as a mist. The authors estimated that about one collision out of every hundred between molecules of the reacting species was effective. The system described here is comparable to the water-sulfur trioxide system in the respect that it, too, involves hydration of an acid anhydride (that of nitrous acid).

EXPERIMENTAL

In principle, and in many particulars, the procedure was the same as that employed by Johnston and Yost.¹ Essentially, the apparatus comprised four parts: a flow system in which gas streams containing the reacting

substances could be metered and mixed, a device consisting of a reaction cell and quick-acting stopgate by means of which a non-equilibrium mixture could be trapped, an optical system producing a chopped beam of light which passed through a portion of the reaction cell, and a detecting and recording system comprising the multiplier photo-tube with its power source, the oscilloscope and the camera.

Figure 1 shows schematically the arrangement of the flow system. Nitric oxide, prepared as described below, entered the system at *A*, filled the two-liter bulb *B* (which served to cushion the effect of suddenly closing the system) and was divided into two streams. One of these passed through stopcock *C*, flowmeter *D* and water saturator *E*, the other through stopcock *F* and flowmeter *C* to *H*, where a much slower stream of oxygen was introduced. The stopcocks *J* and *K* permitted these sections of the flow system to be cut off from the mixing chamber *L* and from each other. Oxygen from a commercial oxygen cylinder was introduced at *M*; its pressure was adjusted by means of the bubbler *N* and its flow rate measured by flowmeter *P*. Stopcock *Q* served to shut off the oxygen stream. The oxygen served, as a result of its reaction with nitric oxide, to form the necessary small concentration of nitrogen dioxide.

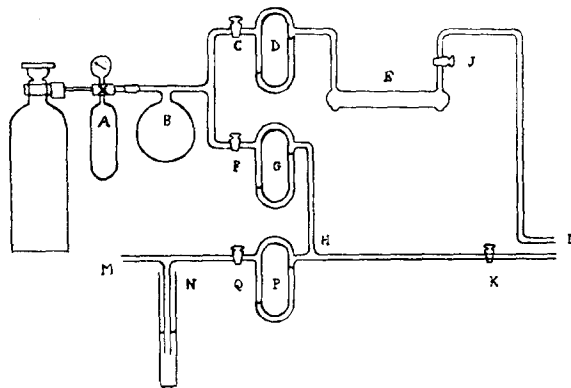


FIG. 1. Diagram of the flow system. *A*: Nitric oxide collecting system. *B*: Two-liter bulb. *D*, *G*, *P*: Capillary flow meters. *E*: Water saturator. *L*: To mixing chamber. *M*: Oxygen inlet. *N*: Bubbler.

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¹ H. S. Johnston and D. M. Yost, *J. Chem. Phys.* **17**, 386 (1949). See also L. G. Wayne and D. M. Yost, *J. Chem. Phys.* **5**, 767 (1950).

² E. H. Melvin and O. R. Wulf, *J. Chem. Phys.* **3**, 755 (1935).

³ Goodeve, Eastman, and Dooley, *Trans. Faraday Soc.* **30**, 1127 (1934).

Dibutyl phthalate was used as the manometer fluid in capillary flowmeters, *D*, *G* and *P*. The capillaries were calibrated at several points throughout their ranges of utility by timing the displacement of a known volume of water.

Water saturator *E* consisted of a 120-cm length of 12-mm tubing filled with glass beads and sufficient water to occupy half the remaining volume. It was kept immersed in water at room temperature. A gravimetric water vapor determination showed it to be more than 99 percent efficient at the flow rates used.

Concentration of water vapor in the reaction mixture could be adjusted by diverting more or less of the total nitric oxide flow through stopcock *C*; the concentrations obtainable in this way ranged from about 0.5 to about 2.4 mole percent. The total nitric oxide flow rate was fixed by adjusting the valve on the supply cylinder.

The temperature of the flowing mixture was measured by means of a thermocouple of No. 50 *B* and *S* gauge constantan and 36-gauge copper placed axially in the stream issuing from the reaction cell. No attempt was made to control the temperature, which therefore varied slowly, usually between 23° and 25°C.

Tygon tubing was used for all connections. Since it was found that this tubing is slowly attacked by nitrogen dioxide, connections were arranged so as to expose a minimum of the tygon surface to the stream containing this component.

For experiments concerning possible time lag in the $\text{NO}_2 + \text{NO} = \text{N}_2\text{O}_3$ equilibrium, the water saturator was removed from the system and nitrogen from a commercial "dry nitrogen" cylinder was introduced into the mixing chamber.

The mixing chamber and reaction cell were constructed on the same plan as those previously described¹ but were smaller. The cell was built of 1-mm

Pyrex capillary tubing, its total volume being about 0.12 ml. The volume of the mixing chamber was found to be about 0.05 ml, and the total volume was, therefore, less than 0.2 ml. With a gas flow of 10 m/sec, the average age of the mixture in the light path was about 0.01 sec.

Apparatus and procedure for trapping a non-equilibrium system in the reaction chamber and for recording the progress of the reaction were essentially as described by Johnston and Yost.¹ Photographs of the oscilloscope screen (such as Figs. 2 and 3) provided a record of NO_2 concentration vs. time. Suitable amplification was secured by adjusting the oscilloscope controls so that the pattern appearing on the screen represented only the peaks of the square-wave modulated light intensity, the beam being off the screen during the dark period of each cycle. The position of the pattern envelope was sufficiently reproducible to be calibrated with respect to the control settings and the magnitude of the applied signal; such calibration was useful in permitting the approximate determination of the equilibrium constant from the photographic data.

Each photographic negative recorded the appearance of the trace through several sweeps of the beam across the screen (*ca.* 0.3–0.5 sec) as seen in Fig. 2, except in a few experiments made to demonstrate the absence of lag in the N_2O_3 dissociation equilibrium; in these a single-sweep device was used (Fig. 3). For measurement, the negative was projected in a microfilm reader onto a sheet of squared paper and the positions of successive peaks recorded.

Nitric oxide was generated by the method given by Johnston and Giauque⁴ in which 50 percent sulfuric acid is dropped into a solution approximately 4 *N* in sodium nitrite and 1 *N* in potassium iodide. The gas evolved was passed through concentrated solutions of

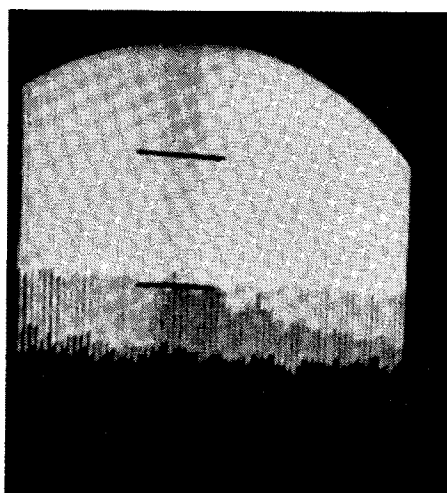


FIG. 2a. Run IV-59. N_2O_3 0.0078 atmos;
 H_2O 0.0151 atmos; half-time 0.083 sec.

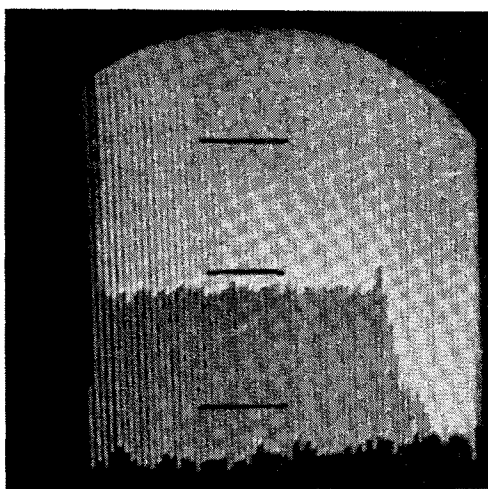


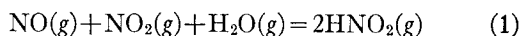
FIG. 2b. Run IV-52. N_2O_3 0.0148 atmos;
 H_2O 0.0230 atmos; half-time 0.014 sec.

⁴H. S. Johnston and W. F. Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).

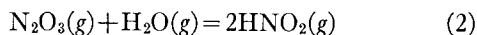
sodium hydroxide and potassium iodide and dried over phosphorous pentoxide, and finally condensed in a glass bulb at liquid-air temperature. It was then redistilled (the last five percent or so of each batch being discarded) and stored in a supply cylinder. Occasional testing showed not more than $\frac{1}{2}$ percent of the stored gas unabsorbed by ferrous sulfate solution. No nitrogen dioxide could be detected.

THE EQUILIBRIUM CONSTANT

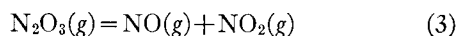
Because the reaction



does not proceed to completion, a knowledge of its equilibrium constant is essential in interpreting its kinetics. Abel and Neusser⁵ in reporting on the vapor pressure of HNO₂ above its aqueous solutions, have incidentally provided data from which the constant, K_2 , for the equilibrium

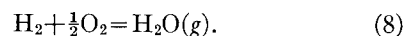
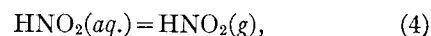


can be estimated to be of the order of magnitude of 2.4. On combining this with the value $K_3 = 2.1$ atmos found by Verhoek and Daniels⁶ for the dissociation



one readily calculates for K_1 the value 1.2 atmos.⁻¹ However, Abel and Neusser expressly pointed out that their experiments were not designed to permit an accurate determination of the quantities on which this

estimate is based, and it is probably indicative of their lack of confidence in such a calculation that they made no attempt to correct their vapor pressure measurements for the effect of this equilibrium. (Their value of $P_{\text{HNO}_2}/(\text{HNO}_2)$, given as 0.0352 l. atmos/mole, is doubtless too high by 10 to 20 percent for this reason.) Thermodynamic data now available permit a more reliable calculation. The result still depends upon the vapor pressure data of Abel and Neusser and is therefore subject to the same 10 to 20 percent uncertainty, but the much more refined treatment of the thermodynamic properties of nitric acid given by Forsythe and Giauque⁷ removes the order-of-magnitude uncertainty inherent in the above estimate. Consider the reactions



Combining these in the proportions 2(4)+2(5)-(6)-(7)-(8) yields the net reaction (1). Extrapolation of the results of Abel and Neusser to ionic strength zero gives $K_4 = 0.0305$, from which ΔF_4^0 is calculated to be 2080 cal/mole. Corresponding values for reactions (5) to (8) are, respectively, -13,020,⁸ 12,275,⁷ 20,650⁷ and -54,507,⁹ leading to the total -300 cal/mole and the value $K_1 = 1.65$ atmos⁻¹, in reasonable

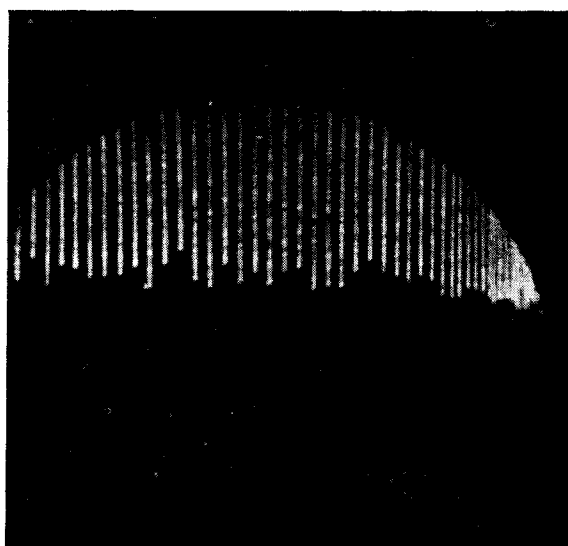


FIG. 3a. Blank for N₂O₃ dilution test.

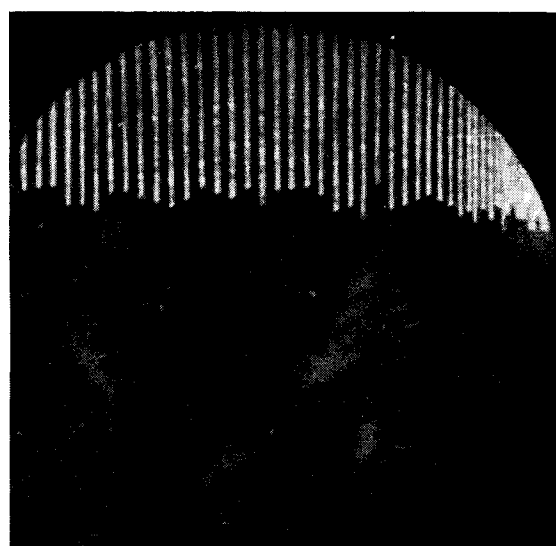


FIG. 3b. N₂O₃ dilution test, N₂/NO, 4.5.

⁵ E. Abel and E. Neusser, *Monatsh. Chem.* **54**, 855 (1939).

⁶ F. H. Verhoek and F. Daniels, *J. Am. Chem. Soc.* **53**, 1250 (1931).

⁷ W. R. Forsythe and W. F. Giauque, *J. Am. Chem. Soc.* **64**, 48 (1942).

⁸ W. M. Latimer, *Oxidation Potentials* (Prentice-Hall, Inc., New York, 1938).

⁹ G. N. Lewis and Merle Randall, *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill Book Company, Inc., New York, 1923).

TABLE I. The equilibrium constant at 25° for reaction (1).

No.	$a \times 10^2$ atmos	$b \times 10^2$ atmos	$x_e \times 10^2$ atmos	K_1 atmos ⁻¹
29	1.80	1.89	1.54	3.1
31	1.80	1.89	1.54	3.1
33	1.80	1.49	1.12	1.67
35	1.80	1.49	1.14	1.68
38	1.85	0.96	0.82	1.28
39	1.90	0.95	0.78	1.08
45	1.43	0.98	0.78	1.44
46	1.46	0.98	0.78	1.44
49	1.49	1.47	0.82	0.92
51	1.49	2.3	1.26	1.68
52	1.48	2.3	1.26	1.68
average:				1.74

agreement with that calculated from the data of Abel and Neusser. Multiplying by K_3 gives $K_2=3.5$.

An experimental confirmation of this predicted value was obtained by the interpretation of data from a number of the runs in which a relatively reliable estimate of equilibrium concentrations could be made. The results are shown in the last column of Table I. In Table I, a is the initial pressure of "available" N_2O_3 , that is $P_{NO_2} + P_{N_2O_3}$; b is the initial water vapor pressure; x_e is the calculated equilibrium pressure of HNO_2 .

Although individual values of K_1 differ from the logarithmic mean by factors of from *ca.* 0.5 to 2, the values which were considered most reliable for experimental reasons were those for runs 51 and 52, which fell very close to the mean; the agreement of this mean with the predicted value therefore provides satisfactory confirmatory evidence concerning the order of magnitude of K_1 .

RATE OF DISSOCIATION OF NITROGEN SESQUIOXIDE

In order to explore the possibility that reaction (3) or its reverse proceeds slowly enough to cause complications in interpreting the kinetics of the main reaction, several tests were made in which NO-NO₂ mixtures were diluted with 2.1 to 4.5 volumes of nitrogen in the mixing chamber, then trapped in the reaction cell. For each test, a blank was provided by photographing a single-sweep trace on the oscilloscope while the diluted mixture was flowing through the cell.

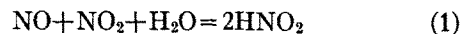
Comparison of the blank with the test photograph showed no evidence of lag in attaining equilibrium. One such pair of photographs is shown in Fig. 3, from which it is seen that no significant increase in NO₂ concentration occurs during the 0.15 sec recorded by the camera.

From this observation it may reasonably be assumed that the lapse of at least two half-times for the dissociation required not more than 0.01 sec, leading to a lower limit of 150 sec⁻¹ for the rate constant K_3 (assuming the dissociation is first order).

ORDER OF THE REACTION

In the system NO-NO₂-H₂O, equilibrium considerations exclude the possibility of the formation of

oxygen or higher valent oxides and oxyacids of nitrogen, so that the only important product molecules are N₂O₃ and HNO₂. As shown in the previous section, there is no lag in the establishment of the N₂O₃ equilibrium, at least within the limits of observation with the apparatus. The only reactions to be considered are, therefore,



and



The experiments were not designed to distinguish between these reactions. By maintaining the pressure of nitric oxide always at substantially one atmosphere, the advantage was gained that simultaneous occurrence of (1) and (2) would not complicate the rate expression, since the ratio $P_{NO_2}/P_{N_2O_3}$ was kept constant (=2.1). The differential rate equation can thus be written

$$dx/kdt = Y[(a-x/2)(b-x/2) - x^2/K] \quad (9)$$

where x denotes P_{HNO_2} as a function of the time t , a is the initial value of $P_{NO_2} + P_{N_2O_3}$; b is the initial value of P_{H_2O} ; k is the assumed rate constant of the forward reaction; K is a composite equilibrium constant for the over-all reaction, given by $K_1 P_{NO} / (1 + P_{NO}/K_3)$, which is about 1.1 for $P_{NO}=1$, (this is necessitated by the fact that NO₂ and N₂O₃ disappear at proportional rates,

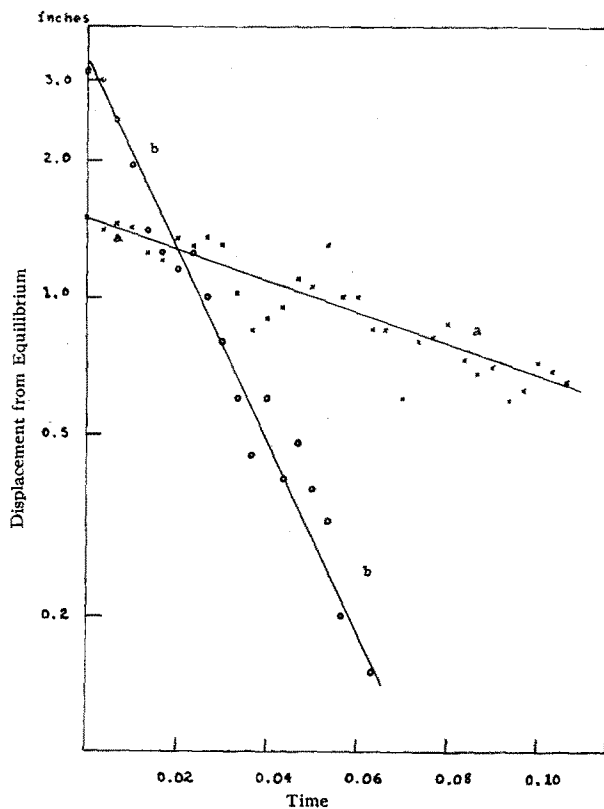
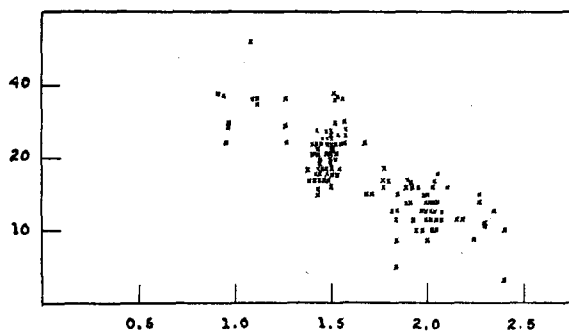
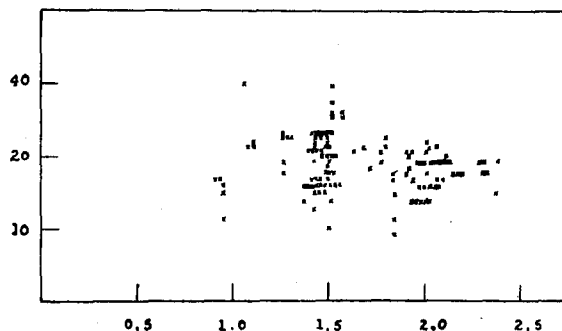


FIG. 4. Displacement from equilibrium vs. time in seconds (semi-log plot). Curve a, Run IV-59, corresponding to Fig. 2a. Curve b, Run IV-52, corresponding to Fig. 2b.


 FIG. 5. $\tau F \times 10^4$ vs. $P_{H_2O_i} \times 10^2$.

 FIG. 7. $\tau F \left(b - \frac{x_{\infty}}{2} \right) \times 10^6$ vs. $P_{H_2O_i} \times 10^2$.

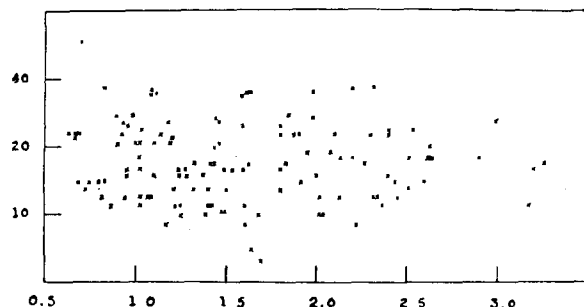
but requires no assumption as to the mechanism of the reaction); and Y is a factor which may be variable, to represent any catalytic or inhibitory influence affecting the rate.

It is readily seen that if Y is constant (corresponding to the assumption that the reaction rate is proportional to the rate of bimolecular collisions between N₂O₃ and H₂O, or of ternary collisions involving NO, NO₂, and H₂O), and if K has the value 4, the polynomial in Eq. (9) reduces to the first degree in x . The solution of (9) is then of the form

$$x_e - x = x_e \exp(-mkt), \quad (10)$$

where x_e denotes the equilibrium pressure of HNO₂ and $m = (a+b)/2$. Under these conditions a plot of $\log(x_e - x)$ vs. t would produce a straight line whose slope would be proportional to m .

If Y is constant but K differs from 4, it can be shown that a plot of $\log(x_e - x)$ vs. t would produce not a straight line, but a curve having the asymptotic slope $-Fk/2$, where $F = [(a-b)^2 + 16ab/K]^{\frac{1}{2}}$. Furthermore the slope of the curve increases monotonically with time, and it is found that, for K not less than one, the initial value can never be less than $\frac{3}{4}$ of this limiting value. To test the second-order hypothesis, therefore, the data were plotted in terms of distance from equilibrium (in terms of the measurements made with the aid of the microfilm reader, as described above) vs. time, on semi-log paper, as shown in Fig. 4; the half-time τ (inversely proportional to the slope) was measured from the most plausible straight line through the


 FIG. 6. $\tau F \times 10^4$ vs. $P_{[N_2O_3]} \times 10^2$.

experimental points, and the constancy of the product τF was investigated.

When plotted against the initial pressure of water vapor (Fig. 5) the values of τF thus obtained revealed a distinct trend in the sense of inverse variation. A comparable plot of τF vs. the initial pressure a due to NO₂ and N₂O₃ (Fig. 6) displays no such trend; the individual values scatter widely throughout the range of initial pressures employed.

From this result it is clear that the dependence of the rate on pressure of water vapor must be of order higher than the first. The most satisfactory simple formulation proves to be that the rate is proportional to the square of the water vapor pressure; i.e., in Eq. (1), $Y = b - x/2$. As is shown in Appendix I, the constancy of the product $\tau F(b - x_e/2)$ affords a convenient test of the applicability of this hypothesis. When plotted against the initial pressures a and b (Figs. 7 and 8, respectively), the values of this product show no significant trend and noteworthily less scatter than the corresponding values of τF . The rate constants reported below are therefore based on the third-order formulation.

THE RATE CONSTANTS

Assuming the rate law

$$dx/dt = k(b - x/2)[(a - x/2)(b - x/2) - x^2/K] \quad (11)$$

the rate constant may be calculated from the relation

$$k = 2 \ln 2 / \tau F (b - x_e/2)$$

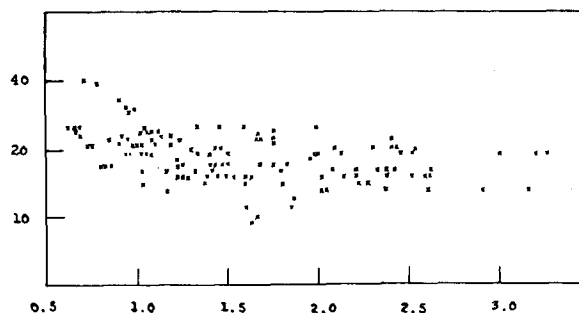

 FIG. 8. $\tau F \left(b - \frac{x_{\infty}}{2} \right) \times 10^6$ vs. $P_{[N_2O_3]} \times 10^2$.

TABLE II.

$a \times 10^2$ atmos	$b \times 10^2$ atmos	$F \times 10^2$ atmos	$A \times 10^2$ atmos	$B \times 10^2$ atmos	$C \times 10^2$ atmos	a_e/s_i
0.5	2.5	4.7	0.65	2.9	5.0	1.06
1.5	2.3	7.1	0.25	4.1	4.6	0.95
1.5	1.5	5.7	1.02	3.3	3.0	0.87
2.5	1.0	6.2	1.03	3.7	2.0	0.62

where the denominator is the product represented in Figs. 7 and 8. The median value of this product from 123 experiments is 1.9×10^{-5} , leading to the result (at 23 to 25°C with $P_{\text{NO}}=1$ atmos) $k=7.3 \times 10^4$ atmos $^{-2}$ sec $^{-1}$ or $\log k=4.86$ with a probable error of 0.09, corresponding to a factor of 1.2.

Treating the forward reaction separately, one finds, if

$$\begin{aligned} -dP/dt &= k' P P^2_{\text{H}_2\text{O}}, \\ P &= P_{\text{NO}_2} + P_{\text{N}_2\text{O}_3}, \\ k' &= \frac{1}{2}k = 3.7 \times 10^4 \text{ atmos}^{-2} \text{ sec}^{-1} \\ &= 2.2 \times 10^7 l^2 \text{ mole}^{-2} \text{ sec}^{-1}. \end{aligned}$$

If the assumption be made that N_2O_3 is the reacting species, so that

$$\begin{aligned} -dP/dt &= k'' P_{\text{N}_2\text{O}_3} P^2_{\text{H}_2\text{O}}, \\ k'' &= 3.1k/2 = 1.1 \times 10^5 \text{ atmos}^{-2} \text{ sec}^{-1} \\ &= 6.8 \times 10^7 l^2 \text{ mole}^{-2} \text{ sec}^{-1}. \end{aligned}$$

Finally, for the reverse reaction if

$$\begin{aligned} -dP_{\text{HNO}_2}/dt &= k''' P^2_{\text{HNO}_2} P_{\text{H}_2\text{O}}, \\ k''' &= k/K = 6.6 \times 10^4 \text{ atmos}^{-2} \text{ sec}^{-1} \\ &= 4.0 \times 10^7 l^2 \text{ mole}^{-2} \text{ sec}^{-1}. \end{aligned}$$

Appendix II contains a discussion of the approximations, assumptions, and uncertainties involved in arriving at these results.

DISCUSSION

Since the reaction proves to be very rapid in spite of the rather small concentrations of the reactants, it is of interest to determine whether the simple kinetic theory predicts a sufficiently high rate of triple collisions to account for the observations. For a typical mixture in which the pressures of water vapor and available N_2O_3 were both 0.015 atmos, the required collision rate at 25°C would be about 3×10^{18} per cc per sec. The number of binary collisions to be expected in this system is estimated, following Hinshelwood,¹⁰ to be about 1.7×10^{14} per cc per sec, using 4×10^{-8} cm as a reasonable guess for the average of the molecular diameters of water and nitrogen sesquioxide molecules. As a simple approximation, the ratio of ternary to binary collision rate is taken to be the same as the ratio of the diameter of the third molecule to the mean free path for that species. Assuming 3×10^{-8} cm for the

molecular diameter of H_2O , the number of ternary collisions per cc per sec is found to be about 8×10^{19} . Thus, assuming that N_2O_3 is the participating species, approximately one ternary collision in twenty-five results in reaction.

While this is a comfortable margin from the standpoint of collision frequency, it must be observed that the requirement of a certain spatial configuration for the reaction complex might easily reduce the probability of reaction for each otherwise suitable collision by an order of magnitude. If this picture is to apply it is necessary to conclude that the energy of activation must be practically nil. This, of course, is a common characteristic of third-order gas reactions and, in view of the probability that the heat of reaction (as well as the free energy change), is very small for this system, it is perhaps reasonable to expect it to be the case here also.

Since the rate of the reverse reaction is of the same order of magnitude as that of the forward reaction and since the amounts of products and of reactants in equilibrium mixtures are comparable, the considerations given above apply equally well to the reverse process. A curious consequence of the third-order law is that water vapor is apparently a catalyst in the formation of an acid anhydride (N_2O_3) from the acid vapor.

It should perhaps be remarked that although the third-order hypothesis is reasonably satisfactory in explaining both kinetics and mechanism of the reaction, yet because of the rather limited range of concentrations used in this study it cannot be regarded as well-established. The true explanation of the observed behavior may well be essentially more complex.

We wish to express here our great appreciation for the many helpful discussions with Dr. Oliver Wulf. We are thankful to Dr. Norman Davidson for general criticism. The work was supported in part by a grant from the Research Corporation, for which we are very grateful.

APPENDIX I

To investigate the properties of its solution, Eq. (11) may be conveniently rearranged to give

$$Rkdt = 8dx/(a-x)(B+x)(C-x) \quad (12)$$

where $R=(4-K)/K$ and A , B , and C are the magnitudes of the roots of the polynomial in the denominator; specifically,

$$A = (F-a-b)/R = x_e, \quad (13)$$

$$B = (F+a+b)/R = x_e + 2(a+b)/R, \quad (14)$$

$$C = 2b. \quad (15)$$

Re-expressing (8) in terms of partial fractions, it becomes

$$\begin{aligned} \frac{1}{8}Rkdt &= \frac{dx}{(A+B)(C-A)(A-x)} \\ &\quad + \frac{dx}{(B+A)(B+C)(B+x)} - \frac{dx}{(C-A)(B+C)(C-x)} \end{aligned}$$

or, remembering that $dx=d(B+x)=-d(A-x)=-d(C-x)$,

$$-\frac{1}{8}Rkdt = \frac{d \ln(1-x/A)}{(A+B)(C-A)} - \frac{d \ln(1+x/B)}{(B+A)(B+C)} - \frac{d \ln(1-x/C)}{(C-A)(B+C)}. \quad (16)$$

¹⁰ C. N. Hinshelwood, *The Kinetics of Chemical Change* (Oxford University Press, London, 1940).

In view of (13), therefore,

$$\frac{d \ln(x_e - x)}{kdt} = \frac{1}{8}R(A+B)(C-A) + \frac{(C-A)d \ln(1+x/B)}{(B+C)kdt} + \frac{(A+B)d \ln(1-x/C)}{(B+C)kdt} \quad (17)$$

As t increases without limit the last two terms of (17) approach zero, so that using (13), (14) and (15) the asymptotic slope is found to be

$$\frac{d \ln(x_e - x)}{kdt} = -\frac{F}{2} \left(b - \frac{x_e}{2} \right).$$

Since the half-time τ is inversely proportional to this slope, the product $\tau F(b - x_e/2)$ must be constant for a system conforming to the given rate law.

A straightforward extension of this analysis shows that the ratio of the final slope to the initial slope of the desired solution can be given by

$$s_e/s_i = 1 + \frac{CA(C-A) - AB(A+B)}{BC(B+C)}.$$

To illustrate the magnitude of this ratio, results of calculation for a few typical cases are shown in Table II.

APPENDIX II

For purposes of discussion, three principal approximations may be recognized: (i) the assumption of linear response of the detecting and recording system; (ii) neglect of complicating factors in interpreting the composition of the reacting mixture; (iii) uncertainty in the determination of the asymptotic half-time for each run. The first assumption was checked by calibration, as mentioned above; the errors due to nonlinearity of this sort in all probability would affect observed amplitude differences by less than five percent. A systematic error is indeed introduced in assuming that the quantity $(x_e - x)$ is linearly dependent on the distance of the transmitted light in an exponential function of the concentration. This may be illustrated by a calculation which shows that in the most adverse case (amplitude change being the largest) the half-time calculated on this basis would be shorter than the true value by six percent. In most runs the error caused by this procedure would be certainly less than five percent.

Complicating factors in determining the composition of the reacting mixture are the presence of nitrogen tetroxide, the change of pressure of nitric oxide as a result of reaction, and the fact that the gas mixture at the exit end of the light path is older than that near the inlet. At 25°C, the dissociation constant of N₂O₄ is 0.14 atmos, from which it may be shown that $P_{N_2O_4} = 7P_{NO_2}^2$, so that the pressure of N₂O₄ ranges up to about 10 percent of the total

available N₂O₄, being in most cases nearer to five percent. If the tetroxide is a nonparticipating molecular species it should affect the half-time by providing a reservoir of N₂O₄ which would not be detected by absorption of light. This effect should be comparable in magnitude but opposite in sign to that of the systematic error discussed in the previous paragraph, providing some compensation in this respect. The change in P_{NO} due to its disappearance in the reaction is of the order of one percent and may legitimately be neglected. Non-uniformity of the gas mixture in the light path is not particularly disturbing because of the fortunate circumstance that the course of the reaction is approximately exponential, so that the half-time is roughly the same for all parts of the system and consequently is given by that of the integrated system. At any rate, the maximum age difference to be considered was about one hundredth of a second, so that no important effect would be expected except perhaps for those runs giving the very shortest half-time.

Uncertainty in the determination of the half-time is due to two principal causes, namely uncertainty in determining the proper slope on the semilog plot, due to scatter of the individual points, and uncertainty in the determination of the value $x_e - x$ for the individual points due to drift of the pattern. As may be seen by examining Fig. 5, the points which are useful in the semi-log plot range over a period of only two or three half-times, so that the half-time estimated is likely to fall between the asymptotic value and the initial value. Since the slope changes most rapidly during the first half-time of the reaction, it is likely that the slope of the line chosen will differ from the asymptotic slope by considerably less than is indicated by the ratio s_e/s_i (Table II). The average error from this cause is probably of the order of 10 percent or less, except possibly in a few cases where the ratio a/b is unusually high.

The drift of the pattern on the oscilloscope screen following its sudden displacement presents a less easily handled problem. This effect is clearly evident on those photographs in which the half-time is very short; the observed displacement rises sharply to a maximum, then falls off more slowly. If it be assumed as a first approximation that this drift also follows an exponential law, its half-time may be estimated as about 0.10 to 0.15 sec. An attempt was made to estimate the magnitude of the uncertainty from this cause in the following way: on tracings derived from several runs of very short half-time, the sloping envelope of the latter portion was extrapolated linearly and the half-time was determined from a semi-log plot representing the data as distance from this line. This resulted in an increase of 20 to 25 percent for half-times estimated by the ordinary method as less than 0.02 sec. Since this process could not be applied in most cases, the trend of the discrepancy with increasing half-time could not be determined, but it seems likely that as the prominence of the maximum lessens, the disturbance of the measured half-time does also.