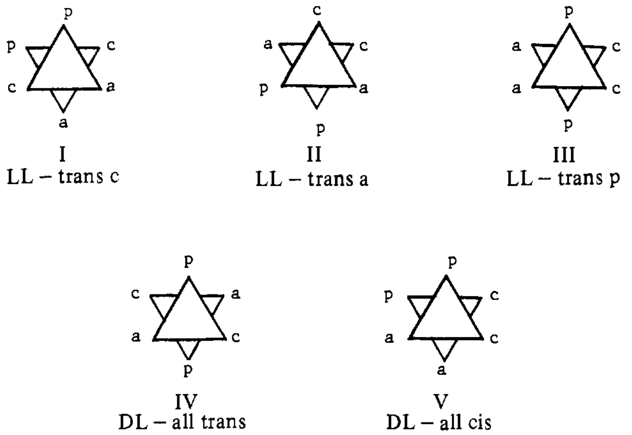
Chart I. Possible Diastereoisomers for Facial Bis-tridentate Six-Coordinate Complexes As Could Be Formed by *O*-Phospho-DL-serine[a]



I
LL – trans c

II
LL – trans a

III
LL – trans p

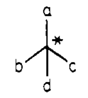
IV
DL – all trans

V
DL – all cis

[a] Abbreviations: a = amino; c = carboxylate; p = phosphate.

groups and steric effects are considered. The only isomer where all groups are trans is IV. It can only be formed from a D and an L ligand. For the optically active bis complexes, I is the most stable on the basis of Coulombic repulsions between donor sites. It is not obvious to us why this isomer should be sufficiently more stable than IV to account for the large stereoselectivity we observe. It would seem that the usual expectation would be that DL complexes should be favored if the ligands are tridentate and coordinate in a facial fashion.

However, meridional coordination can lead to stereoselectivity of the type we observe. For a tridentate ligand with a chiral center engaging in meridional coordination, three diastereomers are possible for the bis complex. There are two for the LL (or DD) complex and one for the DL complex. The DL complex exists as an enantiomeric pair, and so it may be formed two different ways. In the absence of steric or Coulombic effects the diastereomers would ideally exist in a 1:2:1 ratio. In any real case, however, the chances are that one of the LL isomers will be more stable than the DL isomer. Consider an idealized tridentate ligand, VI, with substituents b and c on a chiral center and meridional coordination along the line a–d. For a DD or LL complex, two diastereomers are formed. For each ligand of a given diastereomer, the steric or Coulombic interligand interactions of b or c will be the same. In the DL complex, the chiral centers are different and so b on one ligand will not have the same interactions as b on the other ligand. The symmetry is such that a given steric repulsion between two different parts of each ligand will occur twice in the least stable LL isomer, once in the DL isomer, and not at all in the most stable LL isomer. In other words, the DL isomer is always a "steric compromise" between the two LL isomers. When all steric effects are considered, this should generally lead to one of the LL (or DD) isomers being more stable than the DL isomer. Similar arguments can be made in the case of electrostatic repulsions and the *mer* bistridentate coordination should lead to the favoring of LL (or DD) over DL. For a very different system, we have previously demonstrated a number of instances of such stereoselectivity observed for meridional coordination.[20]



VI

The conclusion that may be drawn is that one would expect that facial bistridentate six-coordinate complexes with one chiral center per ligand should display DL stereoselectivity, if any. Meridional complexes should display DD or LL stereoselectivity.

Acknowledgment. M.S.M. thanks the council of Scientific and Industrial Research, New Delhi, India, for a research associateship. The research was supported by Grant AM 21669 from the National Institutes of Health.

Registry No. *O*-Phospho-L-serine, 407-41-0; *O*-phospho-DL-serine, 17885-08-4.

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[20] E. H. Abbott and A. E. Martell, *J. Am. Chem. Soc.*, **92**, 5845 (1970).

Contribution from Materials Development Division I and Exploratory Chemistry Division I,
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Nitrate/Nitrite Chemistry in $NaNO_3$–KNO_3 Melts

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By chemical analysis of samples taken under carefully controlled conditions, we have been able to show that the only reaction of any consequence that takes place in the equimolar binary $NaNO_3$–KNO_3 system over the temperature range 500–600 °C is represented by $NO_3^- \rightleftarrows NO_2^- + {}^1/_2O_2$. Over this temperature range there is no evidence of the formation of any anionic oxygen species such as oxide, peroxide, or superoxide at concentrations greater than 10^{-5} mol/kg. Equilibrium constants for the above reaction have been determined over the temperature range 500–600 °C. The standard free energy for this reaction [$\Delta G°$ (kcal/mol) = 23 000 + 20.6T] has been derived from the experimental data and is in good agreement with similar results for the single salts. A study of the kinetics of the oxidation of nitrite showed the rate of that reaction to be overall second order, first order with respect to both nitrite and oxygen. The rate constants have been measured from 400 to 500 °C, and from their temperature dependence the activation energy for the oxidation of nitrite was calculated: 26.4 kcal/mol.

Introduction

Molten alkali nitrates and, in particular, the equimolar mixture of $NaNO_3$ and KNO_3 have become attractive candidates for heat transfer and thermal energy storage media in solar thermal energy systems.[1] As such, they will be subjected to temperatures in the range 500–600 °C, several hundred degrees above their melting point (222 °C for $NaNO_3$–KNO_3). It is well-known that heating nitrates to

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(1) Farrow, R. L.; Rahn, L. A. "Proceedings of DOE Large Solar Central Power Systems, Semiannual Review", Report SAND80-8805; Sandia National Laboratories: Livermore, CA, June 1980.

elevated temperatures results in their thermal decomposition with the formation of nitrite

$$NO_3^- \rightleftarrows NO_2^- + {}^{1}/{}^{2}O_2 \qquad (1)$$

however, other products have been detected.[2] The ability to understand the reaction among nitrate salts, containment materials, and the atmosphere, and to interpret changes in the physical properties of the melt, requires a thorough understanding of the reactions that are intrinsic to the melt itself. These include the extent of thermal decomposition, the nature of the thermal decomposition products, whether self-dissociation in the melt takes place to any appreciable extent, and the kinetcs of the thermal decomposition reaction.

The thermal decomposition reaction of the single salts $NaNO_3$ and KNO_3 has been thoroughly studied.[2–6] The concensus is that the principal mode of thermal decomposition is given by reaction 1. At temperatures greater than about 700 °C, further decomposition takes place with the evolution of the oxides of nitrogen.[2,3,7] However, with the exception of a very limited study by Kust and Burke[8] over the temperature range 295–340 °C intrinsic reactions in equimolar $NaNO_3$–KNO_3 have not been studied, particularly over the temperature range 500–600 °C.

For a number of years the chemical behavior of the nitrate ion was interpreted on the basis of the Lux–Flood acid–base concept. That is, the nitrate ion was postulated to be a Lux–Flood base that dissociated to produce the conjugated acid (nitronium ion) and oxide

$$NO^{3-} \rightleftarrows NO_2^+ + O^{2-} \qquad (2)$$

The nitronium ion has never been directly observed in low temperature (250–300 °C) nitrate melts although the results of emf studies have been interpreted as evidence of its existence and an equilibrium constant for reaction 2 has been calculated from these measurements: 6×10^{-24} at 300 °C.[9]

In addition to these reactions, the existence of species such as peroxide and superoxide have been postulated. It is suggested that the reactions (3)–(6) take place, depending on the

$$O^{2-} + NO_3^- \rightleftarrows O_2^{2-} + NO_2^- \qquad (3)$$

$$O_2^{2-} + 2NO_3^- \rightleftarrows 2O_2^- + 2NO_2^- \qquad (4)$$

$$O^{2-} + {}^{1}/{}_{2}O_2 \rightleftarrows O_2^{2-} \qquad (5)$$

$$O_2^{2-} + O_2 \rightleftarrows 2O_2^- \qquad (6)$$

experimental conditions. These reactions have not received complete acceptance;[10] the pertinent literature has been reviewed by Zambonin[11] and Burke and Kerridge.[12]

Like the nitrate ion, the nitite ion has been treated as a Lux–Flood base. The dissociation of the nitrite ion has been postulated to occur with the formation of the nitrosonium ion and oxide

$$NO_2 \rightleftarrows NO^+ + O^{2-} \qquad (7)$$

As in the case of the nitronium ion, the nitrosonium cation has not been directly observed. Its existence has been inferred from emf measurements and an equilibrium constant determined. Because the dissociation constant for this reaction is significantly larger than that for reaction 2 (1×10^{-9} vs. 6×10^{-24} at 300 °C),[9] reaction 7 could be considered to be a significant source of oxide ion. If we assume that the heat of reaction for reaction 7 is the same as that for reaction 2 and use the equilibrium value of the concentration of the nitrite ion at 600 °C (vide infra), the oxide ion concentration resulting from reaction 7 is found to be $\sim 10^{-8}$ mol/kg. Consequently, it appears that neither reaction 2 nor reaction 7 is significant at temperatures between 500 and 600 °C. At higher temperatures then employed in this study (650–700 °C) thermal decomposition of the nitrite ion can be expected to occur with the formation of oxide and superoxide.[2]

In this study we have determined the principal chemical species produced in equimolar $NaNO_3$–KNO_3 and measured their concentration dependence on time and composition of the atmosphere over the temperature range 500–600 °C. From these data, the enthalpy, entropy, and free energy for reaction 1 were determined as well as the rate of oxidation of nitrite and the activation energy for that reaction.

Experimental Process

In previous studies the composition of the $NaNO_3$–KNO_3 melt was inferred from analysis of the gas phase.[2–6] In this investigation, reaction products were identified and studied by taking samples of the $NaNO_3$–KNO_3 melt periodically and chemically analyzing their composition. The reason for this approach is that we have found at temperatures in excess of 500 °C a thin film of molten salt will form over the insde of the experimental apparatus. This behavior is a consequence of the ability of these salts to wet and spread spontaneously over almost any surface they contact. Whenever this salt film comes in contact with such materials as stainless steel or quartz at temperatures >500 °C, there is extensive corrosion with the liberation of nitrogen oxides, e.g.

$$Cr + 2NO_3^- \rightleftarrows CrO_4^{2-} + 2NO \qquad (8)$$

$$SiO_2 + 2NO_3^- \rightleftarrows SiO_4^{2-} + 2NO_2 \qquad (9)$$

The presence of these corrosion product gases could lead to erroneous conclusions regarding reactions taking place in the melt.

Figure 1 is an illustration of the experimental apparatus used in the equilibrium chemistry studies. So that reactions could be avoided between the nitrate melt and the container which might affect the results, the melts were held in a gold crucible. The chromel–alumel thermocouple used to monitor the melt temperature was sheathed in gold, and the gas inlet tube was made from recrystallized alumina. There was no visual evidence of a reaction between any of these materials and the nitrate melt in either oxygen or argon, even at 600 °C and in experiments that lasted in excess of 200 h. Furthermore, once equilibrium had been attained, no systematic variation in the nitrate concentration could be detected (Figure 2). The crucible was contained in a flanged stainless-steel vessel with a removable quartz liner. The liner was added to decrease corrosion of the vessel. The stainless-steel top had various compression fittings that secured the thermocouple and gas-inlet and -outlet tubes and permitted their vertical movement while maintaining the integrity of the atmosphere. A separate fitting allowed melt samples to be withdrawn. The top was maintained at room temperature by means of a chilled-water cooling collar.

Dependence of the reaction rate on mass transport of reactants during the kinetics experiments was eliminated by the use of a specially designed aluminum centrifugal agitator coupled with high gas flow rates. The centrifugal agitator was driven at 2500 rpm by a Caframo Type RZR1 motor. A Teflon sleeve, which was press-fit into a stainless-steel fitting on the vessel top, provided a gastight seal as well as a bearing surface for the agitator.

All the gases used in this study were carefully purified before being admitted to the reaction vessel. High-purity argon was passed through a heated titanium bed to remove oxygen and water and then through an Ascarite column to remove any carbon dioxide. Oxygen, which was reagent quality, was also passed through an Ascarite column. So that back-diffusion of atmospheric gases could be prevented, the effluent gas was passed through a sulfuric acid bubbler. In addition to careful purification of the gases, all the salts used in this program were routinely purified by recrystallization from distilled H_2O.

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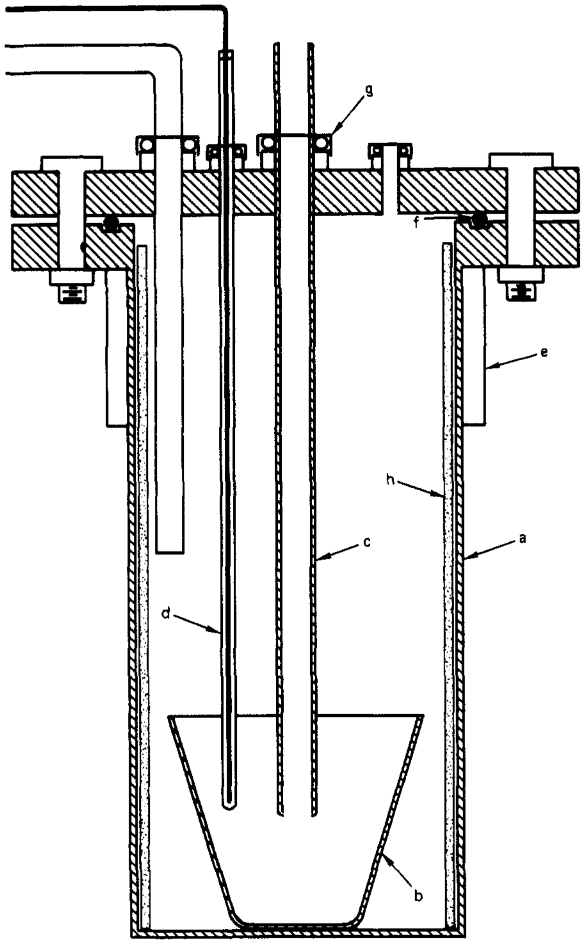

Figure 1. Experimental apparatus: (a) stainless-steel vessel (diameter 7.6 cm, height 38 cm); (b) gold crucible; (c) alumina gas-inlet tube; (d) gold-sheathed thermocouple; (e) chilled-water cooling collar; (f) copper gasket; (g) Cajon-Ultratorr compression fittings; (h) quartz sleeve.

Following recrystallization, $NaNO_3$ and KNO_3 were stored in a vacuum oven at 150 °C.

The approach taken in this investigation was to generate various concentrations of nitrite by holding a $NaNO_3$–KNO_3 melt at the selected experimental temperature while argon was bubbled through the melt until a predetermined nitrite level was reached, as determined by chemical analysis of the melt. Once this nitrite concentration had been reached, the argon was replaced by oxygen, or an oxygen–argon mixture if the influence of oxygen pressure was being studied. In those cases where the influence of oxygen partial pressure was being studied, the oxygen partial pressure was considered to be equal to its concentration in an oxygen–argon mixture. The flow rates of oxygen and argon were measured and controlled within 1% by a set of Tylan Model FC-260 flow controllers. The total gas flow rate was 100 mL/min for the equilibrium experiments. During the kinetic experiments the total gas flow rate was 600–800 mL/min.

Samples of the melt were taken with a quartz pipet at periodic intervals in order to determine the chemical species, other than nitrite, present in the melt and their concentrations. These samples were weighed and dissolved in distilled H_2O, and the pH was measured. If any of the several oxygen species previously discussed (oxide, peroxide, superoxide) were present in the melt sample, they would be detected because of hydrolysis and their concentration could be determined by a conventional acid–base titration. In no case did we find evidence for any of these oxygen species.

A titrimetric method was developed to determine the nitrite concentration. Rather than the conventional method employing $KMnO_4$, we used Ce(IV) as the oxidizing agent.[13,14] An excess of $Ce(NH_4)_2(NO_3)_6$ in 2 N HNO_3 was added to the dissolved sample. The unreacted cerium was then back-titrated with 0.1 N $Na_2C_2O_4$ with ferrous *o*-phenanthroline as the indicator. This method of analysis for nitrite offers several advantages over the more traditional method using $KMnO_4$. In the first place, nitrites do not react with $KMnO_4$ in a neutral or alkaline medium; consequently, it is necessary to acidify the solution. This generally results in low values because the nitrous acid formed is unstable and volatile. Even if acidified $KMnO_4$ is added to the nitrite solution, the reaction between $KMnO_4$ and nitrite is slow enough that some loss of nitrite can occur as a consequence of the formation of nitrous acid. Furthermore, acidic $KMnO_4$ solutions are unstable and must be frequently standardized. Acidified ceric salt solutions, on the other hand, are quite stable and $Ce(NH_4)_2(NO_3)_6$ can be obtained in primary standard purity. Ceric ammonium nitrate is a more powerful oxidizing agent than potassium permanganate, and the reaction between cerium(IV) and nitrite appears to be very rapid; consequently, there is very little, if any, loss of nitrite due to the formation of nitrous acid mixtures. The titration error is about 1.5%. This analytical method is discussed in more detail elsewhere.[13] In addition to direct chemical analysis, several melt samples were analyzed by X-ray diffraction. Only nitrate and nitrite were found to be present.

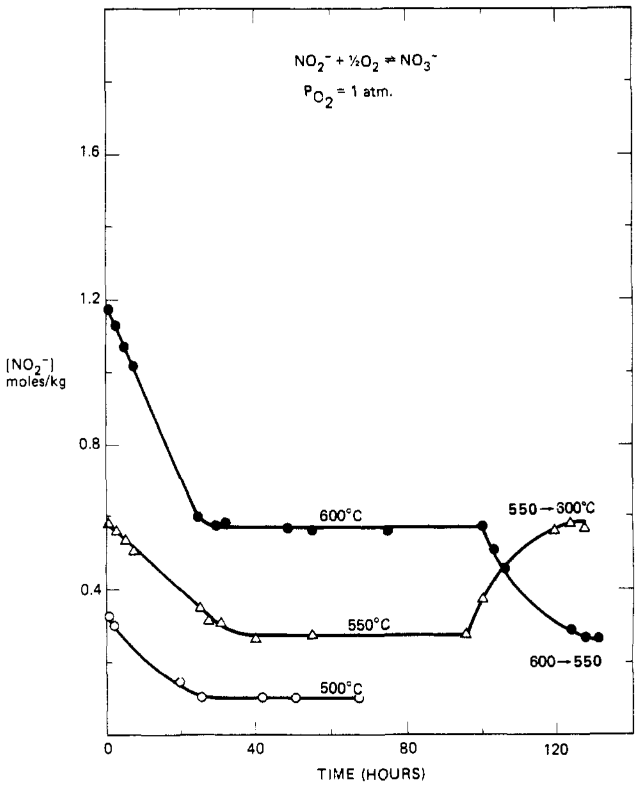

Figure 2. Nitrite concentrations vs. time at 500, 550, and 600 °C. (At 100 h the temperature is changed in the direction indicated and equilibrium reestablished.)

Results

Equilibrium Chemistry. None of the melt samples showed evidence of any anionic oxygen species, i.e., O^{2-}, O_2^{2-}, or O_2^-. This means that, if any of these species were indeed present, their concentration would have to be less than 10^{-5} mol/kg; the lower detection limit of the pH measurements. Therefore, we conclude that reaction 1 represents the predominant, if not the only, reaction that is intrinsic to the $NaNO_3$–KNO_3 melt over the temperature range 500–600 °C. Figure 2 shows typical variations in the nitrite concentration with time at 500, 550, and 600 °C at P_{O_2} = 1 atm. Also shown in Figure 2 is the effect of increasing or decreasing the temperature after equilibrium had been reached. It can be seen that once

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Table I. Equilibrium Constant for the Oxidation of of Nitrite (P_{O_2} = 1 atm)

T, °C	K, $atm^{-1/2}$	T, °C	K, $atm^{-1/2}$
500	100.0	600	18.6
550	40.3	620	12.5

Table II. Nitrate/Nitrite Equilibrium Constant as a Function of Oxygen Partial Pressure

T, °C	P_{O_2}, vol %	$[NO_2^-]$, mol/kg	K, $atm^{-1/2}$
550	100	0.26	40.3
550	21 (air)	0.56	40.0
600	100	0.55	18.6
600	80	0.58	19.9
600	60	0.71	18.5
600	40	0.88	18.0
600	20	1.13	19.4
600	21 (air)	1.13	18.9

equilibrium was achieved, the nitrite concentration was very stable even for extended periods of time. Furthermore, the same value of the nitrite concentration is attained at equilibrium regardless of the direction. From these data it is possible to calculate the equilibrium constant for reaction 1 which we rewrite as

$$NO_2^- + {}^1/_2O_2 \rightleftarrows NO_3^- \qquad (1a)$$

For this reaction the equilibrium constant is given as

$$K = \frac{[NO_3^-]}{[NO_2^-]}P_{O_2}^{-1/2} \qquad (10)$$

where $[X_i]$ represents the concentration of X_i.

The substitution of concentration for activity in eq 10 is only justifiable if the solution is ideal. Heat of mixing studies have shown that the $NaNO_3$–KNO_3 system exhibits essentially random mixing on the cation sublattice.[16] Therefore, we may consider $NaNO_3$–KNO_3 to behave as an ideal solution.

Values of the equilibrium constant for reaction 1a, calculated from the analytical data at P_{O_2} = 1 atm, are listed in Table I. Each value of the equilibrium constant is the average of at least three values. The uncertainty in K is 2%.

In addition to studies of the effect of temperature on the intrinsic reactions of the equimolar binary NaNO–KNO mixture, the influence of oxygen partial pressure on these reactions was examined. As in the case where P_{O_2} = 1 atm, we found no evidence of formation of any anionic oxygen species as the partial pressure was varied. That is, reaction 1 still represents the principal reaction in this molten salt system at oxygen partial pressures less than 1.0 atm. This being the case, the expression for the equilibrium constant, eq 10, should still be valid. In Table II the value of K, calculated from the equilibrium values of the nitrite and nitrate concentrations, for various partial pressures of oxygen at 550 and 600 °C is shown. It can be seen from these data that at a given temperature K is indeed constant regardless of the oxygen partial pressure.

Figure 3 is a plot of the logarithm of the ratio of the nitrate to nitrite concentrations against the logarithm of the volume fraction of oxygen in the gas stream at 600 °C. Linear regression analysis of these data gives a slope of 0.5 with a correlation coefficient of 0.994. The equilibrium constant K is thus directly proportional to $P_{O_2}^{-1/2}$. These data support the conclusion that reaction 1 represents the predominant reaction in the equimolar $NaNO_3$–KNO_3 melt between 500 and 600 °C in the absence of H_2O and CO_2.

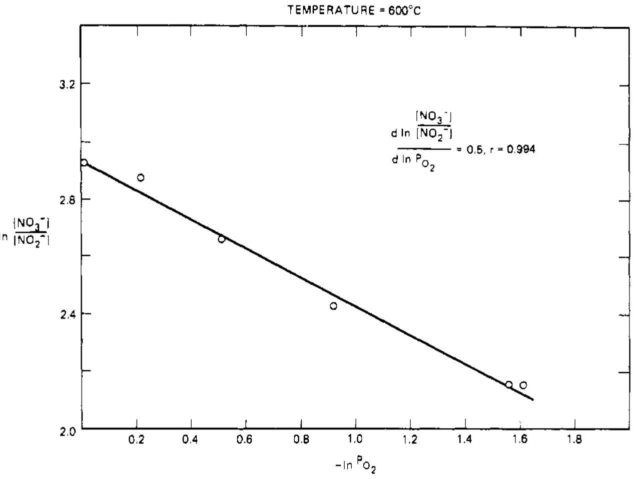

Figure 3. Logarithm of the nitrate: nitrite ratio vs. logarithm of the oxygen partial pressure.

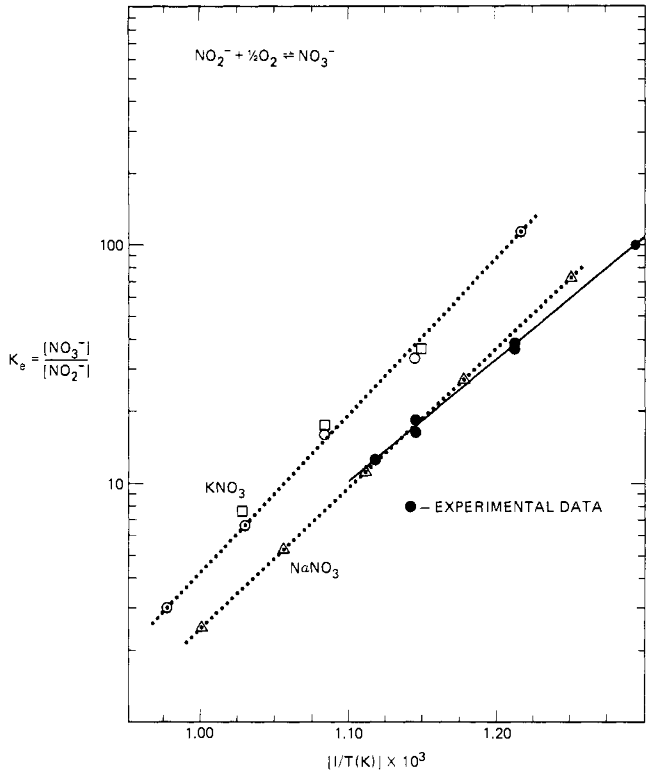

Figure 4. Nitrate–nitrite equilibrium constant vs. 1/[T (K)].

In Figure 4 the values of K, derived from the experimental data, are plotted against 1/[T (K)]. From these data the standard free energy of reaction 1a is given by

$$\Delta G^\circ \text{ (kcal/mol)} = 23\,000 + 20.6[T\text{ (K)}] \qquad (11)$$

No other evaluation of the thermodynamics of reaction 1 in $NaNO_3$–KNO_3 over the temperature range 500–600 °C has been published. Therefore, we are unable to compare our results with extant literature values. These data are, however, consistent with phase stability calculations that have been made by Nagelberg.[17] Literature values for the equilibrium constant for reaction 11 for the pure components KNO_3 and $NaNO_3$[3,4] are included in Figure 4. It can be seen that the data for the binary $NaNO_3$–KNO_3 mixture compares favorably with that for the pure components.

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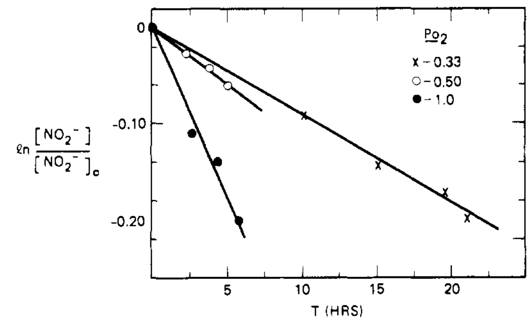

Figure 5. Logarithm of the fraction of nitrite reacted vs. time. T = 404 °C.

Table III. Forward Rate Constants for the Oxidation of Nitrite of Nitrite (T = 404 °C)

P_{O_2}, atm	10^6k_1, s^{-1}	P_{O_2}, atm	10^6k_1, s^{-1}
1.0	9.17	0.50	6.66
0.67	6.22	0.33	8.42

Reaction Kinetics. From measurement of the changes in oxygen gas pressure Freeman[2] has shown that over the temperature range 600–800 °C, the rate of oxidation of sodium and potassium nitrites (reaction 1a) may be described in terms of a simple reversible reaction with a first-order dependence on nitrite concentration. Using a similar technique, Paniccia and Zanibonin[18] have determined that the rate of this reaction in a $NaNO_3$–KNO_3 matrix is overall second order with respect to both oxygen and nitrite. On this basis, the reaction rate may be written as

$$-d[NO_2^-]/dt = k_1[NO_2^-][O_2] - k_{-1}[NO_3^-] \quad (12)$$

From the stoichiometery shown in reaction 1a it follows that

$$[NO_2^-] + [NO_3^-] = [NO_2^-]_0 \quad (13)$$

and then

$$-d[NO_2^-]/dt = [NO_2^-](k_1[O_2] + k_{-1}) - k_{-1}[NO_2^-]_0 \quad (14)$$

and

$$[NO_2^-] = [NO_2^-]_0 \exp[(-k_1[O_2] - k_{-1})t] - \left(\frac{k_{-1}}{k_1}\right)\frac{[NO_2^-]_0}{[O_2] + \left(\frac{k_{-1}}{k_1}\right)}\{\exp[(-k_1[O_2] - k_{-1})t] - 1\} \quad (15)$$

Over the temperature range of these experiments (400–500 °C, the equilibrium constant for reaction 1a, $K - k_1/k_{-1}$, ranges from 1000 to 100 (vide supra) so that the quotient $k_{-1}/k_1 \cong 0$; i.e., $k_1 >> k_{-1}$. Thus, at high oxygen levels eq 15 may be reduced to

$$[NO_2^-] \cong [NO_2^-]_0 \exp(-k_1[O_2]t) \quad (16)$$

or

$$\ln\frac{[NO_2^-]}{[NO_2^-]_0} = k_1[O_2]t \quad (17)$$

Figure 5 shows the experimentally measured values of the fraction of nitrite reacted as a function of time at 404 °C and various oxygen partial pressures. The values of the pseudo-first-order rate constant k_1 calculated from these data are shown in Table III. The rate of decrease of the nitrite concentration was also determined at 453 and 502 °C. As was the case at 404 °C, the logarithm of the fraction of nitrite reacted was a linear function of time at constant oxygen partial pressure. From these data the assumed first-order dependence of the oxidation of nitrite with respect to both nitrite and oxygen in a $NaNO_3$–KNO_3 matrix over the temperature range 400–500 °C was confirmed.

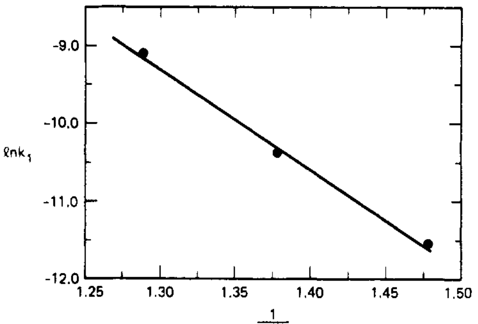

Figure 6. Logarithm of the forward rate constant vs. $1/[T$ (K)].

Table IV. Forward and Reverse Rate Constants for the Reaction

$$NO_2^- + {}^1/_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3^- \quad (P_{O_2} = 1 \text{ atm})$$

T, °C	10^5k_1(exptl), s^{-1}	$k_{-1}(k_1/K) \times 10^7$, s^{-1}
404	0.92	0.11
453	3.2	1.18
502	12.2	12.4

Figure 6 shows a plot of the logarithm of the rate constants determined from these data vs. $1/[T(K)]$. From these data an activation energy of 26.4 kcal/mol is obtained. This value falls midway between the activation energy Freeman measured for the oxidation of KNO_2(l) (34.3 kcal/mol) and $NaNO_2$(l) (20.7 kcal/mol)[2] is in agreement with that of Paniccia and Zambonin for the oxidation of nitrite in $NaNO_3$–KNO_3 (23.2 kcal/mol).[18] On the other hand, the values for k_1 deduced from this study are a factor of 10 greater than those reported by Paniccia and Zambonin.[18]

There are two possible explanations for this pronounced difference in value of the forward rate constant for the oxidation nitrite. The relevant values of Henry's law constant used to transform the second-order constant to the pseudo-first-order rate constant may be incorrect.[18] But we consider this to be unlikely. The most probable explanation for this discrepancy involves mass transport effects. We found, as discussed earlier, that considerable care had to be exercised in experimental design in order to eliminate oxygen mass transport as the rate-controlling step. It was only by the use of a specially designed agitator driven at high speed coupled with high gas flow rates that we were able to eliminate oxygen mass transport effects and achieve values of k_1 that were reproducible and that did not vary with oxygen flow rate, within prescribed limits. To test this hypothesis, we conducted a series of experiments in which the agitator was eliminated and the oxygen gas flow rate reduced to less than 400 mL/min. The rate constants derived from these experiments were within 5% of the published values for k_1 for the oxidation of nitrite.[18] Consequently, the reason for the discrepancy between our values for the forward rate constant for the oxidation of nitrite and previously published values appears to be the presence of mass transport limitations in the earlier work.

Since the rate constants for the oxidation of nitrite and the thermal decomposition of nitrate, reaction 1a, are related by the expression

$$K = k_1/k_{-1}$$

it is possible to calculate values for k_{-1}, the rate constant for the thermal decomposition of nitrate, from the experimentally

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[18] Paniccia, F.; Zambonin, P. G. *J. Phys. Chem.* **1973**, *77*, 1810.

measured values of k_1. These are shown in Table IV as a function of temperature.

Examination of the data shown in Table IV indicates that over the temperature range which this study of the kinetics of the oxidation of nitrite was done the reverse reaction, the thermal decomposition of nitrate to form nitrate and oxygen could be ignored. It must be kept in mind, however, that at temperatures above 500 °C the value of k_{-1}, the reverse rate constant, begins to approach k_1 and this assumption is no longer valid.

Conclusion

We have shown that the principal intrinsic reaction in the equimolar binary $NaNO_3$–KNO_3 system over the temperature range 500–620 °C is the thermal decomposition of the nitrate ion to form nitrite and oxygen. The ratio of nitrate to nitrite has been shown to be proportional to $P_{O_2}{}^{1/2}$, indicating that this reaction scheme is unchanged as the oxygen partial pressure varies. Using the data from these experiments, we have been able to calculate the enthalpy, entropy, and free energy for this reaction. These data are in good agreement with similar thermodynamic data for the single salts.

The kinetics of the oxidation of nitrite in $NaNO_3$–KNO_3 have also been studied over the temperature range 400–500 °C. This reaction has been shown to be second order overall, first order with respect to both nitrite concentration and oxygen partial pressure. The implication of the first-order dependence on oxygen is that oxygen does not dissociate prior to reaction with nitrite. The activation energy for this reaction, calculated from the temperature dependence of the rate constants, was found to be 26.4 kcal/mol. Discrepancies in values of the forward rate constant between this work and earlier published studies were attributed to limitations on the oxidation rate imposed by mass transport of oxygen in the latter.

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1,4-Bis(2,5,5-tris(carboxymethyl)-2,5-diazapentyl)benzene (PXED3A): Synthesis, Binuclear Chelating Tendencies, and Iron(III) μ-Oxo Bridge Formation

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The synthesis of a new decadentate binucleating ligand 1,4-bis(2,5,5-tris(carboxymethyl)-2,5-diazapentyl)benzene (PXED3A, H_6L) and its aqueous equilibria with Cu(II), Co(II), Ni(II), Zn(II), Fe(II), and Fe(III) are described. At 25 °C and 0.100 M ionic strength, the logarithms of the protonation constants for PXED3A are 10.50, 9.83, 5.74, 4.77, 3.00, 2.29, 1.72, 1.2, ~0.9, and ~0.5. The logarithms of the formation constants [ML]/[M][L] of the chelates having a 1:1 molar ratio of metal ion to ligand were found to be as follows: Cu(II), 18.0; Co(II), 15.88; Ni(II), 17.1; Zn(II), 15.93; Fe(II), 13.54. The 1:1 Fe(III) metal–chelate stability constant is estimated to be $10^{21\pm2}$ from the potentiometric data and the Fe(II)/Fe(III) redox potential. Stability constants of the protonated 1:1 chelates, MHL, MH_2L, MH_3L, and MH_4L, are also reported. The logarithms of the formation constants $[M_2L]/[M]^2[L]$ of binuclear chelates of divalent and trivalent metal ions were found to be as follows: Cu(II), 33.6; Co(II), 29.20; Ni(II), 23.2; Zn(II), 29.30; Fe(II), 25.38; Fe(III), 39.03. A spectrophotometric study of the Fe(III)–PXED3A system indicated formation of an intramolecular μ-oxo-bridged species above pH 3.5. Protonation constants for the 1:1 and 2:1 hydrolyzed complexes have also been determined. Probable ligand-bonding sites in the complexes are proposed, and their stabilities are compared with those formed from analogous chelating agents.

Introduction

Binuclear metal complexes have received considerable attention recently. By appropriate adjustment of the ligand backbone, a binucleating ligand is capable of coordinating two metal ions in such a way that both the distance and geometry between the two metal centers are suitable for binding of selected bridging molecules or anions. Binuclear complexes of this type can provide interesting models for studying catalytic reactions of biological systems in which concerted effects of both metal ions are involved.

Several types of binucleating ligands have been reported in the literature. Macrocyclic ligands having relatively rigid structures such as the cryptate compounds reported by Lehn and co-workers[2,3] and the binuclear "face-to-face" metalloporphyrins reported by Collman et al.,[4] in which metal ions are contained in a molecular cavity, provide high selectivity for metal ions and substrates. Another approach incorporates a rigid bridge such as a *p*- or *m*-xylene group in the ligand framework.[5-8] The metal–metal distance in these "wishbone" type binuclear complexes, first reported by Taqui Khan and Martell,[9] is such that a mono- or polyatomic bridging donor group can be bonded to both metal centers. Binuclear copper(I) complexes with a *p*-xylyl or *m*-xylyl backbone were reported to bind dioxygen reversibly[5-7] or to react with dioxygen to hydroxylate the xylyl ligand.[8] The present investigators reported the synthesis of a xylyl-bridged bis-terdentate

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