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Reactions in the System Containing Nitrogen Dioxide, Carbon Monoxide and Oxygen; NO3 as an Intermediate in the Classical Trimolecular Oxidation of Nitric Oxide

G. M. Calhoun and R. H. Crist

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throughout the oil, at the whole surface of the drop, or at one of the interfaces. The fact that the drop grows after the irradiation is discontinued, indicates that the oil-water interface is not the sole place for immediate action. It may be considered possible that activated water molecules contribute to the reaction, but that could hardly explain the delayed effect. More information could evidently be obtained by irradiating the oil before the drop was placed on the water. In the first experiment of this type oil was kept in the same type of containers as used before, namely large watch glasses. A large surface thus was exposed to air. After the irradiation a drop of the oil was placed on a water surface. Such a drop has at first about the same diameter as a drop from unirradiated oil. It spreads, however, rather rapidly and reaches a limiting size after several hours. The final size depends upon the amount of radiation given. It might be expected that the amount of oil surface exposed to the air during irradiation would make a large difference in the chemical change. However, Fig. 4 shows that with oil completely filling a closed container during irradiation with x-rays, this change took place. This does not exclude air from the reaction, as amounts absorbed on the container walls and in the oil may be sufficient for the reaction.

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Reactions in the System Containing Nitrogen Dioxide, Carbon Monoxide and Oxygen; NO_3 as an Intermediate in the Classical Trimolecular Oxidation of Nitric Oxide

G. M. CALHOUN AND R. H. CRIST
Department of Chemistry, Columbia University, New York City

The kinetics of some reactions in the system containing carbon monoxide, oxygen, and nitrogen dioxide have been studied over the temperature range from 658° to 800°K. It has been shown that the reaction is heterogeneous for the lower pressures of nitrogen dioxide and homogeneous for pressures above 10 mm. The homogeneous portion of the reaction appears to include the oxidation of nitric oxide and the oxidation of carbon monoxide by "oxides" of nitrogen. A bimolecular reaction involving nitric oxide and oxygen has been studied. Evidence is presented which indicates that the oxidation of nitric oxide involves two consecutive bimolecular reactions instead of the classical termolecular mechanism.

INTRODUCTION

THE effect of small amounts of nitrogen dioxide upon certain thermal oxidation reactions has been described by several investigators. The rate of the oxidation of hydrogen catalyzed by traces of nitrogen dioxide has been studied by Hinshelwood and co-workers.[1] Norrish[2] has shown that a photochemical reaction proceeds in hydrogen-oxygen mixtures containing nitrogen dioxide at temperatures which are far too low to permit a measurable thermal reaction.

Mixtures of carbon monoxide and oxygen exhibit definite explosion areas which are sharply defined by temperature and pressure of the gases. Semenoff[3] found that these explosive peninsulas could be extended a hundred degrees or more in the direction of lower temperatures if a small quantity of nitrogen dioxide was added to the mixture. This work was primarily concerned with the study of the effect of various inert gases, water vapor, etc. upon the explosion limits. No data relative to the rate of the nonexplosive catalyzed reaction were reported.

A study of the nitrogen dioxide catalyzed oxidation of carbon monoxide in the nonexplosive region has been made by Crist and Roehling.[4] They indicated that the catalytic effect of nitrogen dioxide was probably due to

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[1] (a) Gibson and Hinshelwood, Trans. Faraday Soc. **24**, 559 (1928); (b) Thompson and Hinshelwood, Proc. Roy. Soc. **124A**, 219 (1929).

[2] Norrish and Griffiths, Proc. Roy. Soc. **139A**, 147 (1933).

[3] Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935).

[4] Crist and Roehling, J. Am. Chem. Soc. **57**, 2196 (1935).

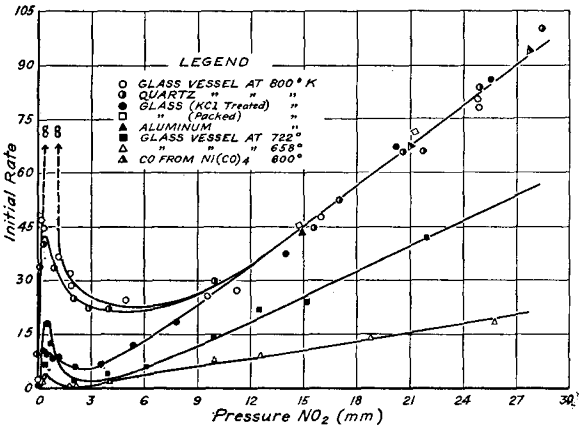

FIG. 1. The effect of surface on the catalyzed oxidation of carbon monoxide.

two processes, one of which was observed at low concentrations of the dioxide, while the other became important when the amount of the catalyst exceeded a certain value.

A preliminary investigation[5] has shown the catalyzed oxidation of carbon monoxide to be heterogeneous for small concentrations of nitrogen dioxide and essentially homogeneous for pressures of the catalyst above 10 mm. The first problem in the present work has been concerned with the measurement of the rate as a function of the surface and temperature over a wide range of catalyst concentration. Since the velocity of the heterogeneous reaction was greatly decreased in a vessel coated with potassium chloride, a separation of the two processes seemed likely, so that a study of the homogeneous catalysis was instituted. Rate measurements under different experimental conditions indicated two bimolecular reactions might be studied. It is with the determination of the rate constants and the temperature coefficients of these reactions that the major portion of this paper is concerned.

EXPERIMENTAL

The apparatus used in this investigation has been described.[4] The reaction vessel was placed in the well of a sulfur thermostat which was equipped with a barostat controlled by a vacuum tube relay.[6, 7] This device maintained the temperature constant to within ±0.3°C. Carbon monoxide and oxygen pressures were measured with mercury manometers and the nitrogen dioxide was measured by a Pirani-Hale type gauge. The progress of the reaction was followed by observing the decrease in pressure as denoted by a capillary mercury manometer.

Oxygen was admitted to the reaction vessel to the desired pressure, then the manometer was filled with oxygen or carbon monoxide to prevent nitrogen dioxide from coming in contact with the mercury surface during a run. Nitrogen dioxide was measured in the Pirani gauge, frozen into small U tube by means of liquid air, allowed to warm up and expand into the reaction vessel, and finally the last traces of the dioxide were carried into the reaction vessel by the carbon monoxide.

Carbon monoxide and nitrogen dioxide were prepared and purified by the methods described in a previous paper.[4] Nickel carbonyl was used as an independent source of carbon monoxide. The liquid carbonyl was taken from a commercial cylinder, fractionally distilled, then decomposed by passing the vapor through a furnace at 300–350°C. Great care was taken to remove traces of finely divided nickel and undecomposed nickel carbonyl. The purification train consisted of several liquid nitrogen traps and U tubes of activated charcoal cooled by liquid nitrogen. Oxygen was prepared by the electrolysis of a 15 percent potassium hydroxide solution using nickel electrodes. The gas was passed through a trap cooled by solid carbon dioxide into a furnace containing copper oxide at a dull red heat, then through a second dry-ice trap, and finally over phosphorous pentoxide.

RESULTS

The rate of oxidation of carbon monoxide in the presence of different quantities of nitrogen dioxide (0.1 to 30 mm) was observed for a variety of reaction vessels. The velocity of

TABLE I.

Standing Time for O_2 (min.)	0	1	5	10	15	45	100
ΔP (mm) 5→35 min.	48.0	45.8	41.8	36.4	34.8	28.8	26.0

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[5] Crist and Calhoun, J. Chem. Phys. 4, 696 (1936).

[6] Rittenberg and Urey, J. Am. Chem. Soc. 56, 1885 (1934).

[7] Coffin, J. Am. Chem. Soc. 55, 3646 (1933).

reaction for small nitrogen dioxide pressures is greatly affected by the surface, but with greater pressures the surface dependence is decreased, and finally disappears when the nitrogen dioxide exceeds 10 mm.

The heterogeneous reaction

In this study the carbon monoxide and oxygen were constant at 500 and 250 mm, respectively. A reaction vessel was selected and the relative rates were observed over the whole range of nitrogen dioxide pressures. In Fig. 1 the initial rate is shown as a function of nitrogen dioxide. The initial rates for the fast reactions were determined by drawing tangents to the rate curves at 1 min., and the relative rate was expressed for a ten minute interval. For the slow reactions, the pressure change from 5 to 15 min. was taken to represent the rates.

The reaction in glass at 800°K exhibits an explosive area between 0.3 and 1 mm of nitrogen dioxide. This region corresponds to the maximum rate in vessels which gave no explosions. The position of the maximum is practically the same as that found by Norrish[2] for the nitrogen dioxide sensitized hydrogen oxidation. The rate of the heterogeneous reaction was greatly decreased in a Pyrex vessel which had been treated with a potassium chloride solution. Results obtained in an aluminum vessel were very similar to those observed in quartz. Fig. 1 also includes runs in which carbon monoxide prepared from nickel carbonyl was used.

When quartz vessels were used, a slight modification in the experimental method was necessary, as it was found that the rate of the reaction depended on the length of time the oxygen was allowed to remain in contact with the quartz surface before introducing the other gases. A systematic study was made to determine this effect. The results are summarized in Table I. The rates in the second row are the pressure changes over a 30 minute time interval, and the other variable in this case is the standing time of oxygen in the quartz reaction vessel. The pressure of carbon monoxide and oxygen were constant at 500 and 250 mm, respectively, the nitrogen dioxide was 2.02 mm in all cases, and the temperature was 800°K. It can be seen that the effect is practically constant after 1 hr. and so, in rate measurements at low catalyst concentrations, the oxygen was always allowed to stand one hour before introducing the other gases. It must be pointed out that this phenomenon was *not* observed at *high* pressures of nitrogen dioxide, in fact the reaction in quartz at low pressures of the catalyst furnished the only example of this effect.

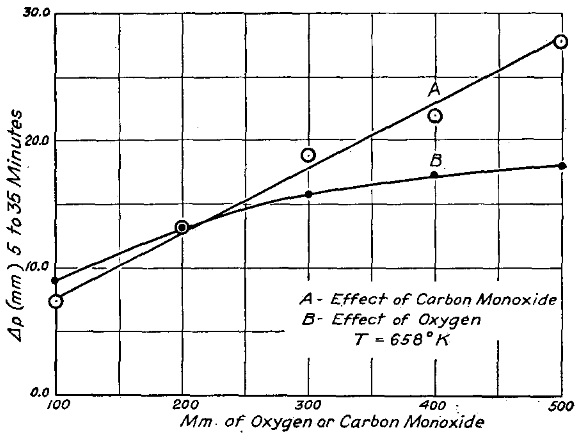

FIG. 2. The effect of carbon monoxide and oxygen on the homogeneous reaction.

The homogeneous reaction

A Pyrex reaction vessel, the surface of which was rinsed with a saturated solution of potassium chloride, was used in all measurements of the homogeneous reaction. In order to minimize any surface effect only the higher concentrations of the nitrogen dioxide were used.

A general study of the effect of the several components of the reacting system was made. The nitrogen dioxide was constant at 15.4 mm and the effect of the other gases was obtained by alternately keeping each constant while the other was varied. The results are shown in Fig. 2. The rate is expressed as the pressure change over a 30 min. time interval. This is a good measure of the rate because at this temperature (658°) the ration $\Delta P/\Delta t$ does not change appreciably during the interval selected. Fig. 2 shows that the rate is proportional to the first power of the carbon monoxide and to some lower power of the oxygen concentration.

Experiments with large excess of oxygen

Since no measurable homogeneous reaction between carbon monoxide and oxygen has been

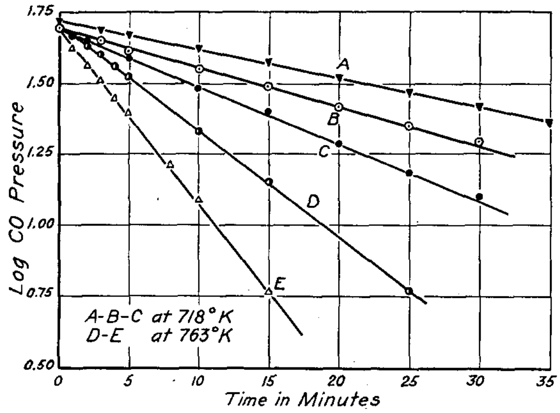

FIG. 3. Typical runs at high oxygen concentration: CO=50 mm; O_2=600 mm; NO_2=1.52, 2.30, 3.22, 1.67, 2.42×10^{-7} mole cc^{-1} for *A*, *B*, *C*, *D* and *E*, respectively.

observed, it is quite likely that the formation of carbon dioxide in the gas phase is dependent on the nitrogen dioxide. Hence the results relative to the effect of oxygen shown in the preceding section would be expected on the basis of the equilibrium relation between nitrogen dioxide and oxygen, namely,

$$[NO_2]=A[O_2]^{\frac{1}{2}}/(K^{\frac{1}{2}}+[O_2]^{\frac{1}{2}});$$
$$A=[NO]+[NO_2],$$

as the observed rate was proportional to (NO_2) calculated from this equation over the range of oxygen pressure used. Further, with a large excess of oxygen the equilibrium concentration of nitrogen dioxide will probably be maintained. If also the carbon monoxide is quite low in concentration, the amount of oxygen lost during reaction will not be great enough to change the equilibrium concentration of nitrogen dioxide appreciably. The conditions for this series of experiments were: oxygen 600 mm, carbon monoxide 50 mm, and nitrogen dioxide 10 to 30 mm.

Representative experiments are shown in Fig. 3. Since the nitrogen dioxide is constant during any particular run, it is apparent that the rate is first order with respect to carbon monoxide. The constants calculated for curves *B* and *D* are given in Table II. Assuming that the reaction is principally between carbon monoxide and nitrogen dioxide with the latter constant and given by the equilibrium expression,[8] the constant, k_3, in the equation

$$-d(CO)/dt=k_3(CO)(NO_2)$$

may be calculated. The summarized results are given in Table III. Column 1 gives the experimental constant k'' which has already been defined, column 2 the equilibrium concentration of nitrogen dioxide, and the last column gives the bimolecular constant k_3 which is of course $k''/(NO_2)$.

The temperature dependence of k_3 can be expressed by the Arrhenius equation, namely,

$$k=A\exp(-E/RT).$$

Fig. 4 shows log *k* plotted against $1/T$. The constants in the preceding equation may be evaluated from the data to give

$$k_3=1.3\times 10^{13}\exp(-32{,}200/RT).$$

The activation energy in this case is of the same order of magnitude as other homogeneous bimolecular reactions.[8]

Numerical errors in k_3 at 658° and 800° reported previously[5] have been corrected in Table III.

Experiments with low oxygen concentration

In preliminary experiments with the oxygen quite low, the slight temperature dependence

TABLE II. *Data for curves D and B of Fig. 3.*

763°K	$(NO_2)_{eq.}=1.67\times 10^{-7}$mole cc^{-1}	
t (min.)	Press. CO (mm)	$k''\times 10^3$ sec.$^{-1}$
1	46.7	
2	43.1	1.30
3	39.9	1.30
4	36.3	1.39
5	33.5	1.38
10	21.5	1.43
15	14.3	1.40
25	5.9	1.44
		Av.=1.38±.05
718°K	$(NO_2)_{eq.}=2.30\times 10^{-7}$mole cc^{-1}	
t (min.)	Press. CO (mm)	$k''\times 10^4$ sec.$^{-1}$
1	48.5	
3	44.5	5.17
5	41.3	5.65
10	35.3	5.40
15	30.9	5.10
20	26.1	5.23
25	22.5	5.16
30	19.7	5.02
35	17.3	4.95
40	14.5	5.05
		Av.=5.24±.17

The constant k'' is defined by the first-order equation $-d(CO)/dt=k''(CO)$.

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[8] Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, 1932).

suggested that a reaction, other than the bimolecular process already mentioned, was being measured. The experimental conditions for this study were: oxygen 20–25 mm, carbon monoxide 600 mm, and the nitric oxide 10–30 mm (measured as nitrogen dioxide but largely dissociated into nitric oxide and oxygen after introduction into the reaction vessel). The total oxygen present was obtained by adding to the original oxygen introduced that produced by the decomposition of nitrogen dioxide. These gases were allowed to come to equilibrium before introducing the carbon monoxide. At equilibrium the oxygen furnished by the dioxide may be obtained from the expression

$$(NO_2)=A(O_2)^{\frac{1}{2}}/(K^{\frac{1}{2}}+(O_2)^{\frac{1}{2}}),$$

where A is the original nitrogen dioxide and K is the equilibrium constant.

The effect of oxygen on the rate was found by the examination of individual runs where the pressure change is a direct measure of the oxygen lost. The results in Table IV represent typical runs and show that the rate is first order with respect to oxygen. These results indicate that the effect of nitric oxide is constant during an individual run. The effect of changing the original nitric oxide may be seen in Fig. 5 in which the first-order constants k' for the individual runs are plotted against the corresponding nitric oxide concentration for several temperatures, the data for each point being similar to that represented in Table IV.

TABLE III. *Summary of results for runs with high oxygen.*

658°K	Equil. conc. NO_2	
$k''\times10^5$ (sec.$^{-1}$)	mole/cc$\times10^7$	$k_3\times10^{-2}$ (cc mole^{-1} sec.$^{-1}$)
8.45	3.11	2.72
10.8	4.20	2.57
7.08	2.34	3.03
		Av. = 2.76 ± .17
718°		
52.4	2.30	22.8
81.4	3.22	25.3
43.8	1.85	23.7
63.0	2.66	23.7
35.4	1.52	23.2
		Av. = 23.8 ± .50
763°		
106	1.29	82.3
205	2.18	94.0
81.8	.956	85.5
138	1.67	83.0
244	2.66	91.9
224	2.42	92.5
		Av. = 88.0 ± 4.7
783°		
164	1.14	144
151	1.01	149
292	1.99	146
213	1.52	140
		Av. = 145 ± 3.0
800°		
262	1.20	218
274	1.20	228
120	.575	209
176	.860	205
310	1.42	218
		Av. = 216 ± 7.0

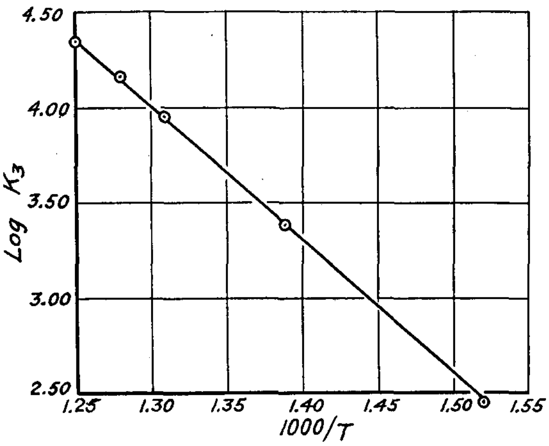

FIG. 4. Temperature dependence of k_3.

It is apparent that the effect is linear and can be expressed by

$$k'=k_1(NO).$$

Most of the runs indicated by Fig. 5 were with 600 mm of carbon monoxide. However, at 800° for (NO) = 37, 33 and at 658° for (NO) = 45, 29 the carbon monoxide was 250, 300, 235, and 300 mm, respectively. These points agree well with the values for the higher carbon monoxide pressures and show that the reaction is independent of this component. Therefore the rate equation expressing these results is

$$-d(O_2)/dt=k_1(NO)(O_2).$$

Table V gives the values of k_1 for the different temperatures as obtained from the slopes of the straight lines in Fig. 5.

The plot of $\log k_1$ against $1/T$ is shown in Fig. 6. The curvature can scarcely be attributed to experimental error and might then be considered as a variation of the activation energy with temperature.

TABLE IV. *Typical runs with low O_2.*

t (min.)	Press. O_2 (mm)	$k' \times 10^4$ (sec.$^{-1}$)
$T=658°K$	(NO) $=4.25\times10^{-7}$mole cc^{-1}	
0	22.9	3.06
5	21.0	3.10
10	19.2	3.15
15	17.4	3.16
20	16.0	3.05
25	14.4	3.20
30	13.3	3.18
35	11.8	2.66*
40	10.8	3.08
60	7.6	Av. $=3.12\pm.05$
$T=800°K$	(NO) $=5.50\times10^{-7}$mole cc^{-1}	
0	(25.0)	
5	20.3	6.90*
10	16.6	5.97
15	13.8	6.45
20	11.6	6.25
25	9.7	6.19
30	8.3	5.97
35	6.8	6.10
		Av. $=6.16\pm.14$

* Not included in average.

La Mer[9] has pointed out that there is no *a priori* reason for assuming the energy of activation to be independent of temperature. On integrating the Arrhenius equation, one ordinarily neglects the heat capacity of activation which, according to this author, has no more justification than the omission of the corresponding entropy terms in the calculation of a thermodynamic equilibrium. He suggests further, that since the temperature variation of activation energy is frequently within the limits of experimental error, it is usually detectable only in those measurements which carry high enough precision or in which the temperature interval can be made comparatively large. The activation energies obtained from the slopes of the curve in Fig. 6 are about 1000 and 5500 cal. for 680° and 780°, respectively. Assuming the foregoing interpretation to be applicable to the case at hand, the heat capacities of activation are calculated to be roughly 25 and 78 cal. per degree at 680° and 780°, respectively.

DISCUSSION OF RESULTS

The heterogeneous reaction

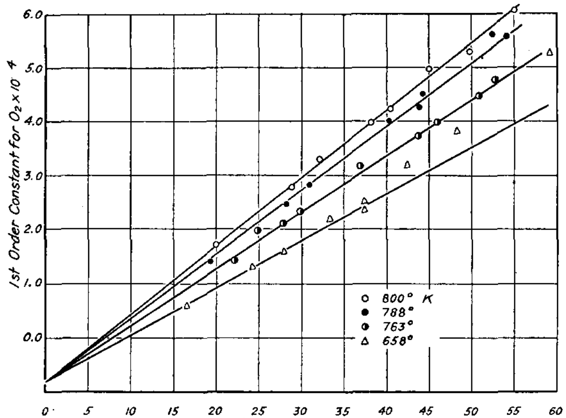

FIG. 5. The effect of nitric oxide at low oxygen concentrations.

The explosive character of the heterogeneous reaction for proper conditions of surface and nitrogen dioxide concentration indicates that chains are initiated at the walls and extend out into the gas phase in sufficient numbers so as to produce explosion.[10] When the nitrogen dioxide pressure is below that required for an explosion, the rate is proportional to the concentration of the catalyst, so that the initiation or the propagation of the chains or both are directly dependent on this component. That the initial process involves a selective adsorption on the surface is shown by the data giving the effect of allowing the various gases to stand in contact with the surface before introducing the other reactants. No effect was observed for carbon monoxide and nitrogen dioxide, but there is a considerable retarding effect for oxygen in quartz vessels as shown in Table I. The individual runs in quartz could not be subjected to a thorough analysis, but they showed the rate to be quite uniform throughout, i.e., there was no high initial rate as in Pyrex where the rate was quite rapid for the first few minutes and then dropped off abnormally. The oxygen appears to exert a "buffer" action upon the surface of quartz in that it permits only a limited number of chains to be initiated per unit time; on the other hand, oxygen covers less of the glass surface, hence the high initial or explosive rate. The data could be explained on the assumption that chains originate

TABLE V. k_1 *(cc mole^{-1} sec.$^{-1}$)*$\times 10^{-3}$.

T°K	800	788	763	658
k_1	1.28	1.20	1.07	0.865

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[9] La Mer, J. Chem. Phys. **1**, 289 (1933).

[10] Alyea, J. Am. Chem. Soc. **53**, 1324 (1931).

from nitric oxide or nitrogen dioxide adsorbed on the surface, and that the chain originator is displaced from the surface by oxygen molecules.

Norrish[2, 11] has pointed out that the close similarity in photochemical and thermal reactions in the system, hydrogen-oxygen-nitrogen dioxide suggests that chains may be initiated by oxygen atoms. Thus it is clear that in the photo process oxygen atoms may be produced by illumination

$$NO_2+h\nu\rightarrow NO+O$$

but a source of oxygen atoms in the thermal reactions is not quite so obvious. The following possibilities have been suggested

$$NO_2\rightarrow NO+O-72.6 \text{ kcal.},$$
$$NO+O_2\rightarrow NO_2+O-44 \text{ kcal.}$$

The chains might be propagated by ozone molecules as suggested by the work of Jackson.[12]

An empirical equation for the rate as a function of the pressure of nitrogen dioxide over the range of the heterogeneous reaction has been given by Crist and Roehling[4] and Norrish[11] namely,

$$y=ax/(x^2-bx+c),$$

where x is the nitrogen dioxide concentration and y is the rate. The shape of the curve can be accounted for if one assumes with Norrish that the rôle of nitrogen dioxide is threefold: (1) it originates chains by furnishing oxygen atoms, (2) it acts as an inhibitor breaking chains in the gas phase and on the walls, (3) as a branching factor.

The homogeneous reaction between carbon monoxide and nitrogen dioxide

In experiments for which the oxygen was quite high in concentration, it was assumed that the equilibrium amount of nitrogen dioxide was present during a run. It was also found that the rate depends on the oxygen as indicated in the nitric oxide-nitrogen dioxide equilibrium. The results obtained in the system with very low oxygen indicate that NO_3 is formed as an intermediate in the oxidation of nitric oxide. If such is the case, then there is the question as to whether the oxidation of carbon monoxide is by reaction with nitrogen dioxide, NO_3, or both. A bimolecular constant for the oxidation of carbon monoxide was calculated using the nitrogen dioxide concentration given by the equilibrium expression. Of course, if a large portion of the reaction occurs by way of NO_3, the numerical value of k_3 will be in doubt. The relationship of the rate with respect to oxygen suggests that the principal reaction under these conditions is that by way of nitrogen dioxide.

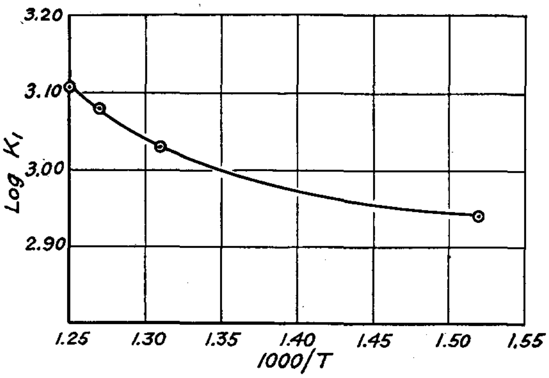

FIG. 6. Temperature dependence of k_1.

An alternative explanation may be advanced if one assumes that carbon monoxide reacts with NO_3 but not NO_2. If such is the case, the observed temperature dependence of k_3 (Table V) might be explained as being essentially due to the rapid decrease in the nitrogen dioxide concentration with temperature. Thus, as the concentration of nitric oxide increases and likewise the amount of NO_3, the rate increases. If the reaction of carbon monoxide and NO_3 is rate determining and has a small temperature coefficient, then the results in question might be accounted for on the basis of the temperature coefficient for the bimolecular decomposition of nitrogen dioxide (E_{ACT} about 30 kcal.). On the basis of the present data one cannot decide definitely which of the above interpretations is correct, but we are inclined to favor the first explanation.

Nitrogen oxide oxidation (low oxygen expt's.)

In a preliminary communication[5] we assumed that the oxidation of nitric oxide was a trimolecular process. Accordingly, a third-order rate constant involving the square of the nitric oxide and the first power of the oxygen con-

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[11] Foord and Norrish, Proc. Roy. Soc. **152A**, 196 (1935).
[12] Jackson, J. Am. Chem. Soc. **56**, 2631 (1934).

centration was calculated. It was suggested that the decrease in our constant at high nitric oxide concentration might be due to the reverse reaction. Subsequent data and a comparison of the relative rate of the reaction of the carbon monoxide with nitrogen dioxide and the bimolecular decomposition of nitrogen dioxide, have shown that the latter reaction could not account for the large discrepancy in the third-order constant.

Let us assume for the present that the following reactions comprise the homogeneous portion of the reaction

$$2NO+O_2\rightarrow 2NO_2, \quad (1)$$

$$2NO_2\rightarrow 2NO+O_2, \quad (2)$$

$$NO_2+CO\rightarrow CO_2+NO. \quad (3)$$

With small amounts of oxygen it was found that the rate was first order with respect to oxygen and nitric oxide and independent of the carbon monoxide. This would eliminate (3) as the rate determining step. It is evident that if the concentration of nitrogen dioxide is too small to influence the rate through (3) it would be much too small for (2) to be important. Hence (1) is left as the rate determining step and this requires the square of the nitric oxide rather than the first power as found in the experiments. Consider then the following reactions:

$$NO+O_2\rightarrow NO_3, \quad (4)$$

$$NO_3+CO\rightarrow NO_2+CO_2, \quad (5)$$

$$NO_2+CO\rightarrow NO+CO_2, \quad (3)$$

$$NO_3+NO\rightarrow 2NO_2, \quad (6)$$

$$2NO_2\rightarrow 2NO+O_2. \quad (2)$$

Nos. (3) and (5) are eliminated because the rate does not depend on carbon monoxide. (6) would show a tendency to change to second order with respect to nitric oxide which was not observed within the precision of the data except at the lowest temperature. This leaves (4) as the rate determining reaction.

It must be added that at the lowest temperature, reactions (2) and/or (6) are probably important, for the points (Fig. 5) deviate considerably from the straight line at high nitric oxide values. The uncertainty in the initial oxygen pressure might account for this deviation. In all these measurements the *total* oxygen was about 20–25 mm; the oxygen furnished by the decomposition of nitrogen dioxide was about $0.6\,A/2$ because the equilibrium concentration of the latter at 658°K for 20–25 mm oxygen is approximately $0.4\,A$, where A is the original nitrogen dioxide. For relatively small A values, the amount of oxygen furnished by the nitrogen dioxide is a smaller fraction of the total oxygen than the quantity contributed by the dioxide when the A value is large since in all cases the total oxygen was 20–25 mm. By comparison of the rates of disappearance of nitrogen dioxide by way of bimolecular decomposition and by reaction with carbon monoxide, it can be shown that the amount of dioxide lost by the former process is appreciable when A is large. This means that more oxygen is being furnished to the reaction mixture during the run, which of course affects the estimate of the original oxygen concentration.

A calculation for two A values gives an indication of the error in the estimation of the initial oxygen concentration. Using $A=3\times10^{-7}$ (equilibrium concentration) the loss of nitrogen dioxide per second by reactions (2) and (3) would be

$$\begin{aligned}-d(NO_2)/dt&=k_3(NO_2)(CO)\\&=2.70\times10^2\times3\times10^{-7}\\&\quad\times1.46\times10^{-5}=11.9\times10^{-10}, \quad (3)\\-d(NO_2)/dt&=k_2(NO_2)^2\\&=5\times10^3\times9\times10^{-14}\\&=4.5\times10^{-10}. \quad (2)\end{aligned}$$

Thus (2) represents 27 percent of the total loss of nitrogen dioxide in this case and a similar calculation using $A=1\times10^{-7}$ shows that (2) would account for only 11 percent of the total. From the consideration of the several rate equations it is possible to estimate the rate of change in nitrogen dioxide concentration with time. Then calculation shows that the estimates for the original oxygen concentration may be too small by approximately 10 percent in the case of the high nitric oxide values at 658°K. The points at the higher temperature are not likely to be much in error due to these competing reactions because the value of nitrogen dioxide at equilibrium is only $0.1A$ as compared to $0.4A$ at the lowest temperature.

Concluding Remarks

The rate of the nitric oxide oxidation has been measured by Bodenstein,[13] Briner, Pfeiffer and Malet,[14] and others. The third-order constants obtained by these investigators do not distinguish between a trimolecular process and two consecutive bimolecular reactions. Kassel[8] has estimated the number of trimolecular collisions in an imperfect gas and the results of his calculation show that the collision number is certainly large enough to account for the observed rate. Gershinowitz and Eyring[15] have obtained a theoretical expression for the rate of trimolecular reactions which involves a ratio of partition functions for the "activated" complex and the normal reactant molecules. Their calculated values for the oxidation of nitric oxide agree well with experiment. This theoretical treatment, like previous experimental work, cannot distinguish possible intermediate reactions which may lead finally to the formation of the activated state.

Recently, Rice[16] has suggested that the oxidation may occur in two steps

$$2NO \rightleftarrows (NO)_2, \tag{1}$$

$$(NO)_2 + O_2 \rightarrow 2NO_2. \tag{2}$$

If the equilibrium in (1) is maintained, the rate should be determined by (2) and the observed order of the reaction would be unchanged. The abnormal entropy of vaporization of liquid nitric oxide is taken as evidence for the existence of $(NO)_2$ in the gaseous phase. He estimates the heat of dissociation in the gas phase to be 2–3000 cal. and this could account for the negative temperature coefficient of (2) since the concentration of the associated complex should decrease with temperature. Trautz[17] suggested some years ago that the oxidation of nitric oxide might include the formation of a complex, NO_3, as an intermediate.

$$NO + O_2 \rightleftarrows NO_3, \tag{1a}$$

$$NO_3 + NO \rightarrow 2NO_2. \tag{2a}$$

This author's justification for the intermediate complex included the idea that the number of three-body collisions could not account for the observed rate. The data given in the present paper requires this intermediate on the grounds that the observed rate is dependent on the first power of the nitric oxide concentration. It is only necessary to postulate that the NO_3 is removed rapidly by the carbon monoxide, thus preventing its dissociation or reaction with nitric oxide.

The temperature coefficient of (1a) indicates a small positive activation energy, hence the rate of formation of NO_3 will not increase greatly with temperature, but the unimolecular decomposition of this complex might have a somewhat greater temperature dependence. If this is true, the concentration of the NO_3 will decrease with temperature and reaction (2a) should show a negative temperature coefficient. In the absence of carbon monoxide, the equilibrium in (1a) will be maintained and the rate determining reaction would be (2a) which involves the second power of the nitric oxide concentration. Thus, one can correlate the present work with that of Bodenstein and others.

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