

When a hydrogen atom or a hydroxyl group is joined directly to the central nitrogen atom of the ammonium ion, the constant reaches very low values. This may be ascribed to hydrogen bonding with the negative ion. Thus, the dissociation constant of trimethylammonium picrate is only  $1.5 \times 10^{-4}$ . In the case of ions having an —OH group directly attached to the nitrogen atom, the bonding effect is even greater, the dissociation constants for trimethylhydroxyammonium picrate and phenyldimethylhydroxyammonium picrate being  $1.7 \times 10^{-5}$  and  $1.9 \times 10^{-5}$ , respectively. Clearly, here we have energy effects of considerable magnitude appearing as a result of other than coulombic interaction.

Some preliminary measurements were carried out with phenyldimethylammonium picrate. On extrapolation of the Fuoss plot, which was found to be linear, a  $\Lambda_0$  value of 9.54 was obtained. It seems evident that this salt dissociates into free acid and base in nitrobenzene solution. The conductance of solutions of this salt was greatly increased by adding either picric acid or dimethylaniline. The same salt undergoes acid-base dissociation in tricresyl phosphate as Elliott and Fuoss<sup>12</sup> have shown. The results of a detailed study of systems of this kind will be presented in another paper of this series.

### V. Summary

1. A method is described for the preparation of nitrobenzene having a specific conductance of  $2-4 \times 10^{-10}$ .

(12) Elliott and Fuoss, *THIS JOURNAL*, **61**, 294 (1939).

2. The results of conductance measurements at concentrations below  $2 \times 10^{-3}N$  are given for the following salts: the picrates of tetramethylammonium, tetraethylammonium, tetra-*n*-propylammonium, tetra-*n*-butylammonium, tetra-*n*-amylammonium, trimethylammonium, trimethylhydroxyammonium, methoxytrimethylammonium, ethyltrimethylammonium, bromomethyltrimethylammonium, hydroxyethyltrimethylammonium, methoxymethyltrimethylammonium, phenyltrimethylammonium, phenyldimethylhydroxyammonium and phenyltrimethylammonium picrate and for tetra-*n*-butylammonium triphenylborofluoride.

3. The higher members of the homologous series of tetraalkylammonium picrates give results which closely approximate the Debye-Hückel-Onsager equation. For these salts, values of  $\Lambda_0$  have been obtained by extrapolation of the  $\Lambda_0\sqrt{C}$  plots to the  $\Lambda$ -axis.

4. The results for other picrates, which show ion-pair association, have been treated by the method of Fuoss to obtain values of  $\Lambda_0$  and  $K$ .

5. The conductance of various ions in nitrobenzene has been approximated by the method of Fowler and Kraus.

6. The influence of various constitutional factors on ion conductance and on dissociation constants is discussed.

7. It has been shown that phenyldimethylammonium picrate dissociates into free acid and base, which dissociation is repressed by addition of these constituents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## A Study of the Kinetics of the Reaction between Nitrogen Pentoxide and Nitric Oxide<sup>1,2</sup>

BY J. HAROLD SMITH<sup>3</sup> AND FARRINGTON DANIELS

The reaction between nitrogen pentoxide and nitric oxide has been observed previously only in a qualitative manner,<sup>4,5</sup> and it has been described as an extremely rapid, perhaps instantaneous, gas phase reaction. Busse and Daniels<sup>4</sup> in 1927 observed that "nitric oxide reacts immediately with nitrogen pentoxide" to produce brown nitrogen dioxide. Sprenger<sup>5</sup> refers to the reaction as being "immeasurably rapid." No attempt to follow the rate of this very rapid reaction in a quantitative manner has heretofore been reported.

(1) From a dissertation submitted by J. Harold Smith to the Graduate School faculty of the University of Wisconsin in June, 1941, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Presented to the Div. of Phys. and Inorg. Chem. at the St. Louis, Mo., meeting of the A.C.S., April, 1941.

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(4) Busse and Daniels, *THIS JOURNAL*, **49**, 1257 (1927).

(5) Sprenger, *Z. physik. Chem.*, **49**, 136 (1928).

The nitrogen pentoxide-nitric oxide reaction is of interest as a gas-phase reaction which takes place at a rapid rate even at room temperature. Furthermore, this reaction is of special interest in connection with the thermal decomposition of nitrogen pentoxide. The nitrogen pentoxide-nitric oxide reaction is assumed to be a rapid secondary step in a mechanism proposed to account for the first order nature of the nitrogen pentoxide decomposition,<sup>4,6</sup> but a question has been raised<sup>7</sup> regarding the possibility that this reaction may be slow enough at very low pressures to limit the rate of the nitrogen pentoxide decomposition.

This paper describes a method and apparatus devised for the measurement of the rate of the

(6) Bodenstein, *ibid.*, **105**, 51 (1923).

(7) Daniels "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, p. 71.

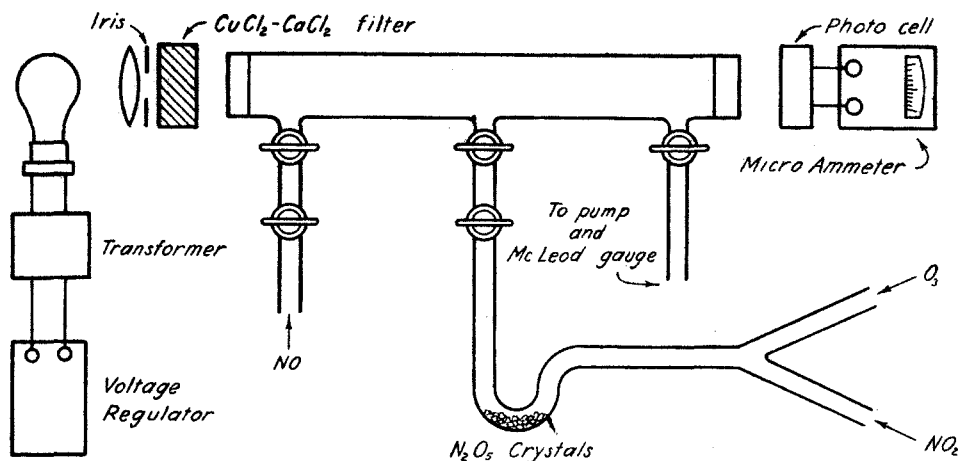


Fig. 1.—Diagram of apparatus.

rapid gas phase reaction between nitrogen pentoxide and nitric oxide. Data are given for measurements made at 0, 15 and 25°, and with pressures ranging from a few hundredths of a millimeter up to approximately 20 millimeters. The kinetics of the reaction are discussed, and a possible mechanism is tentatively suggested.

### Experimental

The reaction between nitrogen pentoxide and nitric oxide is particularly well suited to a colorimetric method for following its progress, since both reactants are colorless and the nitrogen dioxide produced is sufficiently colored to be detected at very low pressures. At room temperature, nitrogen dioxide has an appreciable color at a pressure of only a few tenths of a millimeter in a colorimetric tube two feet in length. The use of the colorimetric method is fortunate since the reaction is so rapid that very low pressures, of the order of only a few millimeters, must be used in order to obtain a conveniently measured rate.

**Apparatus.**—The apparatus used is shown diagrammatically in Fig. 1. Several reaction tubes of optical paths ranging from 18 to 178 cm. were used throughout the course of the investigation. In general the cylindrical reaction tubes were equipped with sealed-in optical Pyrex windows and were immersed in a constant temperature water bath during the measurements. The nitrogen pentoxide and nitric oxide were admitted through large stopcocks from gas at a relatively high pressure in the side tubes. The use of stopcocks in the system was not eliminated, even though undesirable. The thermal instability of the nitrogen pentoxide, coupled with necessary precautions to exclude moisture, and the low pressures of reactants made the use of alternative techniques and devices very difficult. After several unsuccessful preliminary attempts to avoid them, stopcocks were finally resorted to. The use of a good stopcock grease was imperative, since with the low pressures being used a tight system was very essential. Due to the extremely rapid rate of the nitrogen pentoxide-nitric oxide reaction, however, the time of contact of the gases with the grease was short and the amount of reaction with the grease was small.

The progress of the reaction was followed by determining the amount of nitrogen dioxide present at any given time with the aid of a sensitive photocell of the self generating type. A sensitive micro-ammeter of range 0–15 micro-

amp. was used for measuring the current generated by the photo-cell. A parallel beam of light from a single filament incandescent source was used. This was filtered through a 2.5-cm. layer of cupric chloride-calcium chloride solution which transmits only between 480 and 600  $m\mu$ ., and thus removes light which is known to cause photo-chemical decomposition of nitrogen pentoxide if nitrogen dioxide is present.<sup>3</sup>

**Method.**—In general the experimental procedure was to admit a small amount of the washed and carefully dried nitric oxide (obtained from a nitrite-iodide-acid mixture) and then evacuate the system. This was repeated several times in order to thoroughly rinse the reaction vessel, after which nitric oxide was admitted and pumped down to the desired pressure. Measurements of pressure were made with a McLeod type gage of range up to 5 mm. A known amount of nitrogen pentoxide was admitted from the vapor in the side tube at a much higher pressure. The high pressure of the nitrogen pentoxide in the side tube forced the gas instantly into the reaction vessel and helped to complete mixing, which was accomplished rapidly at the low pressures used. The pressure of the nitrogen pentoxide vapor in the side tube was adjusted by controlling the temperature of the nitrogen pentoxide crystals in the U tube, which were produced conveniently in a very pure and dry state by the oxidation of nitrogen dioxide with ozone. The nitrogen dioxide was obtained either by heating lead nitrate crystals or from commercial tanks of liquified gas.

The photo-cell was calibrated empirically against measured amounts of nitrogen dioxide in the various reaction tubes and at temperatures of 0, 15 and 25°. The nitrogen dioxide pressures were measured with the McLeod gage, and were corrected for the variation of the degree of association of nitrogen dioxide with temperature and pressure.

Using calibration curves, the amount of the nitrogen dioxide produced after any given time was easily ascertained, and a continuous physical

(8) Daniels and Johnson, *THIS JOURNAL*, **42**, 72 (1921).

method was available for following the progress of the rapid reaction. At pressures of only a few hundredths of a millimeter, nitrogen dioxide was easily detected and measured. The nitrogen dioxide produced from just 0.013 mm. of nitric oxide reacting with an excess of nitrogen pentoxide in the 178.4 cm. tube caused a micro-ammeter deflection of 5 units. The micro-ammeter reading adjusted in but a fraction of a second to a change in the nitrogen dioxide concentration, and the apparatus was thus ideally suited for following the progress of the very rapid reaction.

### Results

Using this apparatus and procedure, measurements have been made on the rate of the nitric oxide-nitrogen pentoxide reaction at 0, 15 and 25° and at pressures ranging from a few hundredths of a millimeter up to 20 mm. Under these conditions the reaction was found to proceed at a conveniently-followed rate, with a half life at 0° of the order of ten to fifteen minutes.

**The Reaction.**—In order to obtain experimental confirmation of the assumption that the reaction between nitrogen pentoxide and nitric oxide in the gaseous phase is as represented by the equation,  $\text{N}_2\text{O}_5 + \text{NO} \rightarrow 3\text{NO}_2$ , limited, measured amounts of nitric oxide were mixed with an excess of nitrogen pentoxide vapor and the reaction was allowed to go to apparent completion. The amount of nitrogen dioxide produced in each case was determined and compared with that expected on the basis of the above equation. Table I gives data at 25 and 0° which permit a comparison of the amount of nitrogen pentoxide expected (from the limited amount of nitric oxide, on the basis of the equation), and that obtained (as indicated by the previously prepared calibration curve for the photo-cell).

TABLE I

[NO <sub>2</sub> ] calculated (assuming $\text{NO} + \text{N}_2\text{O}_5 \rightarrow$ $3\text{NO}_2$ )	[NO <sub>2</sub> ] produced (using calibration curves)	[NO <sub>2</sub> ] calculated (assuming $\text{NO} + \text{N}_2\text{O}_5 \rightarrow$ $3\text{NO}_2$ )	[NO <sub>2</sub> ] produced (using calibration curves)
moles/liter $\times 10^{-5}$		moles/liter $\times 10^{-5}$	
At 25°		At 0°	
4.6 $\times 10^{-5}$	4.8 $\times 10^{-5}$	4.5 $\times 10^{-5}$	5.5 $\times 10^{-5}$
7.2	7.8	5.0	6.0
12.1	11.7	5.2	6.1
15.9	15.1	8.2	8.5
16.4	15.7	12.7	14.5
24.9	23.8	14.8	15.5
24.9	22.8	21.4	20.5

The good agreement of the data in the two columns indicates that under these conditions the reaction proceeds as written, virtually to completion. Some discrepancies observed in preliminary measurements at 25° were attributed to experimental error.

**Moisture Effects.**—The reaction appears to be strongly catalyzed by moisture. The rate in a new tube was found to be considerably greater than in the same tube after continued evacuation

and heating for drying and outgassing. Furthermore, erratic, non-reproducible rates were generally observed in the new tubes. The rates in tubes coated with paraffin were found to be in good agreement with the quite reproducible rates observed in carefully dried or "aged" tubes. The results suggest that the reaction is catalyzed by moisture, especially in the presence of a new glass surface. To confirm this, moisture was deliberately added during a series of measurements in a carefully dried tube. A definite increase in the rate and generally erratic behavior were observed upon the addition of water vapor.<sup>9</sup>

It is conceivable that the nitrogen dioxide produced by the reaction may influence the rate, particularly if any moisture is present. A generally observed decrease in the rate as the reaction neared completion suggests a possible retarding effect due to nitrogen dioxide. On the other hand, however, limited data which permit a direct comparison indicate that the rate is not influenced by the presence of nitrogen dioxide. It was possible in only two instances to directly compare the rate observed at a high nitrogen dioxide concentration to that found when a small amount of nitrogen dioxide was present (at given concentrations of nitrogen pentoxide and nitric oxide). Approximately equal rates were observed, indicating the absence of any influence due to nitrogen dioxide. It is unfortunate that more data on this point were not obtained. Experimentally, such measurements are difficult with the method employed, since the progress of the reaction was followed by measuring the amount of nitrogen dioxide present, and at high concentrations of nitrogen dioxide the colorimetric measurements of concentration are inaccurate.

**Surface Effects.**—Surface effects are indicated by the pronounced catalytic influence of moisture in a new tube with a fresh surface. To test for surface effects, rate measurements were made using a three-liter spherical reaction vessel in place of the much smaller cylindrical tubes. The surface-volume ratios for the cylinders were approximately six times as great as for the sphere and the physical dimensions were widely different. Table II compares the empirical "specific rate constants"<sup>10</sup> for

(9) It is evident that the reaction is catalyzed by moisture, and also that the more completely traces of moisture are removed the slower the rate. A question arises regarding whether or not the reaction will proceed at all in the complete absence of moisture. A definite answer cannot be given on the basis of the data available, since with the method used absolute exclusion of water vapor was impossible. While the rate did decrease as drying progressed, a point was finally reached where further attempts at drying seemed to be without effect on decreasing the rate. This ultimate rate may then correspond either to the "dry" rate or conceivably to the slowest rate obtainable with the drying methods and apparatus used. All data given in this paper correspond to the fairly consistent slowest rate observed, in each case.

(10) It was found that when the logarithm of the concentration of nitrogen pentoxide is plotted against time reasonably straight lines are obtained, at least for the first half of the reaction, as shown in Fig. 2. The rate values listed in the table were obtained by multiplying the slopes of the straight lines thus obtained for individual runs by  $-2.303$ , and are regarded as empirical "rate constants."

data obtained using the sphere with corresponding values found with a cylindrical vessel.

TABLE II

DATA COMPARING THE REACTION RATE IN CYLINDRICAL AND SPHERICAL VESSELS AT 25 AND 0°

The surface-volume ratio of the cylindrical vessel is approximately six times that of the sphere.

Cylindrical tube (216 ml.)	Paraffined spherical vessel (3,056 ml.)	Cylindrical tube (216 ml.)	Paraffined spherical vessel (3,056 ml.)
25°			
8.4 × 10 <sup>-3</sup>	9.6 × 10 <sup>-3</sup>	2.9 × 10 <sup>-3</sup>	
8.0	6.2	2.9	
7.7	7.3	3.1	
7.8	6.7	3.3	(No measurements at 15°)
8.6	7.1	3.1	
8.1	7.7		
8.3		Av. 3.1 × 10 <sup>-3</sup>	
8.3			0°
8.3		7.3 × 10 <sup>-4</sup>	7.9 × 10 <sup>-4</sup>
8.1		7.0	7.5
Av. 8.1 × 10 <sup>-3</sup>	7.4 × 10 <sup>-3</sup>	7.2	6.3
			7.4
		Av. 7.2 × 10 <sup>-4</sup>	7.3 × 10 <sup>-4</sup>

<sup>a</sup> Values given are for individual runs. Initial concentrations of nitrogen pentoxide and nitric oxide were of the order of 10–15 × 10<sup>-3</sup> mole per liter.

It is seen that the rates at both 0 and 25° are comparable, within the limits of experimental error, in the two types of vessels. The data indicate that, at least in carefully dried vessels, surface effects are not great and that the reaction may be essentially a homogeneous process. There are a number of characteristics of the reaction which definitely suggest complexity, however, and it is possible that some step or reaction in what appears to be a complex process may be influenced by surface factors. The abrupt change to consistent results, corresponding to a slower rate, immediately after paraffining a new tube suggests this to be the case.

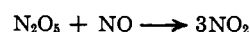
It has been found<sup>11</sup> that the rate of the reaction between nitric acid and nitric oxide is greatly influenced by surface. In view of this it is not surprising that the presence of moisture introduces surface effects in the reaction between nitric oxide and nitrogen pentoxide. If any moisture is present it is likely that the nitrogen pentoxide will rapidly react with it to give nitric acid.

**Temperature Behavior.**—The influence of temperature on the reaction rate is indicated by the data given in Table II. The rate is somewhat more than ten times as fast at 25° as it is at 0°, indicating that a 10° rise in temperature almost triples the rate. This temperature coefficient corresponds to an energy of activation of the order of 15,700 calories per mole. In view of the apparent complexity of the reaction, however, the calculated activation energy is of questionable significance.

**The Nitrogen Pentoxide Concentration Effect.**—Data such as given in Table III indicate

(11) Smith, THIS JOURNAL, 69, 1741 (1947).

that the rate of the reaction



is at least an approximate first order function of the concentration of nitrogen pentoxide. On the basis of the general rate expression

$$-d[\text{N}_2\text{O}_5]/dt = k[\text{N}_2\text{O}_5]^2[\text{NO}]^v$$

if the [NO] is kept constant the rate should be proportional to the [N<sub>2</sub>O<sub>5</sub>], assuming that the reaction is first order with respect to the nitrogen pentoxide. The data given in Table III were taken at a temperature of 0°, and with the [NO] held essentially constant. The rate values were determined by taking the slopes of curves obtained by plotting [N<sub>2</sub>O<sub>5</sub>] against time. Slopes were taken near the start of the reaction in each case.

TABLE III

THE INFLUENCE OF [N<sub>2</sub>O<sub>5</sub>] ON REACTION RATE (AT 0°)

[N <sub>2</sub> O <sub>5</sub> ], (moles/liter × 10 <sup>3</sup> )	$-\frac{d[\text{N}_2\text{O}_5]}{dt}$ , (moles/liter, sec. <sup>-1</sup> × 10 <sup>3</sup> )	$-\frac{d[\text{N}_2\text{O}_5]}{dt} / [\text{N}_2\text{O}_5]$ , (sec. <sup>-1</sup> × 10 <sup>3</sup> )
9.0	4.7	5.2
11.0	7.8	7.1
24.2	17.2	7.1
43.4	28.8	6.7
48.4	47.3	9.8
		Av. 7.2

A trend which is apparently real was noted, with higher rate values at high concentrations of nitrogen pentoxide. This indicates that the reaction, even though near first order with respect to nitrogen pentoxide, may be a complex process with an apparent "order" somewhat higher than first.

Further indication of the approximate first order behavior of the reaction with respect to nitrogen pentoxide is found in the fact<sup>10</sup> that plots of the log [N<sub>2</sub>O<sub>5</sub>] against time give fairly straight lines.<sup>12</sup> Representative behavior is shown in Fig. 2 which gives plots of average values for a number of runs at three temperatures.

The empirical rate constants are obtained by multiplying the slopes of such lines by -2.303. Good agreement is noted between the constants obtained in this way for individual runs (Table II) and those found from the slopes of the rate plots (Table III).

While the first portions of such plots are nearly straight lines, definite deviation is noted as the reaction nears completion, where the rate is obviously less than would be expected, assuming simple first order behavior. Some deviation in this region may quite likely be due to experimental errors, particularly in the determination of the initial concentrations of reactants and in cali-

(12) This would be expected, provided the reaction is first order with respect to nitrogen pentoxide, if the [NO]<sup>v</sup> term is kept constant. That this is conveniently possible, in effect, will be shown by results to be presented in later sections of the paper.

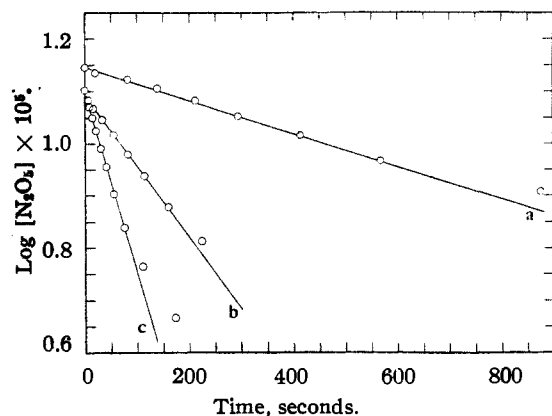


Fig. 2.—Log  $[N_2O_5]$ –time relationship at three temperatures: (a)  $0^\circ$  (av. of 3 runs); (b)  $15^\circ$  (av. of 5 runs); (c)  $25^\circ$  (av. of 9 runs). From results obtained in a 216 ml. (56.9 cm.) cylindrical tube. The nitric oxide concentration factor was essentially constant.

bration. Good accuracy was not attained in the measurement of high concentrations of nitrogen dioxide.

In view of other characteristics of the reaction, however, the deviation may well be taken as real, and considered as further evidence for complexity of the reaction. A similar trend is found in rate values obtained from the slopes of plots of concentration against time. Higher ratios of slope to concentration are found near the start of the reaction than toward completion. These results confirm the trend previously noted in the data of Table III. Also the method of Guggenheim<sup>13</sup> gives substantially higher “ $k$ ” values than those given in Table II.

**The Nitric Oxide Concentration Effect.**—In contrast to the near first order behavior with respect to nitrogen pentoxide, the rate is almost independent of the concentration of nitric oxide. This is shown by data such as given in Table IV which were obtained at  $25^\circ$  at constant nitrogen pentoxide concentration ( $10.8 \times 10^{-5}$  moles/liter), and at various concentrations of nitric oxide. The rate values are given as the slopes of curves obtained by plotting the  $[NO_2]$  against time.

It is apparent from these and similar data that the reaction rate is only slightly influenced by the  $[NO]$ . This is shown further, when the data are plotted as in Fig. 3.

That the nitric oxide is used up in the reaction—and thus is not simply acting as a catalyst—is clearly shown by the fact that the reaction stops when the nitric oxide is all consumed. This is shown very strikingly in the upper two plots of Fig. 3, where a limited amount of nitric oxide is

(13) Guggenheim, *Phil. Mag.*, Series 7, 2, 538–543 (1926).

TABLE IV  
THE INFLUENCE OF  $[NO]$  ON REACTION RATE (AT  $25^\circ$ )

$[NO]$ , (moles/liter $\times 10^5$ )	$d[NO_2]/dt$ , moles/liter, sec. <sup>-1</sup> $\times 10^5$
0.7	0.22
3.1	.26
5.6	.27
(Approx.) 22.0	.29
111.0	.48

present. The reaction begins at a fairly rapid rate, which is only slightly dependent upon the amount of nitric oxide present, but stops quite abruptly at the point where all of the nitric oxide is used up. In the absence of nitric oxide, the nitrogen pentoxide decomposes at the very much slower rate characteristic of the thermal decomposition. This corresponds to the almost horizontal lines on the plot. After any given length of time, the addition of more nitric oxide results in a continuation of the nitric oxide–nitrogen pentoxide reaction at a rate expected with the amount of nitric oxide added.

It is obvious that if a rate expression such as

$$d[NO_2]/dt = k[N_2O_5]^x[NO]^y$$

is applicable,  $y$  must have a value considerably less than unity. Attempts to evaluate  $y$  indicate a value of approximately 0.1 at rather low nitric oxide pressures of a few millimeters. It was found, however, that the “order” with respect to nitric oxide ( $y$ ) is not constant, but it increases as the pressure of nitric oxide is increased. At extremely low nitric oxide pressures, of only a few tenths of a millimeter,  $y$  is almost zero, but it

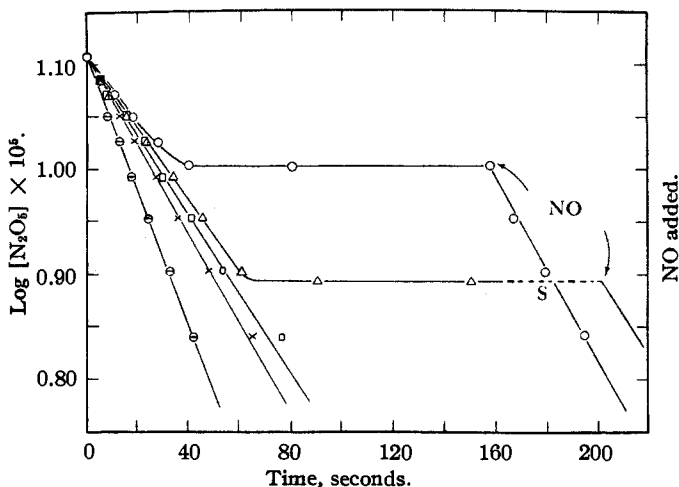


Fig. 3.—Log  $[N_2O_5]$ –time relationship at various concentrations of nitric oxide. Initial nitric oxide concentrations as follows (moles/liter  $\times 10^5$ ): O, 2.7;  $\Delta$ , 5.1;  $\square$ , 7.6;  $\times$ , (approx.) 24;  $\ominus$ , 113. The dashed line at S indicates the lapse of 500 seconds, at the end of which time  $12.4 \times 10^{-5}$  m./l. of nitric oxide was added.

(apparently) increases to a value of several tenths at the highest pressures used. It seems apparent that the simple rate expression is not

adequate to describe the behavior of the complex process.<sup>14</sup>

### Discussion of Results

While the reaction is catalyzed by moisture, especially in a new tube with a fresh surface, reproducible results of fair consistency have been obtained in carefully dried, "aged" or paraffined tubes. The temperature behavior appears to be quite normal. The near first order behavior with respect to nitrogen pentoxide is not unexpected, and it seems possible that the apparent deviation from first order may be due to catalytic influences such as rather minor moisture or surface effects or simultaneous side reactions, as well as in part to experimental errors.

The behavior with respect to nitric oxide is quite unusual, and is a clear indication that the reaction is complex. That nitric oxide is consumed by the reaction is definitely established, but the rate appears to be almost independent of the concentration of nitric oxide, at least at low pressures. To account for this, the possibility of a surface reaction cannot be ignored. It is conceivable that a very low pressure of nitric oxide may suffice to "saturate" the surfaces with this gas. Removal of nitric oxide molecules from the surface by chemical reaction may then not significantly decrease the amount adsorbed, since the nitric oxide which reacts and leaves the surface is at once replaced from the gas phase. Such a mechanism may then account for the apparent near "zero order" behavior observed.

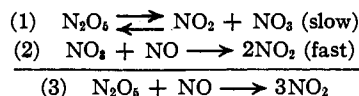
There are several objections to such a mechanism. The good agreement of the results in the spherical vessel with those in the cylinders (Table II) indicate that surface effects are not prominent at least in the "aged" or paraffined tubes which are carefully dried. There is little evidence to show that the reaction is subject to surface influences under conditions where the unusual nitric oxide behavior is observed. Furthermore, the apparent order with respect to nitric oxide seems to be nearest zero at the lowest pressures, contrary to what might be expected if adsorption and

(14) It is conceivable that the rate of nitrogen pentoxide-nitric oxide reaction may be even less dependent upon the concentration of nitric oxide than indicated by the data. The observed slight influence of nitric oxide on the rate may be largely due to rather minor side reactions, such as that between nitric oxide and oxygen, which may be taking place simultaneously. Traces of oxygen may be present from at least two sources: (1) leakage of air into the evacuated apparatus; and (2) the decomposition of nitrogen pentoxide during brief periods prior to the determinations. Since the nitric oxide-oxygen reaction is second order with respect to nitric oxide, the amount of nitrogen dioxide produced by this reaction would be relatively more significant at high than at low pressures of nitric oxide (at a constant nitrogen pentoxide concentration). Furthermore, if any moisture is present, the reaction between nitrogen pentoxide and nitric oxide becomes essentially that between nitric acid and nitric oxide, for which first order behavior with respect to nitric oxide, as well as pronounced surface effects, have been observed.<sup>11</sup> Any traces of moisture present, perhaps from the reaction of nitrogen pentoxide or nitrogen dioxide with the stopcock grease,<sup>15</sup> would consequently be expected to introduce more of a nitric oxide concentration effect than would otherwise have been observed.

(15) Brown and Crist, *J. Phys. Chem.*, **9**, 840 (1941).

a surface reaction are involved. The large temperature coefficient for the over-all reaction is an argument against a surface reaction. If the rate determining steps were the diffusion of nitrogen pentoxide to or from the walls, the temperature coefficient would be much smaller.

The results obtained require a mechanism which does not involve the nitric oxide in the rate determining step. On the assumption that the reaction is not a surface process, the nitrogen pentoxide and nitrogen dioxide (or traces of other substances possibly present) must be involved in some preliminary rate-determining step which does not include the nitric oxide. Such a mechanism as the following, which is only tentatively suggested, may conceivably account for the facts observed



If the rate of reaction (1) is slow enough compared to (2), which may be very rapid since  $\text{NO}_3$  is doubtless a very strong oxidizing agent, then the process may be quite independent of the nitric oxide concentration, as observed. Reaction (1) is likely reversible<sup>16</sup> and the reaction rate should then depend upon the concentration of nitrogen dioxide. The observed decreases in the rate as the reaction proceeds (with the production of nitrogen dioxide) may lend support to this mechanism. On the other hand, limited direct data indicate that the presence of nitrogen dioxide does not retard the reaction. If this is so, it constitutes a serious objection to the above mechanism.

Though  $\text{NO}_3$  is generally unfamiliar, absorption bands attributed to it have been observed by a number of investigators<sup>16,17,18</sup> particularly in mixtures of ozone with nitrogen oxides. Unsuccessful attempts to find these absorption bands in mixtures of nitric oxide and nitrogen pentoxide were made in this investigation, using a Steinheil three prism spectrograph. The  $\text{NO}_3$  bands were observed in mixtures of nitrogen pentoxide with ozone. The failure to find the absorption bands attributed to  $\text{NO}_3$  does not rule out the possibility that it may be present at very low concentration. Certainly one would not expect to find a high concentration of a strong oxidizing agent such as  $\text{NO}_3$  in the presence of the easily oxidizable nitric oxide, particularly if the  $\text{NO}_3 + \text{NO}$  reaction is very rapid.

### Summary

1. A photo-colorimetric apparatus for measuring the rate of the very rapid gas phase reaction between nitrogen pentoxide and nitric oxide (or other similar reactions) is described.

2. Measurements have been made on the rate of the nitrogen pentoxide-nitric oxide reaction at

(16) Schumacher and Sprenger, *Z. physik. Chem.*, **136A**, 77 (1928); **23B**, 267 (1929).

(17) Warburg and Leithauser, *Ann. Physik*, **20**, 743 (1906); **23**, 209 (1907).

(18) Jones and Wulf, *J. Chem. Phys.*, **5**, 873 (1937).

0, 15 and 25°, and at pressures (of reactants) ranging from a few hundredths of a millimeter up to 20 millimeters. While the reaction was found to be strongly catalyzed by traces of water vapor, especially in a new tube, fairly consistent and reproducible results have been obtained in tubes thoroughly baked out and evacuated or in tubes coated with paraffin. Indication that the reaction under these conditions is essentially homogenous is found in the close agreement of measurements taken in tubes of various shapes and of widely different surface-volume ratios (6:1).

3. The reaction proceeds at a conveniently followed rate, with a "half-life" of the order of ten to fifteen minutes at 0°. The temperature dependence is quite normal; a 10° rise in temperature almost triples the reaction rate. An energy of activation of the order of 15,700 cal. per mole is indicated.

4. The rate shows an approximate first-order

dependence upon the nitrogen pentoxide concentration. The behavior of the reaction with respect to the concentration of nitric oxide is quite unusual. At low pressures the rate is almost independent of the nitric oxide concentration, even though the nitric oxide is used up in the reaction. The apparent "order" with respect to nitric oxide is approximately 0.1 at low pressures. The rate equation,  $-d[N_2O_5]/dt = k[N_2O_5]$ , approximately fits the experimental observations, if  $k$  values of the order of  $8 \times 10^{-3}$  and  $7 \times 10^{-4}$  are used at 25 and 0°, respectively. Distinct trends in such  $k$  values are noted, but it is believed that available experimental data are not sufficiently complete or accurate to justify the selection of a more elaborate rate equation.

5. The unique behavior of the reaction is discussed, and the evidences for the complexity of the reaction are pointed out.

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## A Rate Study of the Oxidation of Nitric Oxide with Nitric Acid Vapor

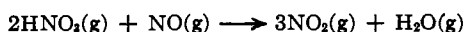
BY J. HAROLD SMITH<sup>1</sup>

The reaction  $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$  has been the subject of considerable investigation, primarily because of its importance in the nitric acid industry. Many investigators<sup>2-7</sup> have studied the equilibrium involved, but little has been accomplished with regard to rate determinations either for the forward or reverse reactions. This is particularly true of the gas phase reaction, for which no rate studies have been reported.

This paper presents the results of some preliminary measurements on the rate of the reaction between nitric acid vapor and nitric oxide, which is the reverse of the above reaction.

### Experimental

**Apparatus.**—Since the nitrogen dioxide produced by the reaction



is the only colored substance involved, the progress of the reaction is easily followed by the photo-colorimetric method and procedure previously described.<sup>8,9</sup>

The relatively large amount of nitrogen dioxide produced by the reaction makes this method particularly advantageous. Rate measurements were made in two vessels with widely different size and shape. One reaction vessel was a cylindrical tube of capacity approximately 250 ml. (diam. 2.5 cm.; length 56.9 cm.), and the other a

3,160 ml. sphere. Each vessel was equipped with side tubes, connected with large bore (4 mm.) stopcocks, to facilitate the rapid admission of the desired amounts of the reactants. A good grade of paraffin stopcock grease was used to prevent leakage into the evacuated system. Some objectionable reaction of the grease with the corrosive gases was noted, but in general the gas pressures were low enough and the time of exposure so short that the amount of reaction was small.

The nitric oxide was generated and purified in the manner described by Johnston and Giauque.<sup>10</sup> Nitric acid (100%) was prepared from dried, C. P. potassium nitrate and concentrated C. P. sulfuric acid as described by Forsythe and Giauque.<sup>7</sup> With vacuum distillation of the nitric acid at low temperatures, decomposition was effectively avoided and the liquid had only a very light yellow color. This nitric acid was frozen in a trap which was attached through a tube and a double stopcock arrangement to the reaction vessel. Maintained at solid carbon dioxide-acetone temperatures, the nitric acid could be kept for long periods without appreciable decomposition.

The desired amount of nitric acid vapor was admitted to the reaction vessel by proper adjustment of the temperature of the liquid in order to control its vapor pressure. The vapor pressure-temperature data for nitric acid from the older literature,<sup>11,12</sup> have been questioned recently and redetermined.<sup>13,14,15</sup> The results of the recent determinations are considerably higher than those given in the "Critical Tables," but they are in good agreement, and were used in the calculation of the nitric acid concentrations.

**Method.**—Due to the rapid rate of the reaction, rather low pressures (of the order of a few millimeters) of nitric oxide and nitric acid were used. A known amount of one of the reactants (usually nitric acid) was admitted to the reaction vessel, and at the time for the start of a deter-

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