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Kinetic Study of the Oxidation of Nitric Oxide with Oxygen in the Pressure Range 1 to 20 Mm.[1]

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The rate of the reaction $2NO + O_2 \rightarrow 2NO_2$ has been measured from 1 to 20 mm. at 0, 25 and 65° using the absorption of light by NO_2. The order with respect to nitric oxide is slightly greater than 2, and the order with respect to oxygen is 1 or slightly less. At higher pressures these orders tend to become 2 and 1. Inert gases, surfaces and temperature have but little influence on the rate. The specific rate is slower at the beginning of the reaction and is slightly decreased by NO_2 addition. A mechanism and a rate expression are proposed.

The reaction $2NO + O_2 \rightarrow 2NO_2$ has been generally accepted as a third-order gas phase reaction with a negative temperature coefficient, the rate constant being proportional to $T^{-3/2}$. It has been studied by many investigators.[3–5] The reaction is important industrially in the production of nitric acid, particularly in a new thermal process for the fixation of nitrogen.[6] The slowness of the reaction with 1 or 2% nitric oxide in air is an important economic handicap. Other reactions involving nitrogen oxides are proving to be more complicated than formerly realized, such as the N_2O_5 decomposition,[7,8] and the reaction of NO_2 with water.[9] Johnston[10] has pointed out the theoretically-possible intermediate reactions.

The purpose of this investigation was to explore the reaction $2NO + O_2 \rightarrow 2NO_2$ under special conditions to reveal any departure from third-order behavior and to contribute to a better understanding of the mechanism. The pressure range was 1 to 20 mm. Possible catalytic effects of surfaces and added gases were explored, but found to be of minor importance.

Experimental Procedure

The rate of the reaction was followed through absorption of light by nitrogen dioxide. The other gases present do not absorb light. A beam of white light, filtered to remove the photochemically-active violet light, was split with mirrors into three beams. One beam passed through a reaction chamber 120 cm. long and 14 cm. in diameter with a volume of 18.500 liters; the second passed through a reaction chamber of the same length, but 4 cm. in diameter with a larger ratio of surface walls to volume; the third beam, which passed through an empty tube, served as a check on the constancy of the light source every minute or so. Dental mirrors reflected the light from each of these tubes onto a photronic cell (manufactured by the Photo-volt Corporation) connected to a sensitive galvanometer. The galvanometer readings were converted directly into nitrogen dioxide pressure (including both NO_2 and N_2O_4 in equilibrium) by means of an empirically-determined calibration curve. Any abnormalities in the response of the photronic cell or deviations from Beer's law were not important because the light readings were calibrated directly against the $NO_2 \rightleftarrows N_2O_4$ equilibrium mixture at known total pressures in the same chamber in which the reaction was carried out. In these chambers, 4 ft. long, it is possible to measure a change of a few hundredths of a millimeter in the partial pressure of the NO_2. The large chamber was provided with plate-glass windows attached with cement.

The small chamber had sealed-in Pyrex windows, and it was connected through a glass circulating pump to a long parallel tube in which catalytic surfaces could be introduced. The reacting gases were circulated in this all-glass system, with double-acting, ground glass plungers and valves operated magnetically by iron bars enclosed in glass and surrounded by solenoids which were activated by interrupted current. The total volume of this system was 2.050 liters and the circulation rate was 70 ml. per second.

The reacting gases, nitric oxide and oxygen, were purified, stored over water, dried and introduced through stopcocks into reservoir bulbs of about 30- and 300-ml. capacity which were attached to the reaction chambers through stopcocks. The pressures of the gases were measured manometrically and the partial pressures which they produced in the reaction chamber were calculated from the measured pressure in the reservoir and the ratios of the carefully

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(1) More complete details of this work may be found in the Ph.D. thesis of John C. Treacy filed in the library of the University of Wisconsin in January, 1953.

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(3) (a) M. Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918); (b) R. L. Hasche, THIS JOURNAL, **48**, 2253 (1926); (c) F. B. Brown and R. H. Crist, *J. Chem. Phys.*, **9**, 840 (1941).

(4) J. H. Smith, THIS JOURNAL, **65**, 74 (1943).

(5) N. Gilbert and F. Daniels, *Ind. Eng. Chem.*, **40**, 1719 (1948).

(6) W. G. Hendrickson and F. Daniels, *ibid.*, **45**, 2613 (1953).

(7) R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337, 613 (1947); **18**, 770 (1950).

(8) A. R. Amell and F. Daniels, THIS JOURNAL, **74**, 629 (1952).

(9) J. K. Rieke, Master's Thesis, University of Wisconsin, 1952.

(10) H. S. Johnston, THIS JOURNAL, **73**, 4542 (1951).

measured reservoir volume to the total volume of the reservoir and reaction chamber. The apparatus was always evacuated to less than 0.05 mm. before introducing gases for an experiment. Leakage and chemical action of NO_2 on the silicone stopcock lubricant and large cemented windows were proved to be negligible by filling the vessels with NO_2 and NO at reduced pressure. The NO_2 concentration remained constant for several days.

The apparatus and reaction chambers were kept at 25 ± 0.50° by thermostating the room. In experiments at 0 and 65° the reaction chamber was a thermostated glass bulb into which the reactant gases expanded after the chamber was evacuated. After standing for the predetermined time, the mixture of gases was then allowed to expand further into the evacuated 4-foot chamber for the leisurely determination of the partial pressure of NO_2 by light absorption.

Experimental Data

Several thousand direct measurements of nitrogen dioxide concentration were made as a function of time, in many different mixtures of nitric oxide and oxygen at 0, 25 and 65°. The complete data are recorded in the thesis[11] and the significant relations are indicated in the graphs.

Typical data are plotted on a semi-logarithmic scale in Fig. 1 where the partial pressure of NO_2 is plotted against the logarithm of the time when the initial pressure of O_2 is 20, 15, 10 and 5 mm.

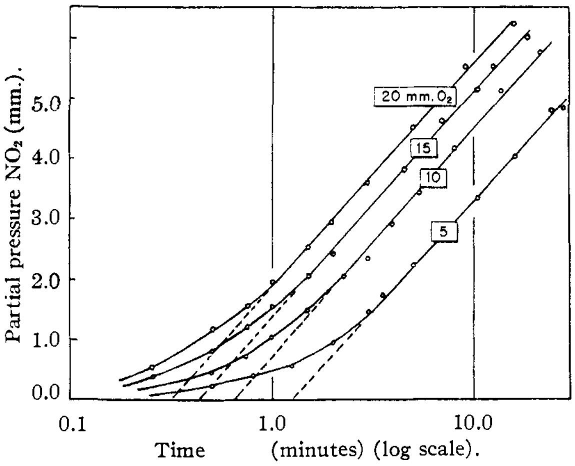

Fig. 1.—Partial pressures of NO_2 at various times after 7.5 mm. NO is mixed with the indicated pressure of O_2. These data are typical of those found in this work and indicate the simplification of calculation involved when logarithmic time plots were used; temperature 25°, no NO_2 initially introduced.

The slope of this line, $dp_{NO_2}/d \log t$, divided by 2.303 and by the time t, gives dp_{NO_2}/dt, at a specified time. This is the desired rate of reaction.

These semilog graphs can be divided into two parts, the latter of which is nearly straight. Anomalies in the reaction rate can be discerned better with this type of graph than with a graph plotted on cartesian coördinates or with data calculated from the integrated rate equation. The concentration of NO_2 was measured at a specified time, and the concentrations of the NO and O_2 calculated from this value and their original concentrations. The initial rate of reaction at time zero was determined from a graph on rectangular coördinates because the semilog graph is not suitable for this calculation.

Tables and graphs[11] similar to Fig. 1 were prepared for 15, 10, 7.5 and 5.0 mm. of NO and of O_2. A few measurements were made at still lower pressures. Additional experiments included a repetition of most of these mixtures with the addition of 2, 4 and 6 mm. NO_2 to the original O_2 and NO.

Tables were then prepared showing the rate of reaction dp_{NO_2}/dt as a function of the concentration of NO, of O_2, and of added NO_2. From these the "order" of each reactant in the reaction was obtained by plotting the rate of NO_2 production against the partial pressure of one reactant on log-log paper, holding the partial pressure of the other constant. The slope of these curves gives the exponent of the reactant, a or b, being varied in the over-all equation $dp_{NO_2}/dt = k(p_{NO})^a(p_{O_2})^b$.

Experimental Results

The apparent order for NO concentration in the rate expression was usually about 2.3, at these low pressures, as shown in Fig. 2, but tended toward the classical value of 2.0 at higher pressures or with higher concentrations of NO_2. The apparent order for oxygen concentration was 1.0 or slightly less. The data were complicated by an apparent increase in specific reaction rate when the reaction is about one-quarter completed.

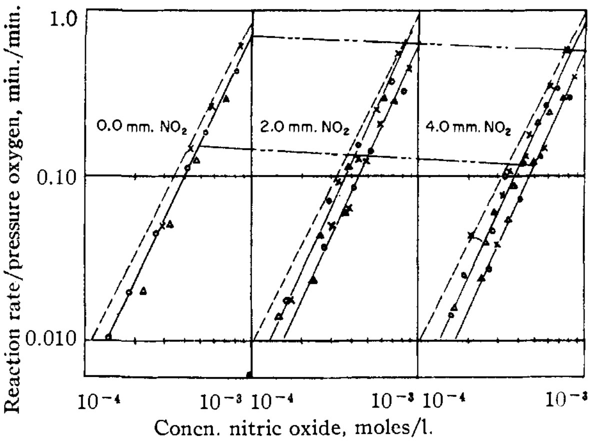

Fig. 2.—Effect of NO concentration, NO_2 partial pressure and temperature on reaction rate. Oxygen partial pressure between 6 and 8 mm. Tie lines indicate slight effect of NO_2 on initial rate. Dashed curves have slope two and are shown for reference purposes. x denotes 0°; O, 25°; Δ, 65°. Both axes are on a logarithmic scale. Lower curves on plots for two and four mm. NO_2, represent initial (time zero) data. Tie lines connect points where all other variables except NO_2 are constant.

Several possible causes of abnormal behavior were investigated. It was shown that surface catalysis is not a factor by the fact that the same results were obtained in vessels with different ratios of surface to volume in tubes of 4 and 14 cm. diameter. They were the same also when the reacting gases were circulated through an auxiliary chamber with glass beads or glass wool. Any deviations from Beer's law caused by irregularities in the photocell circuit would not be a cause of error because the empirically-determined calibration curve was obtained under the same conditions with the $NO_2 \rightleftarrows$

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(11) J. C. Treacy, Ph.D. thesis, University of Wisconsin, 1953.

N_2O_4 gases of measured pressure occupying the same reaction cell. Mixing of the gases was no cause of uncertainty as shown by the fact that forced circulation of the gases with the magnetically operated pump made no difference. Moreover, the same specific reaction rate was obtained in low pressure reactions where the first readable amounts of NO_2 were obtained after an hour, and in reactions at higher pressures where readings were taken after only a few seconds. The time of mixing, if it were appreciable, would affect the initial readings more in the fast, high pressure experiments than in the slow, low pressure experiments.

No detectable change in rate was observed when water vapor up to 0.5 mm. was added. Additions of carbon dioxide and nitrogen also had no effect on the rate. Pressures of water above 0.5 mm. accelerated the reaction. In the experiments without added water, the amount of water accidentally present would be less than 0.5 mm.

The addition of NO_2 at the beginning of the experiment along with NO_2 and O_2 decreased the rate slightly and above 6 mm. of NO_2 the reaction tended to approach the classical third-order behavior in which

$$\frac{\mathrm{d}C_{NO_2}}{\mathrm{d}t} = k(c_{NO})^{2.0}(c_{O_2})^{1.0}$$

The influence of temperature was slight, in agreement with all previous investigations of this reaction. Expressed in partial pressures, the rate constants at 0, 25 and 65° decreased slightly with increasing temperature, but expressed in moles per liter they were nearly the same. The temperature range of the measurements was too small to permit a numerical calculation of the very small temperature coefficient.

Discussion

The data fit the rate equations given here and the data of others are given for comparison.

$k = \mathrm{d}NO_2/\mathrm{d}t(NO)^2(O_2)$

x = extent of reaction, $(NO_2)/(NO)_0$

	10 mm. NO, $x > {}^1/_4$	1 mm. NO, $x > {}^1/_4$	10 mm. NO, $x < {}^1/_4$
Cc.^{2}/mole^2 sec.	1.3×10^{10}	0.8×10^{10}	0.75×10^{10}
Mm.^{2}/min.	2.3×10^{-3}	1.4×10^{-3}	1.3×10^{-3}
	Crist, Brown[3c]	Smith[4]	Bodenstein[3a]
Cc.^{2}/mole^2 sec.	1.5×10^{10}	1.2×10^{10}	1.4×10^{10}
Mm.^{2}/min.	2.6×10^{-3}	2.1×10^{-3}	2.5×10^{-3}

In this table, our values are computed according to the third-order law as are the other values, and the values at 10 mm. and at 1 mm. do not give the same value . . . $2.3/1.4 = 10^{0.22}$. Also "k" for the beginnings of the reaction is lower. Bodenstein's data constants are low also for the very start of the reaction.

The following mechanism is preferred over several others which were critically studied

$$NO + O_2 \rightleftarrows NO_3$$

$$\text{Equilibrium, } K_A = (NO_3)/(NO)(O_2) \quad (1)$$

$$NO_3 + NO \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO_3{\cdot}NO \quad (2)$$

$$NO_3{\cdot}NO + NO_2 \xrightarrow{k_3} 2NO + O_2 + NO_2 \quad (3)$$

$$NO_3 + NO_2 \leftrightarrows N_2O_5$$

$$\text{Equilibrium } K_B = (N_2O_5)/(NO_3)(NO_2) \quad (4)$$

$$NO_3 + NO \xrightarrow{k_5} 2NO_2 \quad (5)$$

$$NO_3{\cdot}NO + NO \xrightarrow{k_6} 2NO_2 + NO \quad (6)$$

NO, O_2 and NO_3 are assumed to be in rapid equilibrium. Several formulations with other intermediates led to final rate equations in which the order of the reaction with respect to NO was less rather than greater than 2.0. The postulation of a dimer of NO, (N_2O_2) which has been assumed by some other investigators, did not permit a set of equations which account for the experimental behavior. The "odd molecule" NO_3 seems to be more helpful in explaining the reaction mechanism. Moreover, the existence of (N_2O_2) has not been satisfactorily established in the gas phase whereas NO_3 has been identified spectroscopically[12] and has been accepted in the kinetics of the N_2O_5 reactions.[3,10]

This series of reactions essentially assumes that all the molecules with an odd number of electrons will interact with each other, including an association between NO_3 and NO, which may well be an isomer of the more common dimer of NO_2. It assumes further that NO_2 is produced from two simultaneous reactions involving reaction of NO with NO_3 and with $NO_3{\cdot}NO$.

N_2O_5 is assumed to be in equilibrium with the other oxides. NO_2 is presumed to have the effect of causing the $NO_3{\cdot}NO$ to react to form other species, thereby reducing the effective concentration of this material at high NO_2 partial pressure. This effect is needed to explain the slight decrease in rate with the addition of NO_2, and the classical third order behavior at higher pressures.

Assuming that the concentration of trace intermediates is substantially constant and that rate of change is zero, the following rate equations may be set up. The rate of N_2O_5 formation is neglected.

$$(NO_3{\cdot}NO) = k_1(NO_3)(NO)/(k_2 + k_3(NO_2) + k_6(NO))$$

$$\begin{aligned}\mathrm{d}(NO_2)/\mathrm{d}t &= k_5(NO_3)(NO) + k_6k_1(NO_3)(NO)^2/(k_2 + k_3(NO_2) + k_6(NO)) \\ &= k_5K_A(NO)^2(O_2) + k_6k_1K_A(NO)^3(O_2)/(k_2 + k_3(NO_2) + k_6(NO))\end{aligned}$$

$$(\mathrm{d}(NO_2)/\mathrm{d}t)/(NO)^2(O_2) = k = k_5K_A(1 + k_6k_1(NO)/k_5(k_2 + k_3(NO_2) + k_6(NO))$$

The last equation is in agreement with the "greater than second order" behavior of rate with NO if k_3 is small with respect to the other constants. At high partial pressures of NO_2 the last term drops out and the reaction becomes second order with respect to nitric oxide.

Reduction in NO_2 rate is due to the withdrawal of NO_2 by a reaction with the NO_3 to give N_2O_5. The rate effects in the production of initial amounts of $NO_3{\cdot}NO$, enable explanations of an anomalous increase in rate at one quarter completion of reaction and the order of less than unity in O_2 which was usually observed. Increased O_2 concentration also increases the amount of NO_3, and hence the amount of N_2O_5 formed, thus removing NO_2 from the system and causing a lower indicated NO_2 formation rate.

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(12) E. J. Jones and O. R. Wulf, *J. Chem. Phys.*, **5**, 873 (1937).

It is believed that this series of reactions, taken together, accounts for the kinetic behavior in the oxidation of nitric oxide by oxygen. The effect of nitrogen dioxide and the greater than second-order dependence of the nitric oxide concentration show that the reaction is complicated and that the classical, simple termolecular mechanism giving a true third-order reaction is an oversimplification—but a surprisingly good one at the higher pressures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Mechanism of the Permanganate–Oxalate Reaction

BY SEYMOUR J. ADLER[1] AND RICHARD M. NOYES

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Ultraviolet absorption spectra of the di- and trioxalate complexes of manganese(III) have been measured for the first time. Studies of the decomposition of these complexes confirm the observations of Taube in a different medium that a monoöxalate complex is kinetically important at low oxalate concentrations. Spectrophotometric and titrimetric studies of solutions containing both permanganate and manganese(III) demonstrate that there are no significant concentrations of the oxidation states +4, +5 and +6. These experiments also show that oxalate can replace manganous ion in providing three of the four electrons involved in reducing permanganate to manganese(III), but manganous ion is much preferred if it is available. Studies at low oxalate concentration support a previous proposal that permanganate itself usually reacts only with an oxalate complex of manganese(II), but the monoöxalate complex of manganese(III) may also be reactive. These observations permit the most detailed mechanism that has yet been proposed for the reduction of permanganate to manganese(III).

Introduction

The reaction between permanganate and oxalate ions has been a subject of kinetic study for almost ninety years, and two recent publications[2,3] have provided independent bibliographies of the extensive literature on the reaction. It has become clear that when manganous and oxalate ions are initially present in excess the reaction involves two processes

$$MnO_4^- + 4Mn^{++} + 5nC_2O_4^= + 8H^+ \longrightarrow 5Mn(C_2O_4)_n^{3-2n} + 4H_2O \quad (A)$$

$$2Mn(C_2O_4)_n^{3-2n} \longrightarrow 2Mn^{++} + (2n - 1)C_2O_4^= + 2CO_2 \quad (B)$$

where n may be 1, 2 or 3. These processes each take place in several steps, and detailed mechanisms are not clear. Also, these two processes are not sufficient to describe the reaction under all conditions. The results presented here supplement previous studies of this system and contribute to the elucidation of the detailed mechanism of the reaction. The data tend to support a partial mechanism proposed earlier,[4] and they permit even more detailed postulates about the nature of some of the individual steps.

Experimental

Reagents.—Solutions of potassium permanganate were prepared by customary procedures and standardized against sodium oxalate. Solutions of sodium oxalate were prepared fresh every two weeks; attempts to stabilize them by addition of acid led to formation of peroxide. Solutions of manganous perchlorate were standardized by precipitation as the ammonium phosphate and ignition to the pyrophosphate. The sodium perchlorate, used to maintain constant ionic strength of 1.00 *M*, was prepared from sodium carbonate and perchloric acid and was analyzed by evaporation. The reagents and analytical procedures are discussed with references in the original dissertation.[1]

General Procedure.—The reactions were started in glass-stoppered Erlenmeyer flasks fitted with a center well into which the permanganate was pipetted. The remaining solutions were pipetted into the outer portion of the flask, and the flask was swept with tank nitrogen while thermostated at 25.00 ± 0.01°. The reaction volume was always 100 ml.

The reaction was started by inverting and shaking the stoppered flask. At specified times, some reaction mixtures were compared with a Beckman Model DU spectrophotometer against blanks containing all the constituents except permanganate. A few supplementary observations were made with a Cary Recording Spectrophotometer, Model 11. The other solutions were titrated for oxidizing power by quenching with sodium iodide at appropriate times.

Titration Procedures.—The titrations were complicated because some solutions formed hydrogen peroxide in spite of efforts to flush out atmospheric oxygen. Two procedures were developed for including and excluding the oxidizing power of this peroxide.

Procedure α was designed to measure total oxidizing power of manganese and peroxide. The reaction mixture was quenched with a solution containing 25 ml. of 2.5 *M* sulfuric acid, 0.5 ml. of 3% ammonium molybdate (to catalyze reduction of peroxide), and 10 ml. of 10% sodium iodide. The quenched solution was allowed to stand for 10 minutes in the thermostat before it was diluted with 200 ml. of water and titrated with thiosulfate with starch as indicator. The procedure gave identical results against the original permanganate whether or not oxalate and manganous ion were present. Negligible blanks were obtained in solutions swept out with nitrogen but containing no added permanganate.

Procedure β was designed to measure oxidizing power due to manganese in states above +2 but not to measure hydrogen peroxide. The contents of the reaction flask were poured rapidly into 100 ml. of water containing 1 g. of sodium iodide and the liberated iodine was rapidly titrated with thiosulfate, the entire operation requiring less than a minute. In experiments containing a large excess of oxalate ion, it was necessary to add some acid to the quench in order to get sufficiently rapid reduction of the higher oxidation states of manganese. The initial titer of a sample of permanganate was a little lower by procedure β than by procedure α, but the difference was usually within 3%.

Results

Equilibria Involving Oxalate Complexes of Manganese(III).—Manganese(III) forms a yellow dioxalate complex,[5] $Mn(C_2O_4)_2^-$, and a red trioxalate

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[1] Based on a Dissertation submitted by Seymour J. Adler to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Persons desiring to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, New York.

[2] R. M. Noyes, *Trans. N. Y. Acad. Sci.*, **13**, 314 (1951).

[3] E. Abel, *Monatsh.*, **83**, 695 (1952).

[4] J. M. Malcolm and R. M. Noyes, THIS JOURNAL, **74**, 2769 (1952).

[5] The formulas do not include water that may also be bound in these complexes. Our data furnish no information on extent of hydration.