and the temperature of 150°, at which the vapor pressure is 78 mm., was chosen for the experiment. These were carried out at a pressure of 53 mm. of disulfide and twice as much of thiol. Under these conditions the exchange is measurable though very slow, the half-time being about 40 hours. As a test of the homogeneity of the reaction, the surface–volume ratio was varied by partially packing the vessel with Pyrex glass rings. The results are given in Fig. 4. Although the errors involved in these experiments are rather large, and therefore the extrapolation of the rate to zero surface–volume ratio rather arbitrary, the fundamentally heterogeneous character of the reaction is evident.

The Non-base-catalyzed Exchange.—It is often reported in the literature that aromatic disulfides undergo homolytic dissociation at low temperatures (∼100°), with the formation of relatively stable sulfenyl radicals. This view is based on optical[21] and magnetic[22] evidence, which is not, however, entirely convincing,[23] so that the matter still seems controversial. It appeared interesting to determine the rate of exchange for diphenyl disulfide under those experimental conditions in which previous workers have proposed that sulfenyl radicals exist in equilibrium with disulfide. In fact, if the disulfide dissociates in free radicals, an alternative path, (C), for the isotopic exchange is offered

$$\text{(C)}\quad C_6H_5S\text{—}SC_6H_5 \rightleftarrows 2C_6H_5S\cdot \qquad (13)$$

$$C_6H_5S\cdot + C_6H_5{}^*SH \rightleftarrows C_6H_5SH + +C_6H_5S\cdot{}^* \qquad (14)$$

Since the hydrogen transfer (14) may be considered very fast, a very high rate of exchange may reasonably be predicted if the concentration of $C_6H_5S\cdot$ radicals is so high as to cause the observed optical anomalies.[24]

In the preceding sections the possibility of this alternative mechanism was not even mentioned, not because it was overlooked, but because it had been proved in some preliminary experiments that at low temperature the reaction is base catalyzed and occurs through the intervention of $C_6H_5S^-$ ions. Other experiments were therefore made in which the concentration of $C_6H_5S^-$ was kept as low as possible in order to make the exchange through mechanism (B) a minimum. This was attained by performing the reaction in anhydrous xylene where dissociation of C_6H_5SH may be thought to occur at a very small extent. Experiments at 100° showed a slow rate: for concentration of reagents 7.5×10^{-2} N the half-time was 10 hours and $R = 7.2 \times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$. This figure shows that if mechanism (C) be assumed, the stationary concentration of sulfenyl radicals must be extremely small and could not possibly be responsible for the observed optical anomalies. Rather, the rate is so slow that it can be perhaps accounted for by mechansim (B) since the concentration of $C_6H_5S^-$, though small, cannot be considered zero. This view is supported by the value of the rate of exchange, in the same experimental conditions, between *n*-butyl disulfide and the corresponding thiol. Experiments gave $R = 4.3 \times 10^{-8}$, that is, less than 1/20 as fast. It is then probable that the mechanism is the same in both exchanges and, since there is no evidence whatsoever for thermal homolytic fission of aliphatic disulfides, that mechanism (B) is likely to be operative also in these experimental conditions. It is realized, however, that only a complete kinetic study can unequivocally assign the mechanism.

Acknowledgment.—The authors are indebted to Prof. M. Calvin for having suggested the experiments with the cyclic disulfide and for the use of the recording spectrophotometer, to Mr. P. M. Hayes of the Radiation Laboratory of the University of California for a sample of trimethylene disulfide and to Professors M. Calvin and R. E. Powell of the Department of Chemistry, University of California at Berkeley, for helpful discussions and suggestions during the preparation of the manuscript.

PADOVA, ITALY

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[CONTRIBUTION FROM THE PYROTECHNICS CHEMICAL RESEARCH LABORATORY, PICATINNY ARSENAL]

The Kinetics of the Thermal Decomposition of Potassium Nitrate and of the Reaction between Potassium Nitrite and Oxygen[1a]

BY ELI S. FREEMAN[1b]

RECEIVED AUGUST 9, 1956

The kinetics of the thermal decomposition of potassium nitrate were studied in oxygen, at a constant pressure of one atmosphere, over the temperature range of 650 to 800°. The rate of reaction was followed by observing changes in volume as a function of time. From 650 to 750° the products of decomposition were found to be potassium nitrite, oxygen and traces of nitrogen dioxide. Equilibrium was also attained between potassium nitrate, potassium nitrite and oxygen. At 800°, decomposition was more extensive, with potassium nitrite decomposing to form nitrogen, oxygen and potassium oxide. The reaction between potassium nitrite and oxygen was investigated from 550 to 790°, by measuring the rate of consumption of oxygen to form potassium nitrate. From 550 to 600°, the reaction goes slowly to completion. From 650 to 750°, equilibrium was attained between the reactants and potassium nitrate. At 790°, decomposition of potassium nitrite was evident. The equilibrium constants of the system were calculated from the data, and on the basis of their temperature dependency, the heats of reaction for decomposition and oxidation were determined. A reaction mechanism is proposed and the kinetics of the reactions as well as the energies of activation were evaluated. In addition, some of the results of this study are compared with those obtained in a previous investigation of sodium nitrate and sodium nitrite.

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[1] (a) This paper was presented, in part, before tbe Division of Physical and Inorganic Chemistry at the North Jersey Meeting in Miniature of the American Chemical Society in Newark, N. J., January 1956, and at the Delaware Valley Regional Meeting in Philadelphia, Pa., February 1956; (b) The Newark Colleges of Rutgers University, Newark 2, N. J.

Introduction

Due to the extensive use of alkali nitrates in pyrotechnics, explosives, rocket ignitors as well as in metallurgical heat treating, there is considerable interest in the high temperature behavior of these salts. Previous work dealt, primarily, with the identification of the reaction products and the determination of the decomposition temperatures.[2-5] Much of the former work, however, was carried out in quartz which led to confusing results due to a reaction between silica and the nitrates.

This investigation is concerned with the reaction kinetics of the thermal decomposition of potassium nitrate. The reaction between potassium nitrate and oxygen was also studied to aid in the elucidation of the mechanism of decomposition. Some of the results of this investigation are compared with the results obtained from a similar study of sodium nitrate and sodium nitrite.[6]

Experimental

The potassium nitrate and potassium nitrite were purchased from the Fisher Scientific Co. and were of C.P. Grade. The oxygen, 99.8% pure, was obtained from the Matheson Co. Of several types of reaction vessels tested, it was found that stainless steel 317 was suitable for this study. Spectroscopic analyses of melts which were heated to the experimental temperatures showed that the extent of attack on the stainless steel vessels was negligible over the experimental times. Furthermore, the inner surface did not appear to catalyze the reaction since varying the dimensions of the vessel had no significant effect on the rate of decomposition.

The experimental procedure and apparatus are identical to that used previously[6]; the gases, however, were analyzed by the Orsat method.[7] The reactions were carried out in oxygen, at one atmosphere of pressure, in Type 317 stainless steel tubes. The dimensions of these vessels are 0.1 cm. wall thickness, inside diameter, 1.6 cm. and 1.3 cm., length, 13 cm. Unless otherwise mentioned, the reactions were conducted in the tubes having an inside diameter of 1.6 cm. X-Ray analysis was used to identify the solid products.

Results and Discussion

Figure 1 shows a graph of the increase in volume *vs.* time for the thermal decomposition of potassium nitrate in oxygen. At temperatures of 650, 700 and 750°, the reaction products were found, by X-ray and gas absorption analyses, to be potassium nitrite, oxygen and traces of nitrogen dioxide (less than 1%). The increase in volume, therefore, is almost entirely due to the evolution of oxygen. After a period of time no further changes in volume were observed, indicating that the system had attained equilibrium. At 800°, the decomposition of potassium nitrite becomes important as indicated by the formation of nitrogen. This was confirmed by analyses of the gases resulting from the decomposition of potassium nitrite. Changing the dimensions of the reaction vessel did not alter the reaction rate significantly.

The variation in weight of potassium nitrate and nitrite was automatically recorded as samples were heated from room temperature to 1000°, at a rate of 15°/min. A Chevenard thermobalance was employed for this purpose. When decomposition was complete (970°) the total weight losses corresponded, within 3%, to the formation K_2O.

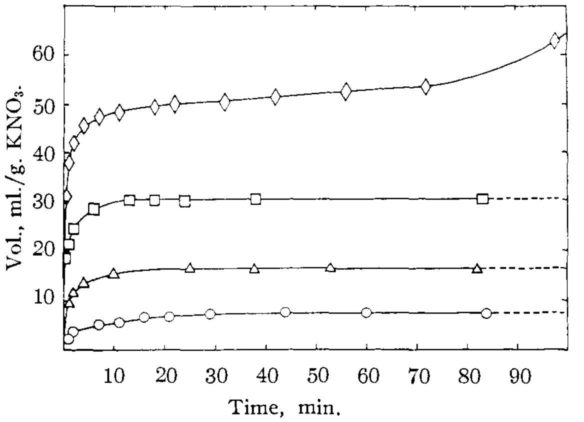

Fig. 1.—The decomposition of potassium nitrate in oxygen (1 atm.), temp., °C.: ○, 650; △, 700; □, 750; ◇, 800.

Potassium nitrite, heated in the presence of oxygen from 550 to 790°, forms potassium nitrate. The course of this reaction is shown in Fig. 2, a graph of the change in volume per g. of potassium nitrite *vs.* time. The rate of reaction increases with temperature, but the extent of reaction decreases. At 550 and 600° the reaction is continuous and eventually goes to completion. From 650 to 750°, as in the case of decomposition of potassium nitrate, the system attains equilibrium. At 790°, a rapid decrease in volume is first observed, followed by a period of 15 min. during which no volume changes occur. This is then followed by an increase in volume due primarily to the evolution of nitrogen, which is attributed to the decomposition of potassium nitrite.

At 750°, the reaction was also carried out in a tube having an inside diameter of 1.30 cm. rather than the usual 1.6 cm. The specific rate was found to decrease from 0.190 min.$^{-1}$ to 0.125 min.$^{-1}$. The ratio of specific rates for the reaction in both size vessels is 1.52 and is equal to the ratio of the corresponding contact areas between the melt and gaseous atmosphere. This indicates that the oxidation process is heterogeneous, taking place, principally, at the liquid–gas interface. A similar surface dependency was observed for the case of the reaction between sodium nitrite and oxygen.[6]

The equilibrium constants, defined in eq. 1 were determined from the data in Figs. 1 and 2.

$$K_e = \frac{N_1}{N_2} \tag{1}$$

K_e = equilibrium constant
N_1 and N_2 = mole fraction of potassium nitrate or nitrite, depending on whether decomposition or oxidation is considered

For this purpose the standard states of the salts were taken as pure molten potassium nitrate and potassium nitrite and for oxygen one atmosphere fugacity. The assumption of ideal behavior of the melt is made since the nitrate and nitrite ions are both univalent and their effective diameters

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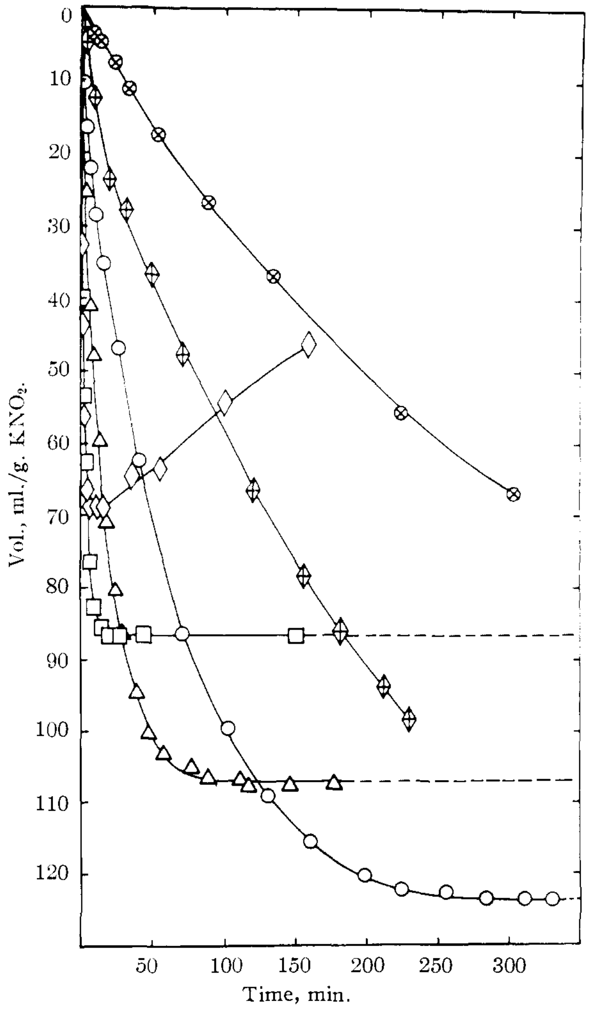

Fig. 2.—The reaction between potassium nitrite and oxygen (1 atm.), temp., °C.: ⊗, 550; ◈, 600; ○, 650; △, 700; □, 750; ◇, 790.

are approximately the same. Furthermore, systems generally approach ideality at high temperatures. The activity coefficients were therefore taken as unity. The respective mole fractions of potassium nitrate and nitrite were determined from the amount of oxygen evolved or consumed during reaction up to the time of equilibrium.

The equilibrium constants, determined from the reaction between potassium nitrite and oxygen are reasonably close to the reciprocals of the equilibrium constants as obtained from the decomposition studies. These values are 14.0, 4.6, 1.9 and 14.1, 5.2 and 2.4 at 750, 700 and 650°, respectively. It should be noted that a small error in the measured volume results in a relatively large error in the calculated equilibrium constants. For example, at 650° a difference of 5% in the volume at equilibrium resulted in a 12% variation between the equilibrium constants.

Figure 3, log K_e *vs.* T^{-1} shows the temperature dependency of the equilibrium constants. The heats of reactions evaluated from the slopes of the lines are 30.8 and −32.8 kcal. mole^{-1} for the decomposition of potassium nitrate and the reaction between potassium nitrite and oxygen, respectively.

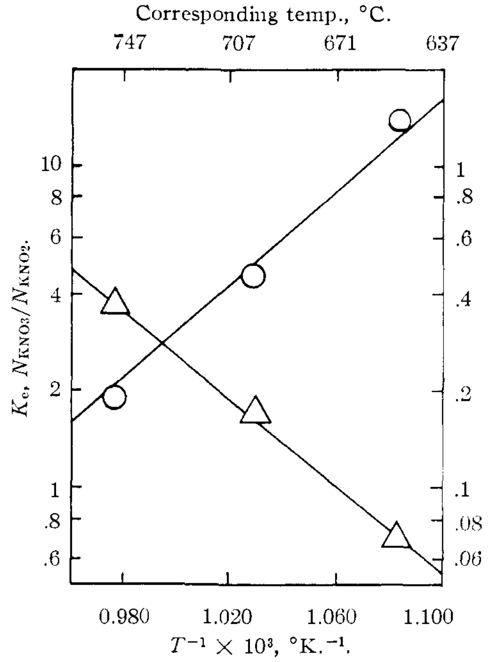

Fig. 3.—Temperature dependency of equilibrium constants: △, right coördinate, $KNO_3 = KNO_2 + {}^1/_2O_2$; ○, left coördinate, ${}^1/_2O_2 + KNO_2 = KNO_3$.

The corresponding values calculated from heats of formation data[8] are 31 kcal.$^{-1}$ and −31 kcal. mole^{-1}. For this calculation an approximate temperature correction has been applied where it was assumed that the difference between the heat capacities of the salts is negligible, and a value of 3.5[9] cal./mole deg. was taken as the average heat capacity of oxygen over the experimental temperature range.

Using the mean experimental value, 31.3 kcal. mole^{-1}, for the heat of reaction and 118.2 kcal. mole^{-1} for the dissociation energy of oxygen[10] the dissociation energy of the N–O bond in potassium nitrate was calculated to be 90.9 kcal. mole^{-1}. From similar experiments with sodium nitrate and sodium nitrite[6] the N–O bond energy was determined to be 83.6 kcal. mole^{-1}. It appears then that the sodium ion weakens the N–O linkage, probably due to its greater polarizing effect on the nitrate ion.

If one assumes that the mechanism of the decomposition of potassium nitrate is similar to that of sodium nitrate,[6] where decomposition and oxidation involve a two-step chain reaction and eq. 2 and 4 are rate determining, the following sequence of reactions is indicated.

$$KNO_2 + O_2 \xrightarrow{k_1} KNO_3 + O \qquad (2)$$

$$KNO_2 + O \xrightarrow{k_2} KNO_3 \qquad (3)$$

$$KNO_3 \xrightarrow{k_3} KNO_2 + O \qquad (4)$$

$$KNO_3 + O \xrightarrow{k_4} KNO_2 + O_2 \qquad (5)$$

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[8] National Bureau of Standards: Circular 500, Selected Values of Chemical Thermodynamic Properties, by F. D. Rossini, D. D. Wagman, W. H. Evans, L. Levine and I. Jaffe, February, 1952.

[9] "Handbook of Chemistry and Physics," 37th Ed., Chemical Rubber Publishing Co., 1955–1956, p. 2107.

[10] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 61.

k_1, k_2, k_3 and k_4 are specific rates referring to the formation of potassium nitrate and nitrite. The reaction $2O \rightarrow O_2$ was not considered since the concentration of atomic oxygen should be negligible compared to the concentration of potassium nitrite and nitrate.

The rate equation[11] for the formation of potassium nitrate, based on the above reactions is

$$\frac{dN_{KNO_3}}{dt} = k_1 N_{KNO_2}N_{O_2} + k_2 N_{KNO_2}N_{O} - k_3 N_{KNO_3} - k_4 N_{KNO_3}N_{O} \qquad (6)$$

N = mole fraction
k_1, k_2, k_3, k_4 = rate constants

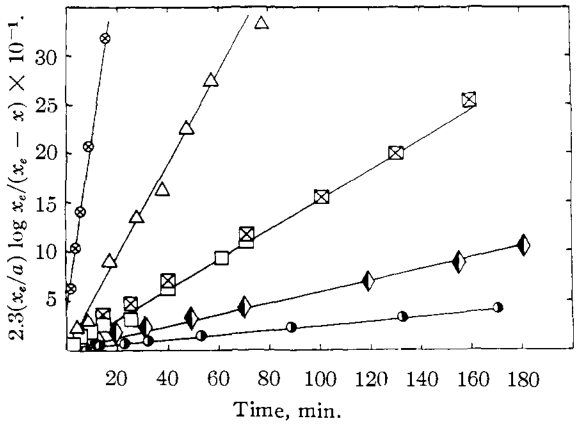

Fig. 4.—Kinetics of reaction between potassium nitrite and oxygen (1 atm.). Temp., °C.: ◑, 550, ◆, 600; ⊠□, 650; △, 700; ⊗, 750.

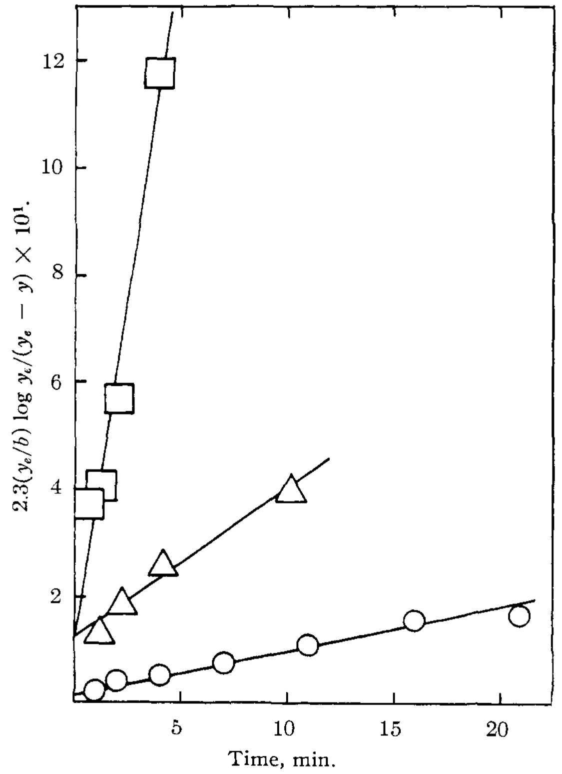

Fig. 5.—Kinetics of the decomposition of potassium nitrate in oxygen (1 atm.), temp., °C.: ○, 600; △, 700; □, 750.

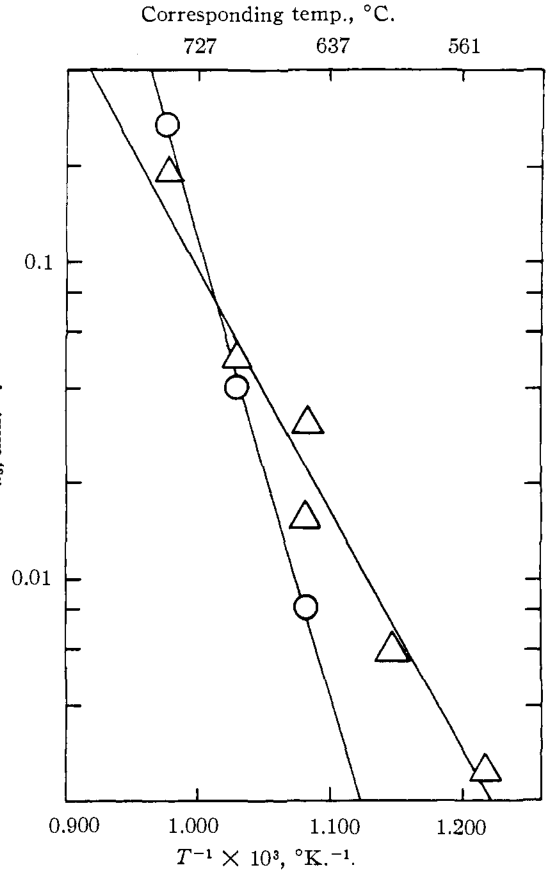

Fig. 6.—Temperature dependency of the rate constants: △, reaction between potassium nitrite and oxygen; ○, decomposition of potassium nitrate.

By applying the steady-state approximation for atomic oxygen at a constant oxygen pressure during the reaction, the terms N_{O_2} and N_O may be incorporated into the specific rates giving:

$$\frac{dN_{KNO_3}}{dt} = k_1' N_{KNO_2} + k_2' N_{KNO_2} - k_3 N_{KNO_3} - k_4' N_{KNO_3} \qquad (7)$$

k_1', k_2', k_4' = new specific rates

At equilibrium $dN_{KNO_3}/dt = 0$. The following equation is therefore obtained

$K_1 = (2.3x_e/at) \log x_e/(x_e - x)$ (8)
$K_1 = k'_1 + k'_2$
x_e = no. of moles of potassium nitrate at equilibrium
x = no. of moles of potassium nitrate formed
a = initial no. of moles of potassiun nitrite
t = time

For the decomposition of KNO_3, one obtains

$K_2 = (2.3\ y_e/bt) \log y_e/(y_e - y)$ (9)
$K_2 = k_3 + k_4'$
b = initial no. of moles of potassium nitrate
y = no. of moles of potassium nitrite formed
y_e = no. of moles of potassum nitrite at equilibrium

Figures 4 and 5 show the result of substituting the data in eq. 8 and 9 and plotting as a function of time. It should be noted that at 550 and 600°, the reaction between potassium nitrite and oxygen goes to completion and consequently $x_e = a$. This reduces eq. 7 to the usual form of a first-order non-reversible expression for these cases.

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[11] The derivation of the rate expressions is given in ref. 6.