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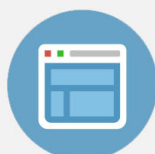J. Chem. Phys. 19, 799 (1951); 10.1063/1.1748373

The Kinetics of the Rapid Gas Reaction between Ozone and Nitrogen Dioxide*

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An apparatus has been designed and constructed which will rapidly mix two gaseous reactants, isolate them in a reaction cell, and, by means of light absorption, follow the course of the reaction photoelectrically in one-tenth of a second or less. The output of the photoelectric tube is recorded by a time-exposure photograph of the screen of an oscilloscope.

The kinetics of the fast reaction between ozone and nitrogen dioxide was studied over a tenfold range of concentration of each reactant. The rate law was found to be

$$-d(O_3)/dt = k(NO_2)(O_3)$$

over the entire course of the reaction. From the temperature coefficient of the rate of reaction the energy of activation was found to be 7.0 ± 0.6 kilo-calories per mole. A mechanism is proposed to account for the observations.

INTRODUCTION

THE rates of very rapid, non-explosive gas reactions have received attention in the recent past, but the cases studied were so rapid, for example the dissociation of nitrogen tetroxide, that very indirect and theoretically complicated methods of experimentation were required. It was deemed of interest, therefore, to study less extreme cases, and thus lay a firmer foundation for any further investigations. To this end it was decided to measure the rate of the reaction between ozone and nitrogen dioxide, which has been shown by Wulf, Daniels, and Karrer[1] to proceed quantitatively according to the equation

$$2NO_2(g) + O_3(g) = N_2O_5(g) + O_2(g). \qquad (1)$$
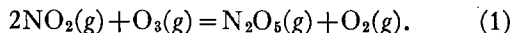
As an additional aspect of interest is the possibility that this reaction may be involved in the atmosphere immediately following a thunder clap.

EXPERIMENTAL METHOD

a. Method Summarized

Three streams of oxygen flowing at known rates from calibrated flowmeters were used (1) to pick up NO_2 from a saturator containing cold, liquid N_2O_4, (2) to dilute the NO_2 stream to the desired final concentration, and (3) to make ozone by passing through a silent electrical discharge tube. The two resulting streams were combined in about 0.01 sec. in a mixing chamber, and the resulting mixture was then passed immediately into a reaction cell of small, 2 mm diameter.

Through the reaction cell passed a filtered, chopped beam of light which fell on an electron

multiplier photoelectric tube. The output of the photoelectric tube was put across the deflection plates of an oscilloscope which, however, was not firing its beam. After a steady state was obtained, a weight was dropped which threw a lever which, in turn, closed a stainless steel stop gate and stopped the flow of the gases; the reacting mixture was thus isolated in the reaction cell. When the stop gate closed it made electrical contact with a brush which caused the oscilloscope to give a single sweep of its beam. During this single sweep the shutter of a camera was open and caught the full sweep on one film. The final data appeared on the photographic negative as a modulated wave packet whose width was simply related to the NO_2 concentration, and whose wave-period was known precisely from the speed of the synchronous motor.

Temperature of the reacting gases was measured by a fine copper-advance thermocouple just below the outlet of the reaction cell.

b. Apparatus

Materials used in this study were compressed oxygen supplied by the Lindé Corporation, and a tank of nitrogen dioxide sold by the Matheson Company.

The flowmeter system, including ozonizer and saturator, is shown schematically in Fig. 1. Flow rates of the oxygen streams were measured by capillary flowmeters using dibutylphthalate as manometer fluid. To remove suspected impurities in the oxygen stream, it was passed through a charcoal trap and a one-liter flask full of P_4O_{10} and glass chips. Even though the vapor pressure of dibutylphthalate is extremely low, an additional charcoal and P_4O_{10} tube was placed between the flowmeter and saturator.

Reservoir bulbs were included to smooth out any instantaneous fluctuations in the output of the ozonizer or saturator and to cushion the effect of

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[1] O. R. Wulf, F. Daniels, and S. Karrer, J. Am. Chem. Soc. **44**, 2398 (1922).

suddenly stopping the flow as readings were being made. In order to make calibrations, it was necessary to bypass the ozonizer and ozone reservoir bulb, or the saturator and the nitrogen dioxide bulb.

A large water-cooled ozonizer was calibrated for various flow rates and voltages by absorbing the ozone in a neutral solution of potassium iodide, which was then acidified with sulfuric acid and titrated with standardized sodium thiosulfate solution. For flow rates below 100 cc per min. the yield was 5.5 percent, essentially independent of flow rate.

The N_2O_4 saturator was an all-glass apparatus which consisted of nine tubes, each six inches long and 12 millimeters in internal diameter, mounted parallel to each other and in a horizontal plane. They were connected from below by tubes which permitted liquid N_2O_4 to flow freely from one to another. Above the ends the tubes were alternately joined in such a manner that the oxygen flowed from tube to tube over the surface of the liquid for a total distance of $4\frac{1}{2}$ feet without bubbling. A well-stirred mixture of water and ice was used as a thermostat for the saturator.

Nitrogen dioxide was passed through P_4O_{10} into the ice-cooled saturator until it was half full of liquid. At first the liquid had a trace of greenish color due to N_2O_3. This color changed to straw orange at 0°C after the liquid had been exposed to an atmosphere of oxygen for a few hours during which time the N_2O_3 was oxidized to N_2O_4. In the calibration of the saturator a stream of oxygen was blown over the liquid N_2O_4, and the vapors picked up were absorbed completely by a known volume of standardized base in a washing column which provided agitated vapor-liquid contact for about 30 seconds. The excess base was titrated with acid to the phenolphthalein end point.

Assuming the perfect gas law to apply inside the saturator, and extrapolating the work of Verhoek and Daniels[2] to get the equilibrium constant for NO_2-N_2O_4 at 0°C, the partial pressure of NO_2 plus N_2O_4 was found to be 0.356±0.003 atm. in nine determinations. Giauque and Kemp[3] found 0.346 atm. as the vapor pressure of N_2O_4 at 273.1°A. Although the difference between 0.356 and 0.346 lies outside the experimental error of the analysis, this difference could easily be due to gas imperfections or to an error in extrapolation of the equilibrium constant.

As an aid to calculation, nomographs were prepared which allow immediate translation to be made from flow rates to equilibrium pressures of

NO_2 and N_2O_4 at any temperature between 0°C and 35°C.

A mixing chamber shown in Fig. 2 was designed after those of Hartridge and Roughton.[4] It was of all-glass construction with four tangential jets on the perimeter of the cylinder, which was 1-mm high and 18 mm in diameter. Mixed gases flowed out of a 2-mm diameter tube co-axial with the mixing cylinder. From the weight of mercury required to fill the mixing chamber and exit tube, the total volume was found to be 0.20 cc. By means of an experiment devised to measure the very fast rate of dissociation of N_2O_4[5] upon dilution with oxygen by this method, it was shown that mixing was at least 99.5 percent complete by the time the gases reached the 2-mm diameter reaction cell.

The two-holed stainless steel stop gate was such that, on suddenly moving it about 3/16 inch by means of a falling weight and a shock cushioning lever, the input and exit channels of flow were simultaneously cut off. The external synchronization circuit for the oscilloscope was a battery which charged a condenser when a key was pressed. When the plunger in the stop gate was closed, it touched a phosphor bronze brush permitting the condenser to discharge through a resistor and thereby initiate the single sweep of the oscilloscope.

The glass reaction cell was *2 mm in internal diameter* and 37 mm long. Its ends were covered with black tygon paint before the windows were sealed on, in order to prevent light from traversing the glass walls and hitting the photoelectric tube, and the light was made slightly convergent in the cell to avoid reflections from the walls. Windows of the cell, consisting of a small lens of 13 mm focal length on one end and a small square of microscope cover glass on the other, were secured by several
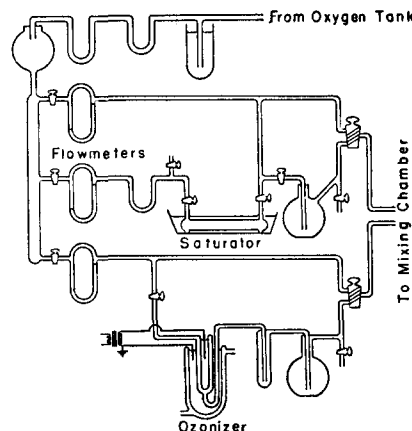

FIG. 1. Flowmeter system including saturator and ozonizer.

[2] F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).
[3] W. F. Giauque and J. D. Kemp, J. Chem. Phys. **6**, 40 (1938).
[4] H. Hartridge and F. J. W. Roughton, Proc. Camb. Phil. Soc. **23**, 450 (1926).
[5] P. D. Brass and R. C. Tolman, J. Am. Chem. Soc. **54**, 1003 (1932).

layers of tygon paint. The reaction cell was fastened to the stop gate by squaring and polishing the ends of the lead-in tubes until they conformed to the countersunk portion of the stop gate, and then sealing wax was applied around the outside.

The flow system was of all-glass construction from the flowmeters to the stop gate. The only material except glass and stainless steel exposed to the corrosive action of the reactants was Dow-Corning silicone stopcock grease and tygon paint, which were attacked only slowly by these gases, very
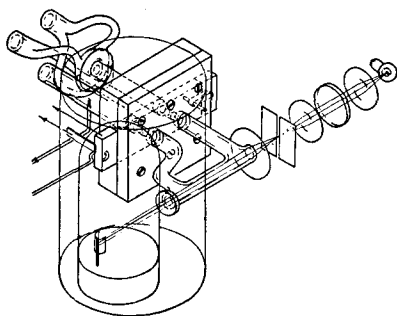

FIG. 2. Isometric projection of mixing chamber, stop gate, and 2-mm diameter reaction cell with schematic drawing of the light source, filters, and lenses.

much slower than the rate of reaction studied and also much slower than the rate of production of fresh quantities of the gases in the flow system.

The light source, shown schematically in Fig. 2, is a 500 watt General Electric projection bulb operated from storage batteries at 80.0 volts. Light was roughly collimated by a pair of condensing lenses and brought away from the hot source. It was filtered by a 1 cm path of 6 percent cupric sulfate solution in order to take out the heat rays, and by a pair of glass filters which transmitted a sharp, photochemically inactive peak between 4400 and 4800A. The beam was then focussed by a second pair of lenses on a hole 0.2 mm in diameter in a securely mounted, small piece of aluminum foil. An image of the 0.2 mm "point" source was formed by the lens-window about a cm beyond the light sensitive surface of the photoelectric tube.

The light chopper was made from a dural disk, $9\frac{1}{2}$ inches in diameter and 1/16-inch thick, in which was machined 10 holes and 10 teeth equi-angularly spaced around the perimeter. This disk was mounted on a 1/15 horsepower, 1800 r.p.m., synchronous motor, and it interrupted the light beam just in front of the 0.2-mm hole 300 times each second. An RCA 931-A photoelectric multiplier tube was used to measure the light emerging from the reaction cell. It was powered by a bank of 18 mini-max batteries rated at $67\frac{1}{2}$ volts each. Selected pairs of 50,000-ohm wire wound resistors were combined to make a voltage divider of 10 equal

steps. A 200,000-ohm potentiometer was adjusted so that at all times during the experiments the ammeter in series with the voltage divider read 0.920 ma when no light fell on the photoelectric tube. No more than a few hundredths of a milli-ampere flowed through the tube itself. A resistor and condenser were put in parallel across the output of the photoelectric tube in order to short out the high frequency components of the "noise" from the photoelectric tube, which was completely unusable at the low intensities employed without this filter. At these low intensities the amplitude of the wave packet on the oscilloscope screen was proportional to the intensity of the light, and this was proved in an experiment in which calibrated wire screens were put in the collimated beam of light. The oscilloscope was a DuMont type 247 with a 5-inch screen, which gave a blue light to which photograph film is quite sensitive. An Argus A-2 camera with its lens re-mounted and set forward was used for this work.

In this study temperature was measured rather than controlled. Temperature of the gases leaving the reaction cell was measured with a thermocouple made of 36 gauge copper and 30 gauge advance wire, protected by three coats of wire enamel. A reference junction was immersed in a well-stirred ice bath, and the potential developed by the thermo-couple was read with a Leeds and Northrup portable precision potentiometer, No. 8662.

Special precautions had to be taken to reduce mechanical vibrations.

RESULTS OF THE RATE MEASUREMENTS

### a. Computation of the Pressure of Reactants

From a knowledge of the flow rates of the oxygen streams, the calibrations of the saturator and the ozonizer, and the temperature, streams of different known NO_2 concentration were made up for calibration purposes and for rate experiments. The system was calibrated by trapping streams of known NO_2 concentration in the reaction cell, and the light transmission which was registered on the oscillo-scope was photographed. Before and after such tests, pure oxygen was similarly analyzed to give a measure of the light intensity I_0. An example of a photograph of the oscilloscope screen for an O_2 blank and an NO_2 blank is shown in Fig. 3. Values of the logarithm of I/I_0 obtained for various pressures are plotted in Fig. 4 against one-half the NO_2 pressure, one-half pressure being used to sim-plify stoichiometric calculations. It can be seen that, with the filters and pressures of NO_2 used, Beer's law is obeyed. From the calibration curve, Fig. 4, the sensitivity of the apparatus can be seen to be about 1×10^{-4} atmosphere of NO_2, and the most efficient working range is between 1 and 10 milliatmospheres.

In a rate experiment, pictures were made respectively of (1) pure O_2 alone, (2) NO_2 diluted by the full amount of O_2 used in the experiment, (3) three or more actual runs with O_2, NO_2, and O_3 with different velocities of the oscilloscope beam across the screen, and finally (2) and (1) again. Examples of the form of the data obtained are shown in Fig. 3. Temperature of the thermocouple junction was read at each stage of the run. The film, plus X, was developed in Defender 777 fine grain developer to a gamma of 1.2.

The traces on the film were projected by a microfilm reader on a sheet of white paper, details of the upper and lower edges were drawn, and the time scale marked and labeled. Upon removal of the paper, a smooth curve was drawn through the slightly ragged edges, and the width of the envelope was measured for each 1/300 sec. The edges were ragged in some cases due to mechanical vibrations from the falling weight, and some scatter was due to random variation in the output of the photoelectric tube.

From an analysis of the O_2 and NO_2 blanks, a portion of the data was found to have as much as two percent distortion. Correction curves for distortion were made from the O_2 and NO_2 blanks, and in view of the fact that these correction curves were reproduced almost identically for different blank runs, it can be stated that distortion was not an important source of error in the final results. A less satisfactorily handled source of error in this work was the drift of I_0 with time. An arbitrary procedure of linear interpolation with respect to the time was used. It was noted that the value of the rate constant which was calculated for a given experiment is very sensitive to the value of I_0 used, and greater precision might be attained if this source of uncertainty were reduced.

The pressure of NO_2, divided by two, was obtained from the value of I/I_0 and Fig. 4. A knowledge of the pressure of NO_2 and the temperature —and thus the equilibrium constant—permitted the calculation of the actual pressure of N_2O_4, and the total formal pressure of N_2O_4. The pressure of O_3 was found from its known initial value and by difference in the total formal N_2O_4 pressure from its initial value, for Wulf, Daniels, and Karrer[1] showed that the reaction between ozone and nitrogen dioxide is given quantitatively by the chemical equation

$$2NO_2 + O_3 = N_2O_5 + O_2. \qquad (1)$$
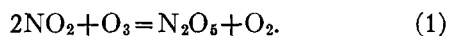
Thus, for each experiment, there was tabulated opposite the time from the start of observations a column for the pressures of $NO_2/2$, N_2O_4, ($NO_2/2 + N_2O_4$), and O_3. An abbreviated but illustrative example is presented in Table I.

b. Differential Rate Equation

The following abbreviations are defined, all pressure units being milliatmospheres; x = pressure of NO_2, y = pressure of N_2O_4, z = pressure of O_3, c = total formal pressure of $N_2O_4 = x/2 + y$. The subscript zero will refer to the initial pressure at the start of the reaction upon mixing, not to the first observation.

The rate of the reaction was calculated by the differential method between two values of the O_3 pressure 1/300 sec. or in some cases 1/60 sec. apart. One column in Table I illustrates this procedure for one experiment, and in a similar fashion the average rate of reaction was computed for the other 42 runs made in this study. An inspection of the tables of the reaction rate lead to the hypothesis that the rate law is

$$-dz/dt = kxz, \qquad (2)$$

that is, the rate of disappearance of O_3 is proportional to the product of the pressures of NO_2 and O_3. To test this hypothesis the average rate obtained for a short interval was divided by the average value of x and z observed at the beginning
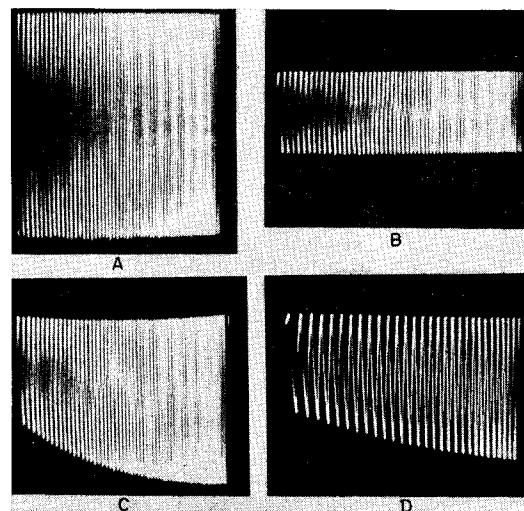

FIG. 3. Examples of photographs of the oscilloscope screen. Respectively, A to D, O_2 blank, NO_2 blank, and two actual runs.

and end of the interval, as is illustrated in the last column on Table I.

Though the individual, instantaneous values scatter fairly seriously, there is no trend in the values of k down the column. Similarly the values of k for the other experiments were computed, and these are tabulated as group averages in Table II-A which summarizes the runs made at room temperature, $21 \pm 1°C$, and in Table II-B which shows the rate constants found at different temperatures. The initial values of c and z each vary over a factor of
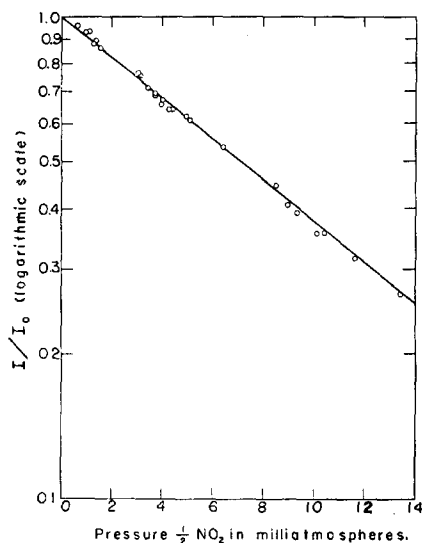
FIG. 4. Calibration of the reaction cell and the photoelectric circuit.

about 10, and the ratio of c_0 to z_0 similarly covers about a 10-fold range.

At one temperature it can be seen that, with some scatter, essentially the same value of the rate constant is obtained for the various concentrations. At 21°C the average value is 3.66×10^7 cm³/mole-sec.; the standard deviation for 27 cases is 0.34 in the same units, and thus the standard error of the mean is 0.07. Hence it is seen that this method has, for a kinetic study, a high degree of precision largely by virtue of the ease of producing a large number of data. In one night, for instance, data for 500 differential rate constants were collected. The deviation of values of k from the mean were not significantly correlated with any of the variables listed in Table II. Inspection of the data showed that no other product of integral powers of the pressures of the reactants gives a satisfactory rate law, and in experiments in which a large excess of NO_2 was present it was possible to decide between kxz and $2kcz$ in favor of the former.

c. Integrated Equation

Using the observed rate equation

$$-dz/dt = kxz,$$

the equilibrium equation between NO_2 and N_2O_4

$$K = x^2/y,$$

and the stoichiometry of the reaction with respect to O_3

$$z = c + (z_0 - c_0),$$

the differential equation can be expressed in terms

of the initial conditions and the pressure of NO_2

$$\frac{(\frac{1}{2} + 2x/K)dx}{[(z_0 - c_0) + x/2 + x^2/K]x} = -k\,dt. \quad (3)$$

This integrates, for $(4/K)(z_0 - c_0)$ less than $1/4$, to give

$$kt = C - \left[\frac{1}{4(z_0 - c_0)} \log \frac{x^2}{z_0 - c_0 + x/2 + x^2/K}\right.$$
$$+ \frac{[\frac{1}{4} - (4/K)(z_0 - c_0)]^{\frac{1}{2}}}{2(z_0 - c_0)}$$
$$\left. \times \log \frac{2x/K + \frac{1}{2} + [\frac{1}{4} - (4/K)(z_0 - c_0)]^{\frac{1}{2}}}{2x/K + \frac{1}{2} - [\frac{1}{4} - (4/K)(z_0 - c_0)]^{\frac{1}{2}}}\right], \quad (4)$$

where C is the value of the terms in the brackets when x is replaced by x_0, and the other terms have been defined above. Data from the experiment, which are summarized in Table I, were substituted in the integrated equation, and the expected linear relationship was found as is seen in Fig. 5. The slope of the line is 1.32 (milliatm. sec.)$^{-1}$ which is in satisfactory agreement with the average value of k, 1.29 in the same units, found from the same data by use of the differential equation.

The integrated equation gives a check on the completeness of mixing of the reactants. The intercept on the time axis of the line found by the integrated equation is -0.032 second, and the flow rate through the reaction cell for this experiment was 9.8 cc per sec. These facts imply a volume of 0.31 cc in front of the cell after mixing has occurred. Since the volume from the center of the reaction cell to the jets of the mixing chamber was 0.35 cc, it appears that mixing was essentially complete early in the stage of the mixing process.

d. Effect of Temperature Changes

Measurement of temperature was somewhat uncertain because of the temperature rise resulting from the heat of reaction. At 18°C the reaction as written above liberates 50 kilocal per mole of O_3,[6] and if the reaction occurred adiabatically, the temperature would rise 8°C when one milliatm. of O_3 reacted in the presence of one atm. of O_3. Actually the reaction occurred neither adiabatically nor isothermally. It required from 10 to 20 minutes for the temperature of the thermocouple to reach its steady state value when the reactants flowed through the reaction cell, and the maximum temperature rise observed was only about 10 percent of

[6] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

that calculated on the assumption of adiabatic conditions.

In order to eliminate some of these uncertainties in the study of the effect of temperature on the rate of the reaction, these runs were made with low pressures of the reactants. A summary of the values of the rate constant for different temperatures is given in Table II-B for two different values of the initial pressures of reactants. The maximum temperature rise observed for the first set of conditions was less than 1°C, and that for the second set of conditions was about $2\frac{1}{2}$°C. In all cases the temperature of the air thermostat around the mixing chamber and reaction cell was within two degrees of that of the thermocouple inside the glass line. Thus, though the temperature control was far from ideal, the errors in the temperature reported in Table II should be no more than about 2°C, and there is no reason to think that the errors are systematic in the sense of giving too great or too small a range of temperature which would invalidate the measurement of the energy of activation.

Rate constants were expressed in terms of moles per cubic centimeter rather than the temperature dependent pressure units, and the energy of activation was computed from the 22 experiments summarized in Table II-B by evaluating the constants in the Arrhenius equation

$$\ln k = -E/RT + \text{constant}$$

by that method of least squares which recognizes the possibility of error in both variables,[7] $\ln k$ and $1/T$. The value found for the energy of activation was 7.0 kilocal per mole, and the standard error of estimate was found to be 0.6 kilocal per mole.

To facilitate the comparison of these results with those of other kinetic studies the rate constant may be expressed in the following forms

$$k = 5.9 \times 10^{12} e^{-E/RT}$$
$$= 3.5 \times 10^{11}(T)^{\frac{1}{2}} e^{-E/RT} \text{ cm}^3/\text{mole-sec.} \quad (5)$$

DISCUSSION OF RESULTS

a. A Mechanism

The mechanism proposed to account for the observation is

(1) $NO_2 + O_3 = NO_3 + O_2$, rate determining
(2) $NO_2 + NO_3 + M = N_2O_5 + M$, fast

where M represents any molecule including the walls of the vessels. The first step is in agreement with the observed second order rate equation; and

[7] R. A. Fisher, *Statistical Methods for Research Workers* (Oliver and Boyd, Edinburgh, 1938), p. 139.

the fact that two molecules of NO_2 react for each one of O_3 requires a reaction such as (2) to remove the second NO_2. Corrections were made for the equilibrium between NO_2 and N_2O_4 the rate of attainment of which is known[5] to be much more rapid than the rate determining step of this reacting system. Inclusion of M in the equations above does not imply that the three molecules collide at exactly the same time, and in fact these experiments gave no evidence as to how closely deactivating collision with M is associated in time with the initial encounter of an NO_2 and NO_3 molecule. NO_3 is a substance frequently postulated to explain the mechanism of reactions of the higher oxides of

TABLE I. An example of the method used to analyze the data Experiment VI-9. Total flow rate 0.594 1 per min., 12°C, $z_0 = 7.28$ milliatmospheres.

Time unit 1/300 sec.	I/I_0	Pressure of gases in milliatmospheres					
		$NO_2/2$ $x/2$	N_2O_4 y	O_3 z	Δz	$\frac{\Delta z/\Delta t}{R}$	R/xz k
0	0.752	2.93	0.67	5.83			
1	0.762	2.79	0.61	5.63	0.20	60	1.83
2	0.769	2.70	0.60	5.53	0.10	30	0.98
3	0.776	2.61	0.55	5.39	0.14	42	1.45
4	0.782	2.53	0.51	5.27	0.12	36	1.32
					0.08	24	0.92
5	0.787	2.47	0.49	5.19			
10	0.813	2.13	0.38	4.74	0.45	36	1.19
15	0.834	1.87	0.28	4.38	0.36	22	1.12
20	0.858	1.59	0.21	4.03	0.35	21	1.45
25	0.876	1.37	0.16	3.76	0.27	16	1.40
30	0.892	1.18	0.12	3.53	0.23	14	1.48
35	0.906	1.01	0.08	3.32	0.21	13	1.68
40	0.915	0.91	0.06	3.20	0.12	7	1.10
45	0.922	0.83	0.06	3.12	0.08	5	0.88
50	0.929	0.75	0.05	3.03	0.09	5	1.11
Average in (atm. $\times 10^{-3} \times$ sec.)$^{-1}$							1.29

TABLE II. Summary of rate constants observed under various conditions. c_0 is the initial pressure of N_2O_4 plus $NO_2/2$. z_0 is the initial pressure of O_3.

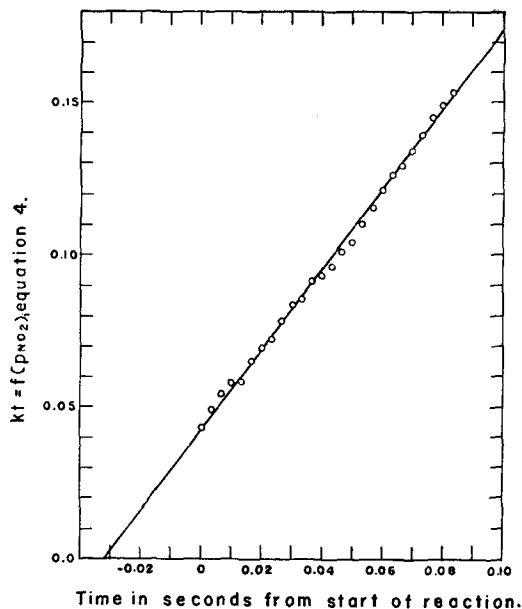| Condition number	Temperature °C	c_0	z_0	Number of runs averaged	Average value of rate constant cm^3/moles sec. $\times 10^{-7}$
		milliatmospheres			
A. Variation of initial pressures of reactants at one temperature					
1	20	1.23	1.92	3	3.7
2	20	1.28	3.68	2	3.5
3	20	1.21	5.70	3	3.5
4	21	5.35	4.69	2	3.9
5	20	5.00	7.52	4	3.9
6	21	4.55	11.35	4	3.3
7	22	13.4	5.60	4	3.4
8	22	14.9	18.0	2	4.1
9	20	12.3	23.8	3	3.6
B. Variation of temperature at constant ratio of initial pressure of reactants					
10	13	1.23	1.92	4	2.8
1	20	1.23	1.92	3	3.7
11	29	1.23	1.92	3	5.0
12	14	5.05	7.28	8	3.0
5	20	5.00	7.52	4	3.9

FIG. 5. Test of the integrated equation (Experiment VI-9)

nitrogen.[8-10] Since its absorption spectrum has been obtained (most recently by Jones and Wulf[11]), NO_3 is more nearly a substantiated compound than a hypothetical intermediate.

If simultaneous differential rate equations are written down for each step in the above mechanism, if the usual assumptions are made about the steady state concentration of NO_3, and if the second reaction is considered fast compared to the first, then

it is found upon solution for the rate of disappearance of O_3 and of NO_2

$$-d(O_3)/dt = k_1(NO_2)(O_3) \qquad (6)$$

$$-d(NO_2)/dt = 2k_1(NO_2)(O_3), \qquad (7)$$

and the rate constant k tabulated above is k_1. Thus the mechanism given above is sufficient to account for the experimental facts found in this study.

b. Relations to Other Kinetic Studies

It should be noted that this reaction and its mechanism is related to and has interconnections with several other kinetic systems involving the higher oxides of nitrogen. The first step of this mechanism is identical with one step in the mechanisms proposed by Schumacher and Sprenger[8] to explain the N_2O_5 catalyzed decomposition of ozone. The second step of the mechanism proposed here is the reverse of the first step of the mechanism proposed by Smith and Daniels[9] for the reaction of NO and N_2O_5, and these two reactions together are the forward and reverse steps of the equilibrium proposed by Ogg[10] as one feature of a new mechanism for the first order decomposition of N_2O_5. It is believed that further work with these four kinetic systems will reveal quantitative interrelations among them.

[8] H. J. Schumacher and G. Sprenger, Zeits. f. physik. Chemie B2, 267 (1929); G. Sprenger, Zeits. f. Elektrochem. 37, 674 (1931).
[9] J. H. Smith and F. Daniels, J. Am. Chem. Soc. 69, 1735 (1947).
[10] R. A. Ogg, Jr., J. Chem. Phys. 15, 337 (1947).
[11] H. J. Jones and O. R. Wulf, J. Chem. Phys. 5, 873 (1937).