

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 8×10^{-3} and 7×10^{-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.

AMHERST, MASS.

RECEIVED JANUARY 16, 1947

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

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

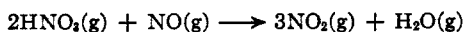
By J. HAROLD SMITH¹

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 investigators²⁻⁷ 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.^{8,9}

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.¹⁰ Nitric acid (100%) was prepared from dried, C. P. potassium nitrate and concentrated C. P. sulfuric acid as described by Forsythe and Giauque.⁷ 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,^{11,12} have been questioned recently and redetermined.^{13,14,15} 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-

(1) Present address: University of Massachusetts, Amherst, Mass.

(2) Burdick and Freed, *THIS JOURNAL*, **43**, 518 (1921).

(3) Lewis and Edgar, *ibid.*, **33**, 292 (1911).

(4) Chambers and Sherwood, *ibid.*, **59**, 316-319 (1937).

(5) Foerster and Kock, *Z. angew. Chem.*, **21**, 2161, 2209 (1908).

(6) Abel, Schmid and Stein, *Z. Elektrochem.*, **36**, 692 (1930).

(7) Forsythe and Giauque, *THIS JOURNAL*, **64**, 48 (1942).

(8) Smith and Daniels, *ibid.*, **69**, 1735 (1947).

(9) Smith, *ibid.*, **66**, 74-78 (1943).

(10) Johnston and Giauque, *ibid.*, **51**, 3194 (1929).

(11) Taylor, *Ind. Eng. Chem.*, **17**, 633 (1925).

(12) "International Critical Tables," Vol. III, 305 (1928).

(13) Wilson and Miles, *Trans. Faraday Soc.*, **36**, 356 (1940).

(14) Klemenc and Rupp, *Z. anorg. Chem.*, **194**, 59 (1930).

(15) Berl and Saenger, *Monatsh.*, **53-54**, 1042 (1929).

mination a measured quantity of the other reactant (*i. e.*, nitric oxide) was admitted from a side tube containing the gas at a relatively high pressure. The progress of the reaction was followed by the rate of appearance of the nitrogen dioxide, as detected by the calibrated photo-cell. The rates at any given time were conveniently determined from the slopes of the smooth plots of nitrogen dioxide concentration against time.

Results

Reversibility of the Reaction.—One of the first factors to be considered is the reversibility of the reaction



Certainly in water solutions equilibrium is established far from completion. The reverse reaction is of fundamental importance in the production of nitric acid. A number of papers^{2,4,6} have reported values for the equilibrium constant.

$$K = P_{\text{NO}} P_{\text{HNO}_3}^2 / P_{\text{NO}_2}^3 P_{\text{H}_2\text{O}}$$

Chambers and Sherwood⁴ report a value of $K = 0.017$ at 25° in good agreement with 0.019 as reported by Abel, Schmid and Stein⁶ for pressures expressed in atmospheres. Calculations using the average ($K = 0.018$) show that at initial pressures of 1 mm. of nitric oxide and 2 mm. of nitric acid the reaction between these substances proceeds 95% of the way toward completion at 25° .

At higher pressures the reaction is less complete, but even at initial pressures of nitric oxide and nitric acid of 5 and 10 mm., respectively, the reaction is 92% complete. Since the pressures used were generally less than this it is safe to assume that the reaction was at least 90% complete. Forsythe and Giauque⁷ have critically considered the experimental determinations and made a thermodynamic calculation of the equilibrium constant. They give a value of 0.0105 for K at 25° . This value for the constant would indicate an even more complete conversion of nitric oxide and nitric acid to nitrogen dioxide and water than has been suggested. The equilibrium is affected only slightly by changing the temperature.

The rate values were determined by taking the slopes of curves obtained by plotting $[\text{NO}_2]$

against time. The slopes were determined near the start of the reaction in each case. This procedure was used to mitigate the error introduced by the reversibility of the reaction for which no correction was made. In view of the near completeness of the reaction, under the conditions used, this error should be relatively small.

Surface Effects.—The rate of the nitric acid-nitric oxide reaction was found to be greatly influenced by the nature and extent of the surface of the reacting vessel. For example, the rate in the relatively small cylindrical tubes was greater than in the much larger spherical vessel with a lower surface-volume ratio (*i. e.*, approximately $1:6$). Furthermore, covering the surface of the sphere with a layer of paraffin decreased the rate tremendously. This retarding effect, due to the paraffined surface, was so pronounced that at 25° the reaction was so slow as to be almost undetectable. On the other hand, the presence of finely divided phosphorus pentoxide powder on the surface of the unparaffined three-liter sphere sharply increased the rate.

The observed catalytic influence of water vapor may be a further indication of surface effects. The accelerating affect of moisture was less pronounced and definite in the paraffined sphere or at high temperature (where absorption would be less) than in the containers of relatively large surface, particularly at low temperatures.

Temperature Behavior.—A pronounced temperature coefficient is found in the range from 0° to approximately 40° , as shown by the plot in Fig. 1. In the cylindrical tubes at higher temperatures the rate slowly increases with temperature, at least up to 90° . This slight increase at high temperatures was not observed in the sphere. A slight decrease in the rate was observed in the sphere as the temperature was raised from 30 to 90° . A very sharp decrease in rate was noted however, as the temperature was raised from 0 to 30° .

The apparent unusual influence of temperature on the rate may be nothing more than a surface phenomenon. A greater extent of adsorption at low than at high temperatures may perhaps explain the unusual behavior. On the other hand, some greater significance may possibly be attached to the temperature behavior, particularly in view of the apparent "third order" characteristics of the reaction, which will be discussed in the next sections. It is well known that several third order reactions (all of which involve nitric oxide) have low or negative temperature coefficients.¹⁶

The Order of the Reaction.—Attempts to determine the "order" of the reaction between nitric acid and nitric oxide confirmed that it is definitely complex. The rate of production of nitrogen dioxide is apparently influenced considerably by the water vapor and nitrogen dioxide

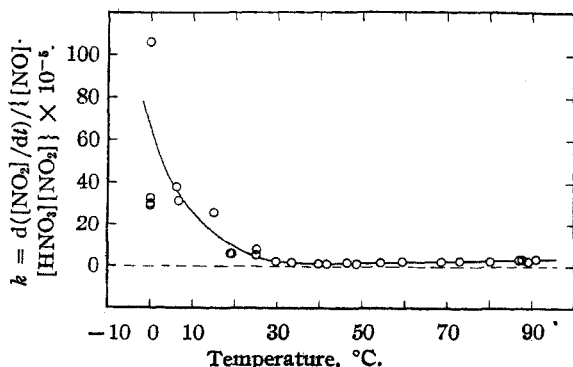


Fig. 1.—Influence of temperature on rate measurements made in a cylindrical tube. Concentrations of reactants and products constant.

(16) Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, England, 1940, Chapter VI.

present, as well as by the concentrations of nitric acid and nitric oxide. In the absence of water vapor or nitrogen dioxide, a distinct "time lag" was observed. During this initial period nitrogen dioxide and water vapor were produced only very slowly at first. The rate gradually increased, apparently because of the auto-catalytic effect due to the products formed, until a maximum rate was attained approximately one-fourth to one-third of the way toward completion of the reaction. Thereafter the rate decreased slowly as the concentrations of reactants diminished. It was observed, however, that the rate did not fall off as rapidly as might have been expected with the decrease in the concentration of the reactants, further indicating an auto-catalytic effect due to the products of the reaction (*i. e.*, nitrogen dioxide and water vapor).

The following results were obtained from measurements on the rate of production of nitrogen dioxide relatively near the start of the reaction (but usually after the initial "induction period"). Insofar as possible, an attempt was made to vary one at a time the concentrations of the various substances involved, with other factors constant, and determine the corresponding rate.

The Nitric Oxide Concentration Effect.—The initial rate observed as just indicated is directly proportional to the concentration of nitric oxide over the entire range studied (*i. e.*, from approximately 1 to 40 mm.). This first order behavior with respect to nitric oxide was found in both the cylindrical and the spherical reaction vessels. Sample data are given for the cylinder in Table I and the sphere in Table II.

TABLE I

THE INFLUENCE OF [NO] ON REACTION RATE
Cylindrical tube, at 25°; $[\text{HNO}_3] = 3.3 \times 10^{-5}$ mole/liter.

$[\text{NO}]$, (m./l. $\times 10^3$)	$d[\text{NO}_2]/dt$, (m./l. $\times 10^3$, sec. ⁻¹)	$d[\text{NO}_2]/dt/[\text{NO}]$, ($\times 10^3$)
7.16	0.0086	1.20
15.5	.0192	1.24
31.2	.0383	1.23

TABLE II

THE INFLUENCE OF [NO] ON REACTION RATE (SPHERICAL VESSEL, AT APPROXIMATELY 35°; $[\text{HNO}_3] = 21.5 \times 10^{-5}$ M./L.)

$[\text{NO}]$, (m./l. $\times 10^3$)	$d[\text{NO}_2]/dt$, (m./l. $\times 10^3$, sec. ⁻¹)	$d[\text{NO}_2]/dt/[\text{NO}]$, ($\times 10^3$)
19.5	0.017	0.87
103	.078	.76
205	.166	.81

The data obtained clearly indicate first order behavior with respect to nitric oxide.

The Nitric Acid Concentration Effect.—The reaction is apparently also first order with respect to nitric acid, as indicated by data such as that given in Table III. Calculations are made on the assumption that the rate is a first order function of the concentrations of both nitric acid and

nitric oxide, at constant nitrogen dioxide and water vapor concentrations. This restriction is necessary since it was observed that the amounts of nitrogen dioxide and water vapor present do influence the rate.

TABLE III

THE INFLUENCE OF $[\text{HNO}_3]$ ON REACTION RATE (CYLINDRICAL TUBE, AT 25°; FIRST ORDER BEHAVIOR WITH RESPECT TO NITRIC OXIDE IS ASSUMED; $[\text{NO}_2] = 6 \times 10^{-5}$ M./L.; $[\text{H}_2\text{O}] = 2 \times 10^{-5}$ M./L.)

$[\text{HNO}_3]$, (m./l. $\times 10^3$)	$[\text{NO}]$, (m./l. $\times 10^3$)	$d[\text{NO}_2]/dt$, (m./l. $\times 10^3$, sec. ⁻¹)	$d[\text{NO}_2]/dt$ [HNO_3][NO] ($\times 10^{-1}$)
2.7	6.8	0.0075	4.1
2.7	6.8	.0089	4.9
2.7	15.5	.0171	4.1
2.7	15.5	.0172	4.1
7.1	15.6	.055	5.0
7.6	15.8	.052	4.3
7.9	8.5	.024	3.6
13.0	16.1	.123	5.9
13.4	16.3	.129	5.9
13.8	7.9	.056	5.1
14.1	15.9	.135	6.0
20.3	16.8	.190	5.6
20.3	16.8	.200	5.9

Av. 4.96

The good agreement of the results over the wide range of nitric acid concentration indicates first order behavior with respect to this reactant even though a slight trend is noted. No trend is found when the results are calculated using the vapor pressure data for nitric acid from the "International Critical Tables."

The Influence of Nitrogen Dioxide.—The catalytic influence of nitrogen dioxide on the rate has been mentioned. It was found that when pure dry nitric acid vapor and nitric oxide were mixed there was a distinct "time lag" with an appreciable interval before the maximum rate was achieved. Typical behavior for the spherical vessel is shown in the lower plots (a, b, c and d) of Fig. 4. This "time lag" effect indicated that one or perhaps both of the products (nitrogen dioxide and water) catalyze the reaction. This was verified by permitting a portion of the products to remain in the reaction vessel from one determination to the next; such runs showed no "time lag" effect.

The immediate problem was then to determine whether the catalytic effect is due to nitrogen dioxide or water vapor (or both). This was answered by making measurements with various amounts of either nitrogen dioxide or water vapor present separately. A third side tube was connected to the three-liter sphere in order to facilitate the admission of nitrogen dioxide or water vapor. In a series of determinations the initial concentrations of nitric acid and nitric oxide were kept constant and only the nitrogen dioxide pressures were varied. Nitrogen dioxide present at the start in this way

was found to have a decided influence upon the initial rate. The effect of the presence of various amounts of nitrogen dioxide is clearly shown in the plots of Fig. 2. If the initial rates, as determined

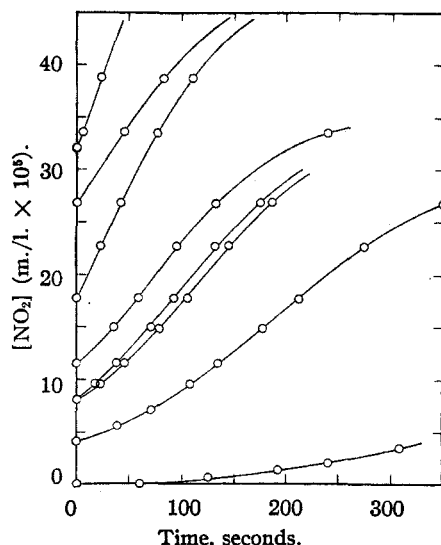


Fig. 2.—Influence of nitrogen dioxide on the rate in a 3-liter sphere at 30°. Initial concentrations of reactants constant: $[\text{HNO}_3] = 31.6 \times 10^{-6} \text{ m./l.}$, $[\text{NO}] = 21.3 \times 10^{-6} \text{ m./l.}$ Initial nitrogen dioxide concentrations as indicated on the ordinate.

from the slopes of the plots in Fig. 2 at zero time are plotted against the nitrogen dioxide concentrations, Fig. 3 is obtained. A rough proportionality between the initial rates and the nitrogen dioxide concentration is noted. Extension of the data to nitrogen dioxide pressures higher than $25\text{--}30 \times 10^{-6} \text{ m./l.}$ is difficult with the colorimetric technique, since the relatively small amounts of nitrogen dioxide produced by the reaction must be determined by difference and the errors are very large.

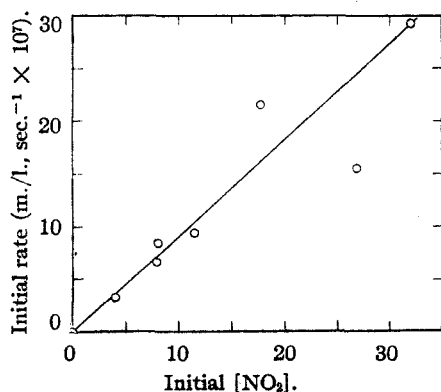


Fig. 3.—Plot showing approximate proportionality between rate and concentration of nitrogen dioxide. Initial rates were determined from the slopes of the plots in Fig. 2 at zero time.

The data indicate that the following rate equation might approximately describe the behavior noted

$$d[\text{NO}_2]/dt = k[\text{NO}][\text{HNO}_3][\text{NO}_2]$$

A check on the applicability of this rate equation is given in Tables IV and V. Values for the constant are calculated at several points in the course of single determinations, on the assumption that the equation applies. Data for a typical run in a spherical vessel are given in Table IV and similar data for a single run in a cylindrical tube in Table V.

TABLE IV

APPLICABILITY OF THE RATE EQUATION $d[\text{NO}_2]/dt = k[\text{NO}][\text{HNO}_3][\text{NO}_2]$ TO DATA OBTAINED IN A THREE-LITER SPHERICAL VESSEL (AT 26.5°)

Concentrations (m./l. $\times 10^6$)				$d[\text{NO}_2]/dt$ $\times 10^6$	k $\times 10^{-4}$
[NO]	[HNO ₃]	[NO ₂]	[H ₂ O]		
19.5	26.5	5	1.7	0.0467	1.80
17.9	23.2	10	3.3	.0728	1.75
14.5	16.5	20	6.7	.0813	1.70
11.2	9.8	30	10	.0298	0.97

TABLE V

APPLICABILITY OF THE RATE EQUATION $d[\text{NO}_2]/dt = k[\text{NO}][\text{HNO}_3][\text{NO}_2]$ TO DATA OBTAINED IN A 250-ML. CYLINDRICAL TUBE (AT 25°)

Concentrations (m./l. $\times 10^6$)				$d[\text{NO}_2]/dt$ $\times 10^6$	k $\times 10^{-4}$
[NO]	[HNO ₃]	[NO ₂]	[H ₂ O]		
7.7	13.8	5	1.7	0.0246	4.6
6.7	11.8	8	2.7	.0223	3.5
5.7	9.8	11	3.7	.0159	2.6
4.7	7.8	14	4.7	.0128	2.5

A trend toward lower k values is observed as the reaction proceeds toward completion. In view of some uncertainties involved, particularly regarding the exact values for the various concentrations and also because of the catalytic effects due to surface and moisture, however, it is believed that the agreement is reasonably good. For a process as complex as this obviously is, particularly because of surface and catalytic influence, the rate equation may have little fundamental significance. The third order rate equation given above at least approximates the behavior of the reaction, however, which is a further indication of near first order behavior with respect to nitrogen dioxide.

The Influence of Water Vapor.—The effect of the presence of water vapor on the rate was similarly investigated. Curves showing the influence of various concentrations of water vapor on the rate of production of nitrogen dioxide in the three-liter sphere are plotted in Fig. 4. Examination of Fig. 4 reveals a rather erratic accelerating influence due to water vapor, and the rate appears to be roughly proportional to the $[\text{H}_2\text{O}]$. The "time lag" is not eliminated, however, even though the rate is increased considerably.

There are reasons to believe that the accelerating influence of water vapor is largely catalytic and primarily a surface phenomenon. In the first

place, the influence of water vapor addition generally diminished with increasing temperature. A much more pronounced effect due to added water vapor was observed at 0°, than at higher temperatures. At the highest temperatures used (80–90°) the addition of water vapor was almost without effect on the rate. Furthermore, in a paraffined three-liter sphere even at 0° the presence of water vapor appeared to have very little accelerating influence. These observations indicate a definite connection between the surface and moisture effects.

It would be interesting to know the rate of the reaction in the absence of moisture. It seemed possible that the presence of a very powerful dehydrating agent might remove water vapor as it is produced, and thus keep the rate at a very low value, corresponding to that observed near the start of the reaction where the water vapor pressure is very low. In an attempt to accomplish this, finely powdered phosphorus pentoxide was spread in a rather thin film over most of the surface of the three-liter spherical flask, and rate measurements were attempted. A very rapid rate and generally erratic behavior were observed at both 0 and 30°. Apparently catalytic effects due to the extensive surface of the powder (or possibly intermediate reaction with it) complicate such measurements.

In view of the influence which water vapor has on the reaction rate, a question arises regarding the inclusion of a $[H_2O]$ factor in the rate equation. There is some indication of an approximate first order effect due to water vapor. It is obvious from a consideration of the data given in Tables IV and V, however, that a first order effect due to water vapor cannot be superimposed on the third order expression given. This would greatly increase the trend which was noted. Certainly one should not expect the order of the equation to be higher than third, and the third order equation seems to be reasonably satisfactory. It is realized, however, that substituting $[H_2O]$ for the $[NO_2]$ in the rate equation would simply multiply all of the constants by a factor of three and not change their relative values or the apparent fair agreement of the third order equation with the observed data. For reasons previously indicated, however, it appears the influence of water vapor may be largely a catalytic surface phenomenon, and thus the $[NO_2]$ is included in the rate expression in preference to the $[H_2O]$.¹⁷

Discussion

The reaction between nitric oxide and nitric acid is obviously complex in many ways. It is complicated by the pronounced and definite autocatalytic influence which nitrogen dioxide has on the rate. Catalytic effects due to surface and

(17) The experimental work was necessarily terminated at this point, and consequently no claim is made that this and several other points were exhaustively investigated, particularly in view of the complexity of the reaction.

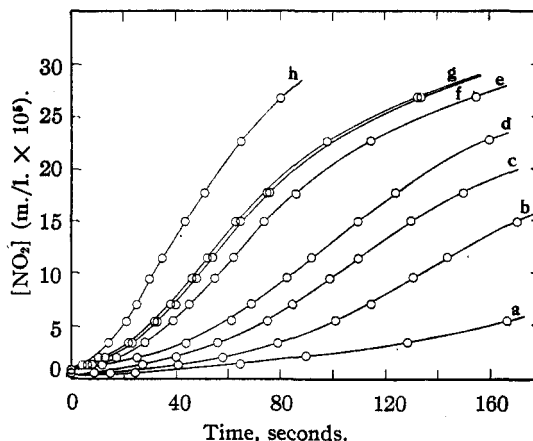


Fig. 4.—Influence of water vapor on the rate of production of nitrogen dioxide in a 3-liter sphere at 28.8°. Initial concentrations of reactants constant: $[HNO_3] \cong 31 \times 10^{-5}$ m./l., $[NO] = 21.3 \times 10^{-5}$ m./l. Initial water vapor concentrations as follows: a = 0; b and c = 3.3×10^{-5} m./l.; d and f = 6.6×10^{-5} m./l.; e and g = 10.0×10^{-5} m./l., h = 13.3×10^{-5} m./l.

moisture are very prominent. Furthermore, the influence of temperature on the rate is very unusual. All these factors combined cast some doubt on the fundamental significance of the results obtained and make any conclusions based upon them quite uncertain. It is possible, for example, that the temperature behavior, the moisture effects and the unusual order of the reaction may be due largely to surface phenomena. Nevertheless, some characteristics of the reaction are of interest even though suggestions regarding their significance are necessarily somewhat tentative.

The influence of nitrogen dioxide on the rate is interesting and perhaps significant. Somewhat similar effects due to nitrogen dioxide have previously been reported. It is known that "colorless nitric acid has either very little or no oxidizing effect on sulfur, metals, etc. If, however, a very little nitrogen dioxide is introduced, oxidation immediately occurs. The nitric acid is thereby reduced, still more nitrogen dioxide is formed, and the rate of oxidation increased with the rising concentration."¹⁸ Mellor¹⁹ indicates that the decomposition of nitric acid is catalyzed by the presence of nitrogen dioxide. "With the pure acid in darkness, there is an induction period occupying about a month, the reaction then proceeds slowly, and after many months, reaches a state of equilibrium."

For a similar reaction



(18) Ephraim, "Inorganic Chemistry," 3rd English ed., by Thorne and Ward, Nordeman Publishing Co., Inc., New York, N. Y., 1939, p. 684.

(19) Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, N. Y., 1922–1937, p. 583.

"nitrogen dioxide appears to be necessary to catalyze this reaction. In the absence of nitrogen dioxide fumes, the reaction may be delayed and then proceed so rapidly as to be of explosive violence."²⁰

Lewis and Edgar²¹ early observed in studying the $\text{HNO}_3 + \text{NO}$ reaction in aqueous solution that "it is remarkable that the reaction does not reach its maximum rate until after a lapse of several hours. It is hardly likely that this can be due to slowness of saturation of the liquid with nitric oxide. It seems more probable that the reaction is in some way auto-catalytic."

It is evident from the references just cited and from the results of this investigation that the presence of nitrogen dioxide has a real influence on the rates of several reactions involving nitric acid. Why these reactions are so strongly influenced by nitrogen dioxide is not clear at this point. An explanation to account for this effect for the $\text{HNO}_3 + \text{NO}$ reaction may perhaps be found in a consideration of intermediates (such as N_2O_3 , $\text{HNO}_3 + \text{NO}_2$, HNO_2 , etc.), but the data at hand are insufficient to justify the selection of any particular mechanism. This is especially true in view of the pronounced catalytic effects due to surface and moisture and obvious complexity of the process.

In spite of the complexity of the reaction, several characteristics suggest that it is a third order process. The reasonably good agreement found between the rates observed and those calculated on the basis of the rate equation, $d[\text{NO}_2]/dt = k[\text{NO}][\text{HNO}_3][\text{NO}_2]$, has been discussed. First order behavior with respect to each reactant is clearly indicated. Furthermore, an approximate first order effect due to either nitrogen dioxide or water vapor is observed. This is assigned to nitrogen dioxide, since water vapor does not eliminate the "time lag" behavior as does nitrogen dioxide, and the influence due to water vapor is apparently directly connected with catalytic surface effects.

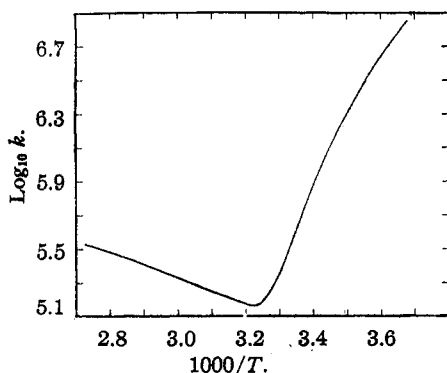


Fig. 5.—Plot of $\log_{10} k$ against reciprocal of absolute temperature. The values for the plot were taken from the curve on Fig. 1.

(20) Booth, *et al.*, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, Vol. I, p. 55.

(21) Lewis and Edgar, *THIS JOURNAL*, **33**, 292 (1911).

A "time lag" effect would of course be expected if the above rate equation is applicable. The rate should be slow near the start of the reaction, when the nitrogen dioxide concentration is low, but should increase as nitrogen dioxide is produced. The rate should obviously reach a maximum and then gradually decrease as the reactants are consumed. The point of maximum rate can easily be found by differentiating the rate equation and evaluating the concentrations when the first derivative is equated to zero. In this way it can be shown that the maximum rate should be attained when the reaction is just one-third of the way toward completion, provided the initial $[\text{HNO}_3]$ is double the initial $[\text{NO}]$. These deductions from the rate equation are at least in qualitative agreement with the observed data.

The apparent third order nature of the reaction is of interest, not only because termolecular gas phase reactions are rare, but particularly because of the first order behavior with respect to nitric oxide. While many of the known termolecular reactions involve this oxide, they are second order with respect to it.

In view of the third order characteristics of the reaction, the influence of temperature is of particular interest. Abnormal temperature behavior is not uncommon for the familiar termolecular gas phase reactions, and, at least for the reaction between nitric oxide and oxygen, a negative temperature coefficient is observed.²² Examination of Fig. 1 reveals that the temperature coefficient which is sharply negative at low temperatures becomes slightly positive (in the cylindrical tube) above 40°. If these data are plotted as a logarithm function of the rate against the reciprocal of the absolute temperature the curve shown in Fig. 5 is obtained.

It is interesting that this curve (Fig. 5) has the same general shape as a plot of collision frequency for an imperfect gas against the reciprocal of temperature, as calculated from theoretical considerations.²³ On the assumption that a termolecular reaction is involved, and that reaction occurs at a constant fraction of the triple collisions, the temperature behavior may constitute an experimental confirmation of the theory. In terms of the intermediate compound theory of termolecular reactions, in which the double molecule $(\text{NO})_2$ has been particularly prominent, intermediates such as $\text{HNO}_3 + \text{NO}$, $\text{HNO}_3 + \text{NO}_2$, $\text{NO} + \text{NO}_2$ (or N_2O_3) may be involved. In any event, a termolecular reaction which is not second order with respect to nitric oxide, and which therefore does not require triple collisions in which two molecules of nitric oxide are involved, is of interest. The present results may indicate that the double molecule intermediates, or at least colli-

(22) Bodenstein, *et al.*, *Z. Elektrochem.*, **24**, 183 (1918); *Z. physik. Chem.*, **100**, 87 (1922).

(23) Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1932, Chap. IV.

sions of some duration, may not be unique with nitric oxide. If the reaction proceeds by some mechanism involving such an intermediate as N_2O_3 (or N_2O_4) the negative temperature coefficient may be understandable due to the thermal instability of these compounds. Certainly little or no N_2O_3 exists in the gas phase at low pressures and high temperatures, but lowering the temperature would at least favor its formation.

If intermediate compound formation is involved in the reaction mechanism, low temperature would favor the formation of intermediates, and a very rapid rate may be expected. Certainly several of the gases (particularly HNO_3 , H_2O and NO_2) are easily condensed even at relatively low pressures at 0° . Intermolecular attractions to form intermediates involving these gases are also high at this temperature. A pronounced negative temperature coefficient might then be expected for this reaction, on the assumption that it is a termolecular process. The negative temperature coefficient is incredibly sharp below 20° , however, and it seems likely that other factors are involved.

In view of the complexity of the reaction, particularly the great effect of surface on the rate, the likelihood of alternative explanations of the temperature behavior cannot be ignored. If, as seems likely, the reaction as observed is largely a surface

phenomenon, the faster rate at low temperatures may perhaps be attributed simply to increased absorption. The extremely rapid, quite erratic, rate in the neighborhood of 0° indicates this. Certainly surface effects are involved in, and perhaps they are largely responsible for, the unusually large negative temperature coefficient in this region.

Summary

1. A preliminary study of the oxidation of nitric oxide with nitric acid vapor in the gas phase at low pressures is reported. Rate measurements show that the kinetics of the reaction are complex and that surface effects are very prominent.

2. The rate is influenced by the reaction products, and some termolecular characteristics are noted. The rate equation $d[NO_2]/dt = k[NO][HNO_3][NO_2]$ approximately fits the data. The high order reaction is further complicated by strong catalytic effects due to water vapor and surface.

3. A pronounced negative temperature coefficient in the range from 0 to 30° further suggests termolecular characteristics, although adsorption and surface effects may provide an alternative explanation.

AMHERST, MASS.

RECEIVED JANUARY 16, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL, AND THE MEDICAL CLINIC, PETER BENT BRIGHAM HOSPITAL]

Preparation and Properties of Serum and Plasma Proteins. XII. The Refractive Properties of the Proteins of Human Plasma and Certain Purified Fractions^{1,2}

BY S. H. ARMSTRONG, JR.,³ M. J. E. BUDKA, K. C. MORRISON AND M. HASSON

The refractive properties of proteins in solution are widely employed both in methods for rapid estimation of protein concentrations⁴ and in the optical systems introduced by the Scandinavian workers for analysis of concentration gradients at boundaries formed in solutions both of pure proteins and of mixtures separable by various types of force.⁵

The general assumption of identity of specific

(1) This work has been carried out in part under contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Harvard University.

(2) This is Number 59 in the series "Studies on Plasma Proteins" from Harvard Medical School, Boston, Massachusetts, on products developed by the Department of Physical Chemistry from blood collected by the American Red Cross.

(3) Welch Fellow in Internal Medicine of the National Research Council.

(4) Earlier literature on rapid protein determinations by refractometric methods, together with the presentation of new measurements on a variety of normal and pathological plasmas of varying protein content, has been recently summarized by F. W. Sunderman (*J. Biol. Chem.*, **153**, 139 (1944)).

(5) O. Lamm, *Nova Acta. Regiae Soc. Sci. Upsaliensis*, IV, 10, 6 (1937); A. Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937); T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford University Press, London, 1940.

refractive increments has been generally recognized as a first approximation,⁶ particularly in instances wherein components are associated with appreciable quantities of non-protein materials.⁷ The early literature yielded considerable discrepancies of the actual values of specific refractive increments for human plasma proteins (for example, 1.66×10^{-4} to 2.00×10^{-4} , in terms of grams per liter, for albumin).⁸

This study presents serial determinations of refractive index increments on pools of normal

(6) L. G. Longworth, *Chem. Rev.*, **30**, 323 (1942); V. P. Dole, *J. Clin. Investigation*, **23**, 705 (1944).

(7) L. G. Longworth, T. Shedlovsky and D. A. MacInnes, *J. Expt. Med.*, **70**, 399 (1939); L. G. Longworth and D. A. MacInnes, *ibid.*, **71**, 77 (1940); L. G. Longworth, R. M. Curtis and R. H. Pembroke, Jr., *J. Clin. Investigation*, **24**, 46 (1945).

(8) The values of the earlier literature have been well summarized, together with consideration of the possible bases for the discrepancies, in the papers of Adair and Robinson (G. S. Adair and M. E. Robinson, *Biochem. J.*, **24**, 993 (1930)) and Putzeys (M. P. Putzeys and Mile. J. Brosteaux, *Bull. Soc. chem. biol.*, **18**, 1681 (1936)). The values of these workers, together with the careful measurements of McFarlane (A. S. McFarlane, *Biochem. J.*, **29**, 407 (1935)), would appear to constitute the most reliable data on animal plasma proteins.