THE KINETICS OF THE THERMAL DECOMPOSITION OF SODIUM NITRATE¹ AND OF THE REACTION BETWEEN SODIUM NITRITE AND OXYGEN

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The kinetics of the thermal decomposition of sodium nitrate and of the reaction between sodium nitrite and oxygen were investigated in the presence of argon and oxygen, at atmospheric pressure, over the temperature range of 600 to 780°. The rate of reaction was followed by observing changes in the volume of the systems as a function of time at constant pressure. Mass spectrometric analyses revealed that the gases formed during the decomposition of sodium nitrate consisted of nitrogen dioxide. The nitrogen and some of the oxygen were due to the decomposition of sodium nitrate and sodium superoxide, intermediate products of the decomposition of sodium nitrate. From the investigation of the reaction between sodium nitrite and oxygen it was found that equilibrium was attained between sodium nitrate, sodium nitrite and oxygen is down 700°. Above 700° the oxidation reaction was followed by the decomposition of sodium nitrate, sodium nitrate from the temperature dependency of the equilibrium constants, the heat of reaction for the formation of nor mole of sodium nitrate from sodium nitrite and oxygen was calculated to be -24.5 kcal. per mole. The rate process for the oxidation reaction appears to be surface dependent, as indicated by the effect of varying the area of contact between gaseous oxygen and the sodium nitrite melt. The kinetics involves a first order reversible reaction with respect to sodium nitrate and sodium nitrite. The entropies and free energies of activation and the nitrogen to oxygen bond energy in sodium nitrate were also determined.

Introduction

Previously, investigations of the thermal decomposition of sodium nitrate dealt with the identification of the gaseous and solid products over various temperature ranges.³⁻⁶ Although there is considerable interest in the high temperature reactions of this compound, especially in the field of munitions, there is apparently a lack of fundamental work concerning the kinetics and the mechanism of the decomposition at normal pressures. In this investigation the reactions of sodium nitrite⁷⁻¹⁰ in argon and oxygen also were studied in order to clarify the origin of the gaseous products as well as the kinetics and the mechanism of the decomposition.

Experimental

The sodium nitrate and sodium nitrite were of C.P. grade and purchased from the Fisher Scientific Company.

The apparatus for this work consisted of a stainless steel thimble (reaction vessel) within a Vycor tube which is connected to a dual system consisting of a gas buret and compensating tube separated by a controlling manometer. The dual system of gas burets makes possible the continual observance of the rate process during the collection of the gaseous decomposition products.

For measuring changes in volume of the system, while automatically maintaining a constant pressure,¹¹ two platinum wires were sealed in the intervening manometer and connected to an electronic relay,¹² used to operate a sole-

(1) This paper was presented, in part, before the Division of Physical and Inorganic Chemistry at the National Meeting of the American Chemical Society in Cincinnati, Ohio, April 6, 1955.

(2) Also at The Newark College of Rutgers University.

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(11) E. S. Freeman and S. Gordon, THIS JOURNAL, **59**, 1009 (1955). (12) A thyratron operated relay similar to the Emil Greiner Co. Model E-2. noid valve¹⁸ (see Fig. 1). When there is a small increase in pressure, mercury-wire contact is made on the compensating tube side of the manometer, opening the solenoid valve. The mercury level in the gas buret falls until the original pressure of the system is restored, at which point the mercury-wire contact is broken and the solenoid valve closes. The change in the mercury level is a measure of the increase in volume at the initial pressure of the system. For reactions involving decreases in volume, the solenoid valve opens when the mercury-wire contact is broken. The position of the mercury leveling bulb is adjusted so that when the solenoid valve is open the mercury level in the buret will rise. A layer of mineral oil, one cm. thick, is used to coat the upper surface of the mercury in the gas buret to minimize reaction with NO₂. It was determined experimentally that losses of NO₂ are almost completely eliminated, in this manner, within the limits of the experimental times used in the decomposition studies. The gases were determined by mass spectrometric analyses and the solid residues by X-ray diffraction and chemical methods.

The mass spectrometer was the G.E. Analytical Model and the instrument was calibrated with O_2 , N_2 , NO, N_2O and NO_2 . The results were confirmed by comparisons with synthetic mixtures of the gases in question.

The Vycor vessel, containing a stainless steel reaction tube, is heated in a resistance furnace which is regulated to $\pm 2^{\circ}$ by means of an indicating pyrometric proportioning controller. The vessel is also provided with an invertible side arm, located out of the heating zone, which contains the sample prior to the reaction. When the furnace has attained the desired temperature and the apparatus is filled with the appropriate gas the side arm is inverted, allowing the sodium nitrate or nitrite crystals (approximately 0.5 g.) to drop into the stainless steel tube where the reaction ensues. All the reactions are carried out at approximately one atmosphere of pressure and in a stainless steel reaction vessel having an inside diameter, i.d., of 1.60 cm., unless otherwise stated.

The Chevenard automatic photographic recording thermobalance was used to obtain the thermograms for sodium nitrate and sodium nitrite in air. The sample weight was approximately 0.5 g. and the reaction was carried out in a Coors crucible (glazed) No. 000. The temperature of the furnace was increased at a rate of 15° per minute, and is noted at the timing marks at 2-minute intervals. The balance was calibrated with standard 100 and 200 mg. weights and the furnace cover adjusted so that buoyancy effects were negligible.

Results and Discussion

Figure 2 is a graph of the change in weight of so-

(13) Automatic Switch Co., Valve #826212.





Fig. 1.—Apparatus: G, water jacket; H, gas buret, 100 ml.; I, controlling manometer (mercury); J, compensating tube; K, platinum leads; L, solenoid valve (stainless steel); M, controlling relay (thyratron); N, leveling bulb; O, to reaction vessel; P, to gas buret; Q, sample container; R, furnace; S, to vacuum and gases; T, stainless steel reaction vessel; U, Vycor vessel.

dium nitrate heated in air vs. temperature. Decomposition, as indicated by losses in weight of the sample, commenced slowly at 600° and was rapid at temperatures exceeding 756°. At 910° the reaction was complete and the total weight loss, 0.277 mg., corresponds to the formation of sodium oxide. The discrepancy between the observed and theotical values is 2.3%.

Figure 3 is a graph of the increase in volume of the individual gases formed as a function of time, due to the decomposition of sodium nitrate in argon, over the temperature range of 650 to 780°. Mass spectrometric analyses of the decomposition gases, which were collected periodically, showed the presence of oxygen, nitrogen and small quantities of nitrogen dioxide. The analytical data are presented in Table I. Several of the points for oxygen, not given in Table I, were obtained by taking the difference between the total volume and the volume of nitrogen plus nitrogen dioxide. The presence of nitrogen dioxide may result from the reac-



Fig. 2.—Thermogram of sodium nitrate in air; weight loss (mg.) vs. temperature (°C.); timing marks at 2 min. intervals; rate of temperature increase, 15° min.⁻¹.



Fig. 3.—Rate of decomposition of $NaNO_8$ in argon at contant pressure (one atm.); volume (ml./g.) S.T.P. vs. time (min.).

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	°C.	Gas		°C.	Gas
0	650	O_2	図	750	N_2
\otimes	650	N_2		750	NO_2 (N_2O_4)
\triangle	700	O_2	¢.	780	O_2
\mathbb{A}	700	N_2	•	780	N_2
	750	O_2	♦	780	$NO_{2} (N_{2}O_{4})$

tion between oxygen and nitric oxide. During the initial stages of the reaction oxygen is the principal gas formed; as the reaction proceeds the proportion of nitrogen increases. The data indicate that the primary stage of the decomposition of sodium nitrate involves predominantly the formation of sodium nitrite and oxygen. X-Ray analyses of the solid residues corroborate these findings. The use of a reaction vessel having a smaller inside diameter, 1.30 cm., had little effect on the reaction rate.

Since sodium nitrite is a product of the decomposition of sodium nitrate, its thermal decomposition was investigated, in argon, over the temperature range of 650 to 780°. The results are shown in Fig. 4, a graph of the increase in volume of the gaseous products vs. time. The decomposition gases were found to consist of nitrogen and oxygen.¹⁴ During the initial stages of the reaction, nitrogen is the predominant gas formed; however, as the reaction progresses the relative quantities of oxygen increase. Relatively good reproducibility of the data is indicated from duplicate experiments carried out at 700°. These results, in addition to the orangebrown color of the decomposing liquid, indicate that the nitrogen formed during the decomposition of sodium nitrate probably originates from the breakdown of sodium nitrite to an intermediate superoxide and nitrogen. The increased proportion of oxygen, as the decomposition of sodium nitrite proceeds, may be accounted for by the decomposition of the superoxide to sodium oxide and oxygen.

X-Ray analyses revealed the presence of sodium nitrate in the solid decomposition products of sodium nitrite. The intensitities of the reflections for sodium nitrate and nitrite were weak due to extensive decomposition, but a pattern was not observed for the oxides. The oxides, therefore, appear to exist in the amorphous state. The formation of sodium nitrate is not attributed directly to the decomposition of sodium nitrite since sodium nitrate is unstable at the experimental temperatures. A reasonable explanation is, however, that when the mass cools, sodium superoxide oxidizes sodium nitrite to the nitrate and itself is reduced to a peroxide or oxide.

Since nitrogen dioxide was not observed during the decomposition of sodium nitrite, in stainless steel, the formation of nitric oxide and/or nitrogen dioxide resulted principally from the decomposition of sodium nitrate. This reaction takes place to a small extent upon heating sodium nitrate as indicated in Table I and Fig. 3.

A graph of the change in weight of sodium nitrite, heated in air, vs. temperature is shown in Fig. 5. At approximately 620° the oxidation of sodium nitrite by oxygen becomes apparent as indicated by increases in sample weight. The maximum weight is attained at 740°. Further increases in temperature resulted in weight losses due to decomposition, which are relatively rapid above 780°. At 920° the decomposition was complete. The total weight loss, 0.327 mg., corresponds to the forma-



Fig. 4.—Rate of decomposition of NaNO₂ in argon at constant pressure (one atm.); volume (ml./g.) S.T.P. vs. time (min.).



Fig. 5.—Thermogram of sodium nitrite in air; weight loss (mg.) vs. temperature (°C.); timing marks at 2 min. intervals; rate of temperature increase, 15° min.⁻¹.

tion of sodium oxide. The difference between the observed and theoretical values is 2.2%.

The effect of oxygen on the high temperature behavior of sodium nitrite over the temperature range of 600 to 780 ° is shown in Fig. 6. Rather than decomposition, as occurs in argon, a decrease in volume is observed due to the formation of sodium nitrate. At 780 and 750° a secondary reaction involving the decomposition of sodium nitrite is indicated. This is evident from the initial decrease in the volume of the system, followed by an increase in volume resulting from the evolution of nitrogen and some oxygen. The amount of sodium nitrate present when the rate of change in volume is zero,

⁽¹⁴⁾ When the reaction was carried out at 600° in a platinum crucible, in nitrogen, traces of NO and/or NO₂ were also observed. This is in qualitative agreement with the results reported by Oza and Walawalker.^{10b}



Fig. 6.—Rate of reaction between NaNO₂ and O₂ at constant pressure (one atm.); volume (ml./g.) S.T.P. vs. time (min.); temp., °C.: \boxtimes , 600; \otimes , 650; \bigcirc , 650; \Box , 700; \triangle , 750; \bigcirc , 780.

and the time for the attainment of this condition, both increase as the temperature is decreased. Although the rate of oxidation increases with temperature, the extent of reaction decreases with increasing temperature. At 600, 650 and 700°, after a period of time which increases with decreasing temperature, the volume of the system remained constant, indicating that equilibrium had been attained between sodium nitrate, sodium nitrite and oxygen. This was confirmed by X-ray analyses of the residues which indicated only the presence of sodium nitrate and sodium nitrite. Duplicate experiments, at 650°, showed good reproducibility of the data.

On the basis of the amount of oxygen at equilibrium, as determined from the above experiments, equilibrium constants were calculated. For this purpose the standard states of the salts were taken as pure molten sodium nitrate and sodium nitrite at the same temperature and pressure. The melt is assumed to approach ideality and the activity of each component was taken as equal to its mole fraction. The assumption of ideality is made since the nitrate and nitrite ions are both univa-

TABLE	Ι
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THERMAL DECOMPOSITION OF NaNO₃ IN ARGON (ONE

		ATMOSPHERE,	•		
Temp., Time,			Volume (ml./g.) S.T.P.		
-0.	min.	Oxygen	Interogen	1002(10204)	
650	160	10 0	0.8	0.1	
700	12	23.5	0.5	0.1	
700	102	31.5	4.3	0.1	
750	15	50.4	0.1	2.1	
750	168	69.0	8.3	2.4	
780	13	59.3	5,1	6.1	
780	123	98.3	30.5	8.7	
780	142	100.1	36.9	8.7	

lent, occupying approximately the same space due to rotation at high temperatures and the cation is common to both salts. Furthermore, in general,

TABLE II

Thermodynami	c Functions and R	ATE CONSTANTS		
1. Net reaction:	$NaNO_2(l) + 1/20$	$P_2(g) = NaNO_3(1)$		
Temp., °C.	Change in free energy ΔF , kcal. mole ⁻¹	Equilibrium constant Ke, NNaNO3/NNaNO2		
600	-3.54	5.88		
650	-1.77	2.61		
700	-0.668	1.41		
2. Reaction: Na Temp., °C.	aNO ₂ (1) + O ₂ (g) \rightarrow Free energy of activation ΔF_1^{\ddagger} , kcal. mole ⁻¹	NaNO ₃ (l) + O(g) Rate constant $k_1' \times 10^4$, sec. ⁻¹		
600	67.7	2.55		
650	70.4	4.52		
700	73.0	8.42		
3. Reaction:	$NaNO_3(1) \rightarrow NaN$	$O_2(l) + O(g)$		
Temp., ° C.	Free energy of activation ΔF_2 ; kcal. mole $^{-1}$	Rate constant $k_2' \times 10^5$, sec. ⁻¹		
600	70.8	4.35		
650	72.3	17.3		
700	73.8	59.7		

systems approach ideal behavior at elevated temperatures.¹⁵ The standard state of oxygen is taken as one atmosphere fugacity since the oxygen pressure was constant, one atmosphere, throughout the reaction. Consequently, the equilibrium constant, K_e , is equal to the ratio of the mole fractions, N, of sodium nitrite and sodium nitrate for the reaction between one mole of sodium nitrite and oxygen to form one mole of sodium nitrate.

$$K_{\rm e} = \frac{N_{\rm NaNOs}}{N_{\rm NaNOs}} \tag{1}$$

(15) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1946, p. 713. The values of the equilibrium constant vary inversely with temperature and are given in Table II.

From a graph of the logarithm of the equilibrium constants vs. the reciprocal of the absolute temperature, Fig. 7, the heat of reaction for the formation of one mole of sodium nitrate from the reaction between sodium nitrite and oxygen was calculated to be -24.5 kcal. per mole. This is in good agreement with the calculated value, -25.6 kcal. per mole, based upon the heats of formation of sodium nitrate (solid), -111.5 kcal. mole⁻¹, and sodium ni-trite (solid), -85.9 kcal. per mole.¹⁶ Other investigators have found that equilibrium exists between lithium nitrate, lithium nitrite and oxygen just above the melting point of lithium nitrate and calculated the heat of reaction for the formation of one mole of lithium nitrate from lithium nitrite and oxygen to be 25.1 kcal. per mole.¹⁷ The change in free energy for the reaction between sodium nitrite and oxygen to form sodium nitrate varies from -3.54 kcal. mole⁻¹ at 600° to -0.67 kcal. mole⁻¹ at 700° (see Table II).

By carrying out the oxidation in a vessel having a smaller inside diameter (1.30 cm.), the rate of reaction was decreased by 40%, which is approximately proportional to the decrease in the contact area between the melt and the gaseous phase. This indicates that the reaction is heterogeneous occurring. principally, on the surface of the melt between oxygen (gas) and sodium nitrite (liquid).

For the deviation of a rate expression the following relationship is considered.

$$NaNO_2 + \frac{1}{2}O_2 \xrightarrow{k_1} NaNO_3$$
 (2)

 k_1 and k_2 = rate constants

The rate of the forward reaction v_1 is

$$v_1 = k_1 \alpha_{0_2} v_2 \alpha_{NaNO_2}$$
(3)

 $\Omega_{0_2} =$ fugacity of oxygen

 α_{NaNO2} = surface activity of sodium nitrite, moles NaNO₂/ cm.²

The activity of sodium nitrite is dependent on the amount of sodium nitrite at the surface of the melt and is proportional to its mole fraction. The fugacity of oxygen is independent of the activity of sodium nitrite and remains essentially constant during the reaction. Therefore, the rate equation takes the form

$$v_1 = k'_1 N_{\text{NaNO}_2} = k'_1 \left(1 - x/a \right) \tag{4}$$

 $k'_1 = a$ new rate constant

- x =moles sodium nitrate in the melt

a = moles sodium nitrate plus moles sodium nitrite x/a = mole fraction of sodium nitrate in the melt (1 - x/a) = mole fraction of sodium nitrite in the melt

The rate of decomposition of sodium nitrate is given in equation 5.

$$k_2 = k_2 \Omega_{\text{NaNO}_3} = k'_2 N_{\text{NaNO}_3} = k'_2 x/a$$
 (5)

The activity of sodium nitrate is taken as equal to its mole fraction, N_{NaNO3} , since the melt is assumed

(16) National Bureau of Standards: Circular 500, Selected Values of Chemical Thermodynamic Properties, by F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, February, 1952.

(17) M. Centnerzwer and M. Blaumenthal, Bull. inter. acad. polon. sci.; sci. math. nat., No. 8-9, 470 (1936).



Fig. 7.—Temperature dependency of equilibrium constant; log equilibrium constant K_{\bullet} vs. $1/T \times 10^3$, °K.⁻¹.

to be ideal. The rate of formation of sodium nitrate is

$$\frac{(x/a)}{dt} = k_1' \left(1 - \frac{x}{a}\right) - \frac{k_2' x}{a}$$
(6)

At equilibrium $v_1 = v_2$. From these relationships the following rate expression is obtained for the case where initially only sodium nitrite is present (x/a = 0 at t = 0)

$$k'_1 = (x_e/at) \ln x_e/(x_e - x)$$
 (7)

 $x_{\rm e}$ = amount of sodium nitrate at equilibrium. If one starts with pure sodium nitrate, an identical expression for k'_2 is obtained, x_e and x being replaced by y_e and y, which refer to moles of sodium nitrite. Figure 8 shows the results of substituting the experimental data in equation 7 and plotting $(x_e/a) \ln x_e/(x_e - x)$ as a function of time. The points fall along a series of straight lines showing good agreement between the theoretical and observed results.

From a graph of the logarithm of the rate constants, k'_1 , vs. \hat{T}^{-1} , Fig. 9, the activation energy was



Fig. 8.—Kinetics of reaction between sodium nitrite and oxygen (x_e/a) ln $x_e/(x_e - x) \times 10^1$ vs. time, min.

calculated to be 20.7 kcal. mole⁻¹. The rate constants, k_2 , for the decomposition of sodium nitrate to sodium nitrite and oxygen were calculated from the relationship between the equilibrium constant, K_{e} , and the rate constants (see Table II).

$$K_{\mathbf{e}} = k_1'/k_2' \tag{8}$$

The graph, $\log k_2 vs. T^{-1}$, for the decomposition of sodium nitrate is plotted in Fig. 9. The activation



Fig. 9.—Temperature dependency of the rate constants: O, left coördinate, $\log k_2' vs. 1/T \times 10^3$, °K.⁻¹; \triangle , right coördinate $\log k_1' vs. 1/T \times 10^3$, °K.⁻¹.

energy was calculated from the slope of the line to be 44.7 kcal. mole⁻¹.

The dissociation energy¹⁸ of oxygen, 118.2 kcal. mole⁻¹, is considerably greater than the activation energy for the formation of sodium nitrate from sodium nitrite and oxygen, 20.7 kcal. mole⁻¹. From this it is clear that a reaction mechanism involving the oxidation of nitrite by atomic oxygen, formed from the dissociation of molecular oxygen, is not probable. Consequently, the energetics and reaction kinetics favor the following mechanism for the oxidation and decomposition reactions.

Oxidation:

$$NaNO_2 + O_2 \xrightarrow{k_1^a} NaNO_3 + O \tag{9}$$

$$O + NaNO_2 \xrightarrow{\kappa_1} NaNO_3$$
 (10)

Decomposition:

$$NaNO_3 \xrightarrow{k_2^a} NaNO_2 + O$$
 (11)

$$O + NaNO_3 \xrightarrow{R_2^\circ} NaNO_2 + O_2$$
 (12)

 $k_1^*, k_1^*, k_2^*, k_2^*$ = rate constants. The reaction, 20 $\rightarrow O_2$, is of minor importance due to the negligibly small concentration of atomic oxygen with respect to the concentration of nitrate and nitrite. The above sequence of reactions is in agreement with the observed kinetics in two respects: reactions (9) and (11) should be slow compared to (10) and (12), respectively; and from general kinetic considerations.

$$v_1 = k_1^a \Omega_{\text{NaNO}_2} \Omega_{\text{O}_2} + k_1^b \Omega_{\text{NaNO}_2} \Omega_{\text{O}} - k_2^b \Omega_{\text{NaNO}_4} \Omega_{\text{O}} - k_2^a$$

$$\Omega_{\text{NaNO}_4} \quad (13)$$

 v_1 = velocity of over-all oxidation reaction. The concentration of atomic oxygen, an unstable intermediate, is assumed to be essentially constant during most of the reaction (stationary state approximation). On this basis the activity of oxygen is incorporated into the rate constant. The fugacity of molecular oxygen is also constant at one atmos-

(18) L. Pauling, "Nature of the Chemical Bond," Cornell Univerity Press, Ithaca, N. Y., 1948, p. 61. phere of pressure. Therefore, the rate of formation of sodium nitrate is

$$v_{1} = K_{1}^{a} \Omega_{NaNO_{2}} + K_{1}^{b} \Omega_{NaNO_{2}} - K_{2}^{b} \Omega_{NaNO_{3}} - k_{2}^{b} \Omega_{NaNO_{4}} = (K_{1}^{a} + K_{1}^{b}) \Omega_{NaNO_{3}} - (K_{2}^{b} + k_{2}^{a}) \Omega_{NaNO_{3}}$$
(14)

where $(K_1^* + K_1^*)$ and $(K_2^* + k_2^*)$ correspond to k_1' and k_2' in equation 6.

The entropies and free energies of activation were determined from equations 15 and 16 assuming that ΔH^{\ddagger} is approximately equal to the energy of activation ΔE^{\ddagger} .

$$k'_{1} \text{ or } k'_{2} - kT/h \ e^{\Delta S^{\dagger}/Re^{-\Delta H^{\dagger}/RT}}$$
(15)

$$h = \text{Planck's constant}$$

$$\Delta H^{\ddagger} = \text{heat of activation}$$

$$k = \text{Boltzmann's constant}$$

$$R = \text{gas constant}$$

$$\Delta S^{\ddagger} = \text{entropy of activation}$$

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$
(16)

 ΔF^{\ddagger} = free energy of activation, kcal. mole⁻¹

The entropies of activation at 650° were calculated to be -53.8 and -29.8 e.u., for the forward and reverse reactions, respectively. The corresponding values for the free energies of activation vary from 67.7 to 73.0 kcal. mole⁻¹ and 70.8 to 73.8 kcal. mole⁻¹, Table II.

A study of the decomposition of sodium nitrate at 700° in an oxygen atmosphere appears to confirm the above treatment and interpretation. After a period of 40 minutes equilibrium was attained and the equilibrium constant, $K'_{\rm e}$, $N_{\rm NaNO_2}/$ $N_{\rm NaNO_3}$, was found to equal 0.342. Figure 10 shows the linear relationship obtained by plotting $(y_{\rm e}/a) \ln y_{\rm e}/(y_{\rm e} - y)$ vs. time. The rate constant for the decomposition was determined from the slope of the line to be 5.60 $\times 10^{-4}$ sec.⁻¹ and is in good agreement with the value obtained from the study



Fig. 10.—Kinetics of the decomposition of sodium nitrate in oxygen; $(y_{\bullet}/a) \ln y_{\bullet}/(y_{\bullet} - y) \times 10^{1} vs.$ time, min.

of the oxidation of sodium nitrite, 5.97×10^{-4} sec.⁻¹. The rate constant for the oxidation reaction is 1.64×10^{-8} sec.⁻¹, approximately two times greater than that found by studying the reaction between sodium nitrite and oxygen, 8.42×10^{-4} sec.⁻¹. This is attributed to a catalytic effect of traces of nitric oxide which was formed during the early stages of the decomposition. Nitric oxide reacts with oxygen to form nitrogen dioxide which reacts with sodium nitrite to form sodium nitrate and nitric oxide. The reactions may be represented as

$$NaNO_2 + NO_2 = NaNO_3 + NO$$
 (17)

$$NO + \frac{1}{2}O_2 = NO_2$$
 (18)
 $NaNO_3 = NaNO_2 + O$ (19)

$$O + NO = NO_2$$
 (20)

The value for the energy of the nitrogen to oxygen bond in sodium nitrate may be calculated from the dissociation energy of oxygen,¹⁸ 118.2 kcal. mole⁻¹, and the energies of activation by the following considerations

$$E_{(N...0)} - E_{0_2} = 20.7 \text{ kcal. mole}^{-1}$$
 (21)

$$E_{(N...0)} = 20.7 + 118.2 = 138.9 \text{ kcal. mole}^{-1}$$
 (22)

$$E_{(N...0...0)} E_{N-0} = 44.7 \text{ kcal. mole}^{-1}$$
 (23)

$$E_{(N-0)} = 138.9 - 44.7 = 94.2 \text{ kcal. mole}^{-1}$$
 (24)

 $(N \dots O \dots O) =$ bonds in transition state. The assumption is made that the temperature dependency of the rate constants for reactions (10) and

(12) are small compared to reactions (9) and (11) due to the unstable nature of atomic oxygen. The value for the nitrogen to oxygen bond in sodium nitrate determined from the heat of dissociation of oxygen and heats of formation of sodium nitrate and nitrite (solid)¹⁵ is 84.7 kcal. mole⁻¹. This discrepancy can be attributed to the assumptions used in the above calculations.

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THIOCYANATE COMPLEXES OF LEAD AND THALLIUM IN SOLUTION

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Polarographic studies of the reduction of lead ions in thiocyanate-perchlorate mixtures of constant ionic strength have shown the existence of the species PbSCN⁺, Pb(SCN)₂ and Pb(SCN)₄⁻ in these solutions. The over-all formation constants at 25° and an ionic strength of 2.00 M are $K_1 = 3.5$, $K_2 = 7.5$ and $K_4 = 7$. The ion Pb(SCN)₈⁻ appears to have a formation constant of the order of 0.1 under the same conditions. Similar studies on thallous ion in nitrate-thiocyanate mixtures show evidence only for un-ionized thallous thiocyanate with a formation constant of about 2.6.

Lead and particularly thallium show relatively little tendency to form complexes with thiocyanate ion in solution, as evidenced by the close correspondence of the half-wave potentials in dilute thiocyanate solutions with those in "non-complexing" electrolytes.^{1,2} For this reason, polarographers have in general assumed the non-existence of complex formation between these metals and thiocyanate, even in relatively concentrated solutions. The conductivity data of Böttger,3 however, suggest the existence of the PbSCN+ with a stability comparable to that of the PbCl+ ion, and the solubility measurements by Bell and George⁴ lead to a formation constant of 6.3 for the species TISCN at 25°. In order to see if the polarographic method could shed further light on this problem, we have studied the dependence of the half-wave potentials of lead and thallium as a function of thiocyanate ion activity in solutions of constant ionic strength.

Experimental

Apparatus and Materials.—Measurements were made either with a Sargent Model XII recording polarograph without damping and equipped with a wave spreader⁶ to expand the voltage scale, or a manual apparatus similar to that of Lingane and Kolthoff.⁶ The dropping electrodes were fabricated of commercial marine barometer tubing and

- (2) J. O. Hibbets and S. S. Cooper, Anal. Chem., 26, 1119 (1954).
- (3) W. Böttger, Z. physik. Chem., 46, 521 (1903).

(5) T. W. Gilbert and D. N. Hume, Anal. Chem., 24, 431 (1952).
(6) J. J. Lingane, J. Am. Chem. Soc., 61, 825 (1939).

the conventional H-type cell with a sintered glass bridge was used. In the lead studies, the reference electrode was a calomel cell 1.9 M in sodium perchlorate, 0.1 M in sodium chloride and 0.001 M in perchlorate solution 0.001 M in perchloric acid. For the thallium studies, a calomel electrode saturated with potassium chloride at 25° was employed, together with a sodium nitrate bridge. A temperature of $25.0 \pm 0.1^{\circ}$ was maintained by means of a thermostated water-bath. All chemicals were reagent quality and distilled water was used throughout. Oxygen was purged from the samples with pre-purified nitrogen.

Technique.—The general method of operation was similar to that described in previous papers.⁷⁻⁹ The half-wave potentials were estimated from plots of log $[(i_d - i)/i]$ versus E, in which duplicate samples checked to within 1 mv. All values were corrected for iR drop in the cell. Good straight lines with slopes in close agreement with the theoretical values were obtained in the above plots, and it was concluded that both systems showed satisfactory reversibility.

Results and Discussion

Lead Thiocyanate.—The half-wave potential and diffusion current of lead were measured in the cell

Hg	Hg_2	NaClO4 NaCl	$1.9 \ M$ $0.1 \ M$	$\begin{array}{c} \operatorname{NaClO_4} \\ 2.0 \ M \end{array}$	NaClO4 NaSCN	$\begin{pmatrix} 2-x \end{pmatrix} M \\ x M$	d.
	Cl_2	HClO₄	0.001 M	$\begin{array}{c} \mathrm{HClO}_4 \\ 0.001 \ M \end{array}$	HClO ₄ Pb(ClO ₄) ₂	0.001 M 5 × 10 ⁻⁴	m le

for values of x from 0 to 2.00 M in steps of 0.1 M. Gelatin (0.01%) was used as a maximum suppressor. The negative shifts in half-wave potential observed

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(8) H. M. Hershenson, M. E. Smith and D. N. Hume, *ibid.*, 75, 507 (1953).

(9) R. E. Frank and D. N. Hume, ibid., 75, 1736 (1953).

⁽¹⁾ I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952.

⁽⁴⁾ R. P. Bell and J. H. B. George, Trans. Faraday Soc., 49, 619 (1953).