temperatures. Unfortunately this possibility was not tested by us in detail. However, some preliminary experiments at 40° (above the temperature of stability of the decahydrate) made by Mr. Robert L. Altman of these laboratories indicate that HCl will add to Na_2SO_4 in the presence of H_2O vapor at about 0.8 relative humidity.

The second possibility, namely, that water acts merely to enhance the surface concentration of sorbed HCl was tested by studying the interaction of HCl at high pressures and thus high relative partial pressures where we might expect to saturate the surface layers of the solid. The tubes used for these experiments were made of 2 mm. i.d. Pyrex capillary tubing bent into the shape of an S and mounted vertically. One end of the S was sealed off, the other open. Very fine (90 mesh) powders of anhydrous Na_2SO_4 were poured into the open end and "tapped" down into the sealed end. Sample sizes were about 150 mg. The capillaries were then sealed at the open, vertical end to a vacuum line and pumped for several hours at 150° in a block oven to less than 10^{-5} mm. pressure to ensure outgassing of sorbed water. The tube was then allowed to cool, some HCl gas was condensed in liquid N_2 in the U-shaped bend of the vertical S and the capillary slowly sealed off while pumping. The tubes were then permitted to warm to 20° where they were kept for several hours. The HCl was then recondensed into the U-bend and this section was sealed off from the dead end containing the Na_2SO_4 powder. Finally this latter section was opened and the powder analyzed for Cl and SO_4. The results of these experiments are shown in Table I.

TABLE I

REACTION OF HCl GAS + ANHYDROUS Na_2SO_4 AT 20°

Pressure of HCl (atm.)	Duration of run (hr.)	Cl, %	SO_4, %	Mole ratio Cl/SO_4
2–25	24	2.30	62.4	0.10
33–42	16	3.88	62.53	.17

As can be seen, there is an extremely slow reaction of HCl, the rate of which appears to increase with increasing partial pressure. It is not, of course, possible to say that there are no traces of water in these systems so that trace catalysis by H_2O is not excluded. However, these rates are at least 10^5 times slower than the rates with the decahydrate so that if there is a direct reaction of HCl gas with the anhydrous salt its rate must be very much slower than the rate of reaction with the decahydrate and the effect cannot be ascribed to low sorption concentration of HCl.[9]

We therefore conclude that the HCl either reacts directly with the decahydrate or else that sorbed H_2O is a true catalyst in the system. These two possibilities should be easily distinguishable experimentally and it appears that this system might then be a very useful one in which to explore quantitatively the heterogeneous catalysis by water.

[9] At the partial pressures used, one would estimate almost complete coverage of the surface.

LOS ANGELES, CAL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Kinetics of the Thermal Decomposition of Nitric Acid Vapor. III. Low Pressure Results

BY HAROLD S. JOHNSTON, LOUISE FOERING AND JAMES R. WHITE

RECEIVED FEBRUARY 14, 1955

The decomposition of nitric acid vapor has been studied at low pressures (0.5 to 20 mm.) in two Vycor bulbs at temperatures between 375 and 425° without and with the addition of argon, carbon dioxide, oxygen, water, nitrogen dioxide or nitric oxide. The broad important features of the mechanism are the same as found before $HNO_3 \underset{b}{\overset{a}{\rightleftarrows}} HO + NO_2$, $HO + HNO_3 \xrightarrow{c} H_2O + NO_3$, ($NO_2 + NO_3 = 2NO_2 + {}^1/_2O_2$ as with N_2O_5). However, an attempt to separate out the unimolecular decomposition, step a, at low pressures revealed the presence of a side reaction (or side reactions) involving water, nitrogen dioxide and nitric oxide. From known kinetic and thermodynamic data it is concluded that these effects might be due to nitrous acid acting as a reactive intermediate. However, the reaction is so complex under these conditions that the secondary processes could not be clearly separated, nor is the reaction a suitable one for unimolecular reaction rate studies.

Introduction

A preliminary study of the reaction

$$2HNO_3 = 2NO_2 + H_2O + {}^1/_2O_2 \qquad (1)$$

in the presence of nitrogen at one atm. total pressure gave first-order kinetics and indicated that an important step in the mechanism is[1]

$$HNO_3 \xrightarrow{a} HO + NO_2$$

Working at low pressures of reactants in the absence of foreign gases, Frejacques found reaction (1) to be second order.[2] An additional study, still at one atm. total pressure, showed inhibition of the first-order rate by nitrogen dioxide and results followed the further mechanism[3]

$$HO + NO_2 \xrightarrow{b} HNO_3$$

$$HO + HNO_3 \xrightarrow{c} H_2O + NO_3$$

$$(NO_3 + NO_2 \longrightarrow 2NO_2 + {}^1/_2O_2 \text{ as with } N_2O_5) \qquad (2)$$

$$(NO_3 + NO \longrightarrow 2NO_2, \text{ as with added NO}) \qquad (3)$$

Over a wide range of temperature, additives such as carbon monoxide, hydrogen, methane and benzene were oxidized at about the same rate as the rate of decomposition of nitric acid alone, which gave support to this mechanism since hydroxyl radicals would attack these molecules. This mechanism reconciled most of the disagreement between ref. 1 and ref. 2 upon the assumption that Frejacques was working close to the second-order region of the unimolecular decomposition a. However, the values of activation energy and the effects of nitric oxide were not completely reconciled.[4]

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(1) H. S. Johnston, L. Foering, Y. S. Tao and G. H. Messerly, THIS JOURNAL, **73**, 2319 (1951).

(2) C. Frejacques, *Compt. rend.*, **232**, 2206 (1951).

(3) H. S. Johnston, L. Foering and R. J. Thompson, *J. Phys. Chem.*, **57**, 390 (1953).

(4) C. Frejacques, Thesis, University of Paris, 1953.

The present study was carried out at very low pressures, both in order to resolve differences between the different investigations and in the hope of separating out the low pressure limit of the unimolecular decomposition, step a.

Experimental

Apparatus.—Two reaction bulbs were used, a 2-liter Vycor flask and a 14.5-liter Vycor flask. The 14.5-liter flask was enclosed in two hemispheres of silver, set inside a can fabricated of heavy 2 S alloy aluminum sheeting, and set inside a larger can of the same material. Heating wires were wrapped uniformly on all sides of the inner aluminum can. Voltage was regulated by a Stabiline Automatic Electromechanical Regulator (Superior Electric Co., Bristol, Conn.) and controlled by a Powerstat variable transformer. The space between the silver shell and the inner can was air filled, and the space on all sides between the inner can and outer can was filled with 6 inches of Santocel-A (Monsanto Chemical Co.) insulation. Light paths were provided through the flask to a photocell (RCA 1P28) mounted outside the furnace. The phototube connected electrically to an electronic voltmeter for slow rates or to an oscilloscope and camera for faster rates. A system of calibrated gas pipets led into the reaction bulb. Pressure inside the reaction bulb could be followed by a very sensitive bourdon gage, read with a microscope with a scale engraved in the eyepiece.

The 2-liter bulb was mounted somewhat similarly. The inner can was nickel-plated copper and the outer can was steel.

Halocarbon (polychlorotrifluorocarbon) stopcock grease was used.

Materials.—Nitric acid was prepared from sodium nitrate and sulfuric acid. Tank nitric oxide and nitrogen dioxide (Matheson Co.) were purified and fractionated. Argon, carbon dioxide and oxygen were obtained from commercial tanks and passed through or liquefied by liquid nitrogen. Distilled water was used as the source of water vapor.

Calibration.—Relative volumes of the pipets were obtained by expanding samples of dry air at known pressures into the various volumes, both at room temperature and at reaction temperature. Thermocouples, which were inserted at various points between the silver shell and the Vycor bulb, were calibrated at the freezing points of tin, lead and zinc. The colorimetric analysis for nitrogen dioxide, using either 436 mμ line of a mercury arc or a band 430–460 mμ from d.c. tungsten lamp, was calibrated by two methods. In one case a measured volume of nitrogen dioxide at room temperature was suddenly expanded into the furnace and the maximum optical density noted. By the other method a sample of nitrogen dioxide was admitted to the furnace and connected to the bourdon gage. The system was left until equilibrium was attained for the reaction

$$2NO_2 \equiv 2NO + O_2 \qquad (4)$$

and then optical density and total pressure were read. At low furnace temperatures (300°) the first method is better, the second method is the only one suitable at high temperatures (500°), but both methods were used at 400°, and they gave the same result.

Stoichiometry.—The observed data were appearance of nitrogen dioxide as a function of time, and most runs were allowed to go until nitrogen dioxide reached a maximum as reaction (4) became important. For nitric acid alone, or for nitric acid in the presence of argon, carbon dioxide, oxygen or water vapor, the final concentration of nitrogen dioxide was equal (±3%) to the initial concentration of nitric acid as computed from initial pressures and volumes. This observation is in agreement with the stoichiometry of equation 1. However, if one integrates the effect of equation 4 over the course of the reaction the final nitrogen dioxide should be substantially less than the observed amount. It appears, therefore, that the reaction follows the stoichiometry of (1) essentially to completion, and only then is reaction (4) allowed to proceed.

In the presence of excess nitric oxide the final concentration of nitrogen dioxide was 150% (±3%) that of the initial nitric acid (the statement of stoichiometry in ref. 3 is in error). The indicated stoichiometry is

$$2HNO_3 + NO = 3NO_2 + H_2O \qquad (5)$$

With excess nitric acid it appeared that essentially all of the nitric oxide disappeared according to (5), and the residual nitric acid disappeared according to (1).

For nitric acid alone and for nitric acid in the presence of gases other than nitrogen dioxide and nitric oxide, the concentration of nitric acid at any time was calculated as $[HNO_3] = [HNO_3]_0 - [NO_2]_{obs}$. For runs with nitric oxide it was impossible to get an exact estimate of nitric acid. It was assumed to be proportional to $D_\infty - D$, where D is optical density due to nitrogen dioxide. For excess nitric oxide this procedure appears valid, but for excess nitric acid it appears to be very uncertain.

Results

Nitric Acid Alone.—In the 2-liter Vycor bulb a series of runs was made at 375, 400 and 425° with nitric acid alone at pressures from 0.5 to 20 mm. Below 5 mm. the rate was first order in nitric acid throughout a given run, Fig. 1. Above 5 mm. inhibition by nitrogen dioxide could be detected, and corrected for by the method of ref. 3. However, the straight line relation, Fig. 5 of ref. 3, was followed for only one or two half-lives, and then anomalous positive curvature set in. Even so, these plots could be extrapolated to zero to give an estimate of the initial first-order rate constant. The empirical first-order rate constants increase with initial concentration of nitric acid as can be seen in Fig. 2. Over a wide range of initial concentration the first-order rate constant is directly proportional to initial concentration. This proportionality constant is an empirical second-order rate constant; and at 375, 400 and 425° these second-order rate constants are, respectively, 0.64×10^5, 2.0×10^5, 5.8×10^5 cc./mole sec. The energy of activation is 38.3 kcal., and the pre-exponential factor is 5.6×10^{17} cc./mole sec.[5]

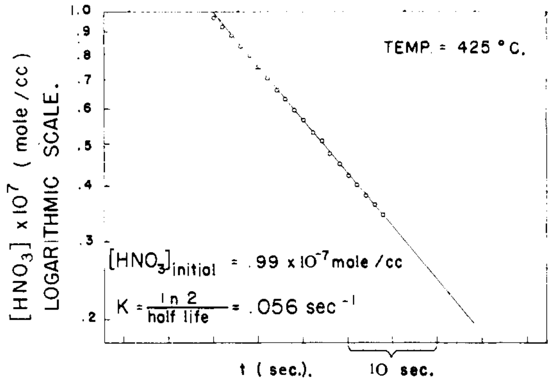

Fig. 1.—Order over the course of a single experiment. The empirical first-order rate constant.

In the 14.5-liter flask numerous runs were made with 2.15×10^{-8} mole/cc. of nitric acid, and also a short series was made with various amounts of nitric acid alone at 400°. Once again the rate was first order in nitric acid during the run, and the first-order constant was proportional to initial nitric acid concentration. This second order rate constant was 3.0×10^5 cc./mole sec. at 400° in poor agreement with the value found in the 2-liter bulb.

Most of the runs made in the 14.5-liter bulb were with constant nitric acid, 2.15×10^{-8} mole/cc., and with varied added gas. In order to make the

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(5) H. S. Johnston, D. Herschbach and J. R. White, Meeting of the American Chemical Society, Los Angeles, Calif., Spring, 1953.

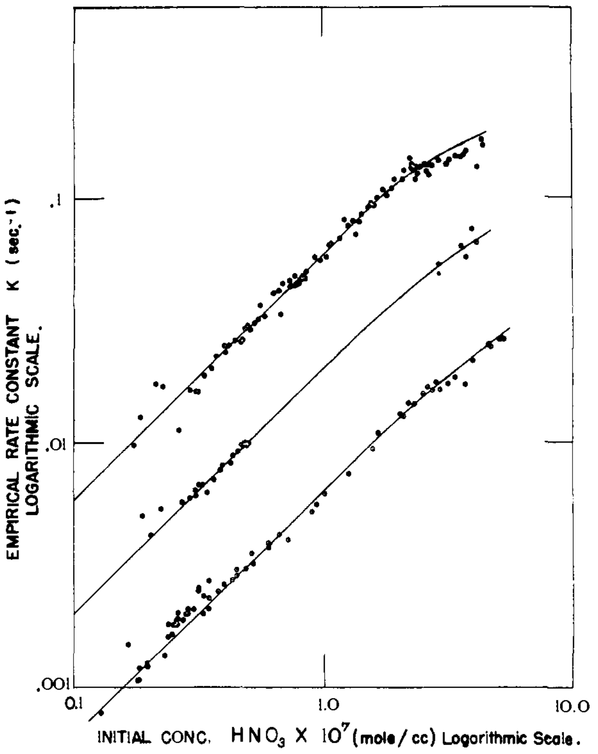

Fig. 2.—Order of the empirical first-order rate constant with respect to varied initial concentration of reactant.

runs with nitric acid alone comparable to those with added gases, the results are plotted as nitric acid in excess of 2.15 × 10^{-8} mole/cc. This plot is shown in Fig. 4.

Nitric Acid in Presence of Various Added Gases.—In the 14.5-liter bulb, the initial nitric acid concentration was held constant at 2.15 × 10^{-8} mole/cc., and various amounts of other gases were added. In the case of water it was added to the reaction bulb first and nitric acid added afterwards. For nitric oxide runs, the nitric acid was run in first and nitric oxide was quickly added afterwards. For argon, carbon dioxide, oxygen and nitrogen dioxide, the foreign gas was mixed with nitric acid at room temperature, and they were passed into the furnace together. All successful runs were made at 400° (see section on "Self-Cooling" below).

During a given run in the presence of argon, carbon dioxide or oxygen, the rate was first order in nitric acid for at least two half-lives. At higher pressures of these gases and at later times, some positive curvature in the plot of log [HNO_3] *vs.* time was noticed, but the initial slope was taken as the empirical first-order rate constant for these cases. During a given run in the presence of nitric oxide the rate was first order in nitric acid for 3 to 5 half-lives. In the presence of water, the plots of log [HNO_3] *vs.* time were linear for 3 or 4 half-lives. In the presence of nitrogen dioxide the plots of log [HNO_3] *vs.* time were linear for at most one half-life and showed positive curvature after that. Empirical first-order rate constants reported here are the initial slopes of these plots. For these runs an attempt was made to correct for inhibition by nitrogen dioxide by the method of Fig. 5, ref. 3. However, the plots were not linear nor were the slopes the same from one plot to another as they should be.

The empirical first-order rate constants for the various gases were averaged in groups of 2 to 7, and these averaged values are plotted against gas concentration in Figs. 3 and 4. In all cases the first-order rate constant is increased by added gases, but the manner of this increase varies markedly from one case to another. These data are available in tabular form.[6]

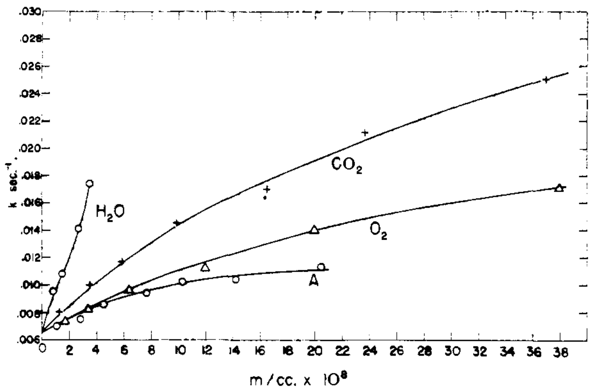

Fig. 3.—Effect of added gases on the empirical first-order rate constant. Initial concentration of nitric acid vapor is 2.2 × 10^{-8} mole/cc. in every case.

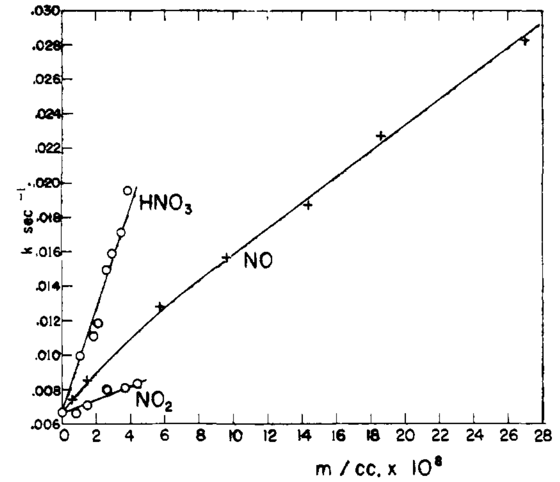

Fig. 4.—Effect of added gases on the empirical first-order rate constant. Initial concentration of nitric acid vapor is 2.2 × 10^{-8} mole/cc. in every case.

Discussion

It was shown previously that the rate-determining step in this system is the unimolecular decomposition of nitric acid, reaction a. At these low pressures the effect of argon, for example, indicates that the reaction is within the "pressure sensitive" region of the unimolecular decomposition. As such, the analysis of mechanism, especially the detection of fine points, is extremely difficult. Every added

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(6) These data have been deposited as Document number 4543 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

gas shows greater or less physical catalysis or activation by collision, and the separation of these physical effects from minor chemical effects may be very difficult. However, from the very general form of the Lindemann mechanism (the form with no models or assumptions about the nature of the detailed functions) one can make several general statements about the signs of certain slopes and curvatures and the values of certain dimensionless ratios.[7] When any effect is found in this system which contradicts these general statements, it will be interpreted as proof of a chemical effect over and above the elementary unimolecular reaction.

In Fig. 3 it can be seen that a plot of concentration of argon *vs.* empirical first-order rate constant is a line with negative curvature. If the only effect of argon is to provide physical activation and deactivation of nitric acid according to a Lindemann mechanism, then one concludes from the rate of curvature that at 2×10^{-8} mole/cc. of nitric acid, one is *not* within the second-order low-pressure region of the unimolecular decomposition. The data for carbon dioxide are in qualitative agreement with those for argon, except that the relative efficiency for energy transfer appears to be about three times as great. The curve for oxygen is intermediate between those of argon and carbon dioxide, and it shows the same qualitative features.

The plots for water, nitric oxide and nitric acid in Figs. 3 and 4 are of a different shape from that for argon, for example. These added gases are linear to much higher values of k than is the case for argon. Also water and nitric acid alone seem to show a slight positive curvature. When these results were first obtained we were tempted to speculate about why these polar gases were so much more efficient in energy transfer than the other added gases. However from consideration of our theorems[7] about what is possible and impossible for plots of this kind, we were quickly convinced that water and nitric oxide exert a chemical effect in this system in addition to the energy-transfer effect. One is forced to assume that water vapor is chemically active in this system, that is, it chemically catalyzes the decomposition of nitric acid at very low pressure. Since water is a molecular product of the over-all reaction (1), the reaction itself must be autocatalytic (it may be recalled that catalytic effects of water were looked for but not found when nitric acid decomposes in the presence of one atm. of nitrogen), and thus the results with nitric acid alone are also anomalous.

According to Fig. 4 nitrogen dioxide is not an effective additive in this system. It was found before[3] that nitrogen dioxide inhibits the decomposition of nitric acid vapor in the presence of one atm. of nitrogen, but under the present conditions of one mm. of reactant the inhibition does not follow the simple linear relationship with $[NO_2]/[HNO_3]$ that was found before. Apparently nitrogen dioxide also has some slight effect different from that of the previous mechanism.[3]

Mechanism.—The primary step in all reactions of nitric acid vapor which have been examined in this series of studies[1,3] is the unimolecular decomposition of nitric acid into hydroxyl free radical and nitrogen dioxide, step a. However, at very low pressures, unlike the case at one atm. total pressure which led to much faster rates, there exists a chemical effect due to water and to nitric oxide, and the effect of nitrogen dioxide differs from that at higher pressures. It could be that several different processes are beginning to be competitive at these low pressures, but the simultaneous appearance of trouble by water, nitric oxide and nitrogen dioxide suggests an examination of nitrous acid as a reactive intermediate. Wayne and Yost[8] have shown this reaction to be extremely fast in both directions at room temperature

$$NO + NO_2 + H_2O = 2HNO_2 \qquad (6)$$

If one proposes a reaction closely analogous to the reverse of (6), one gets

$$HNO_2 + HNO_3 \longrightarrow H_2O + 2NO_2 \qquad (7)$$

Using the known thermodynamic properties of nitrous acid[9] one can estimate roughly the equilibrium constant K_6 to be about 10^{-5} atm.$^{-1}$ at 400°. If reaction (6) is fast enough essentially to maintain equilibrium, then (7) could compete with step a under conditions of these experiments if (7) has a preëxponential factor of 10^{12} cc./mole sec. and energy of activation below 7 or 8 kcal.

Other hypothetical sources of nitrous acid include

$$HO + NO \longrightarrow HNO_2 \qquad (8)$$

$$HNO_3 + NO \longrightarrow HNO_2 + NO_2 \qquad (9)$$

$$H_2O + NO_2 \longrightarrow HNO_2 + OH \qquad (10)$$

Reaction (9) has been proposed by Frejacques,[4] but it is excluded because at constant total pressure it does not lead to a saturation of the nitric oxide effect which has been observed.[3] Step (8) on the other hand, coupled with (7), explains exactly how nitric oxide sustains[3] the initial rate against inhibition by nitrogen dioxide. Step (10) could have a rate comparable to reaction a at 1 mm. total pressure even if (10) has an energy of activation as high as 30 kcal.

In Table I are listed the proposed mechanisms for the decomposition of nitric acid under various conditions. The first entry in the table is regarded as fairly well substantiated.[3] The other entries are not proposed in the sense that these steps have been proven to be important for these cases, but rather these mechanisms are proposed in the sense that the actual mechanism cannot be any simpler.

TABLE I

PROPOSED IMPORTANT STEPS IN THE MECHANISM OF THE DECOMPOSITION OF NITRIC ACID VAPOR AT 400°

Total pressure	Added nitric oxide	Proposed mechanism
1 atm.	No	a, b, c, (2)
1 atm.	Yes	a, b, c, (9), (8)
1 mm.	No	a, c, (2), (6), (7) or (11), (8)
1 mm.	Yes	a, c, (3), (6), (7) or (11), (8)

Self Cooling.—Reaction (1) is about 25 kcal. endothermic at 400°, and thus under conditions of rapid rate (especially in large reaction bulbs),

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(7) J. R. White and H. S. Johnston, *J. Chem. Phys.*, **22**, 1969 (1954).

(8) L. G. Wayne and D. M. Yost, *ibid.*, **19**, 41 (1951).

(9) L. H. Jones, R. M. Badger and G. E. Moore, *ibid.*, **19**, 1599 (1951).

temperature drops due to the cooling effect of the reaction must be guarded against. Using Benson's[10] method of calculating the average temperature drop across a reaction bulb and extending the treatment in an obvious manner to cylinders, one finds the values in Table II. In the 14.5-liter bulb reactants were kept at such a low pressure that the temperature drop did not exceed 1°. However in the 2-liter flask the runs at high pressures and high temperature, Fig. 2, are severely distorted by this effect. For severe temperature gradients such as these, the treatment[11] is oversimplified, and for endothermic reactions it represents the worst possible temperature drop, rather than the expected actual one.

Table II

Calculated Average Temperature Drop in Reaction Bulbs Due to Self-cooling Effect of Endothermic Reaction

Reaction cell	$[HNO_3]$ mole/cc. $\times 10^8$	T, °C.	Av. temp. drop, °C.
2-l. bulb	3	375	0.03
	30	375	3
	3	400	0.1
	30	400	10
	3	425	0.3
	30	425	30
14.5-l. bulb	2.15	400	0.4
2.5 cm. dia. cylinder	100	395	2
	100	475	60

The last two entries are based on Frejacques' values, pp. 49–50 in ref. 4. Reactant pressures were chosen so high that very severe temperature drops occurred even in the small cylinders. This effect of self-cooling is believed to account for the remaining disagreement between our work and Frejacques, especially his low energy of activation.

Acknowledgment.—This study was supported by the Naval Ordnance Test Station, Inyokern, Task Order 2, N123S-80063.

Stanford, Cal.

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[10] S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

[Contribution No. 385 from the Institute for Atomic Research and Department of Chemistry, Iowa State College]

Isotopic Exchange of Manganese during the Reaction between Manganese(II) and Permanganate[1,2]

By James A. Happe and Don S. Martin, Jr.

Received April 20, 1955

Isotopic exchange experiments with Mn^{54} have been performed which involved various chemical forms of manganese existing during the reaction of Mn^{++} with MnO_4^- in acid solutions to give a hydrous oxide containing manganese(IV). A rapid 30 to 40% exchange occurred between Mn^{++} and a freshly formed precipitate. However, 60–70% of the precipitate was unavailable for rapid exchange within 1 to 2 minutes of formation. Isotopic equilibrium during the over-all reaction between Mn^{++} and MnO_4^- required that MnO_4^- be completely reduced to Mn^{IV} before the formation or growth of precipitate grains. Tetraphenylarsonium permanganate was precipitated from solutions of MnO_4^- and Mn^{++} in 1 to 2 molar HNO_3 before the onset of the precipitation of MnO_2 which occurred at *ca.* 10 hours. The permanganate fraction had gained enough activity to correspond to an exchange half-time of 10 to 15 hours. Spectrophotometric studies showed that before a precipitate appeared at least 40% of the MnO_4^- was reduced by a reaction approximately first order in MnO_4^- and without an induction period. In the presence of such large amounts of intermediate species, the exchange between MnO_4^- and Mn^{++} may not be real.

Introduction

The rate and the products of the reaction between manganese(II) and permanganate in aqueous solutions are strongly influenced by the content of the solution. Noyes[3] has reviewed the abundant evidence that in the familiar oxalate reduction of MnO_4^-, Mn^{++} effects an initial rapid reduction of the MnO_4^- to oxalato-complexes of Mn^{III} which slowly yield the products. In the autocatalytic periodate oxidation of Mn^{++}, Waterbury, Hayes and Martin[4] showed that MnO_4^- oxidizes Mn^{++} to iodato complexes of Mn^{III} which are in turn oxidized by periodate. However, in the presence of only dilute nitric or perchloric acids Mn^{++} reduces MnO_4^- to form a hydrous oxide precipitate containing Mn^{IV}. The reaction between these ions in homogeneous solutions is very slow. Tompkins[5] demonstrated quantitatively the autocatalytic nature of the formation of the precipitate. This reaction has been named the Guyard Reaction for which the equation is frequently written

$$3Mn^{++} + 2MnO_4^- + 2H_2O \longrightarrow 5MnO_2 + 4H^+ \quad (1)$$

In excess MnO_4^- the MnO_4^-/Mn^{++} ratio to react is $^2/_3$; however, the indefinite nature of the precipitate is in part indicated by ratios as low as 0.56 which are commonly observed in excess Mn^{++}. Freshly formed precipitates are very finely dispersed, but in a few minutes their color darkens and they are separable by centrifugation and filtration.

The possibility of isotopic exchange between Mn^{++} and MnO_4^- was originally investigated by Polissar[6] who found that negligible exchange occurred at room temperature in the 15 minutes before

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[1] Work was performed in the Ames Laboratory of the United States Atomic Energy Commission.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, April 4, 1955.

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

[4] G. R. Waterbury, A. M. Hayes and D. S. Martin, Jr., This Journal, **74**, 15 (1952).

[5] F. C. Tompkins, *Trans. Faraday Soc.*, **38**, 131 (1942).

[6] M. J. Polissar, This Journal, **58**, 1372 (1936).