Contribution from the Department of Chemistry,
University of Utah Salt Lake City, Utah 84112, U.S.A.

Oxalate Oxidation in Molten Sodium Nitrite[1]

J. D. Burke and R. N. Kust

Received December 19, 1969

The stoichiometry for the oxidation of oxalate ion by molten sodium nitrite has been determined by both qualitative and quantitative methods. The stoichiometry has been found to be given by the variable equation:

$$aC_2O_4^{2-}+(a+\alpha)NO_2^- = \frac{(a-\alpha)}{2}CO_2+\frac{(3a+\alpha)}{2}CO_3^{2-}$$

$$+2\alpha NO+\frac{(a-\alpha)}{2}N_2O$$

A sequence of reactions involving hyponitrite type intermediates and conforming to the observed stoichiometry is proposed as a possible route for the formation of the nitrogenous products observed.

Introduction

Only recently has it been recognized that oxalate ion is oxidized by the nitrate ion when placed in an alkali metal nitrate melt[2] contrary to earlier reports or assumptions of the thermal decomposition of oxalate ion in such melts.[3] In the course of studying the kinetics of oxalate ion oxidation in alkali metal nitrate melt[2c] it was found that nitrite ion, the reduced nitrogen product, also reacted with oxalate ion. Since the reaction between oxalate ion and nitrite ion was found to be sufficiently rapid to alter the simple first order kinetics in oxalate ion for the rate of disappearance of oxalate ion in a nitrate melt, it became of interest to determine the nature of the reaction between the oxalat ion and the nitrite ion. This report is the result of the study of the oxidation of the oxalate ion in a molten sodium nitrite melt.

Experimental Section

Chemicals. The reagent grade sodium nitrite used in the experiments was recrystallized from redistilled water and dried at 200° under a vacuum of less than $5 . 10^{-3}$ torr for at least 12 hours prior to use. Analytical reagent grade potassium oxalate was dried at 110° and used without further purification. Other chemicals were of either reagent grade or analytical reagent grade quality according to their usage.

Procedure. A reaction vessel containing approximately 10.0 grams of sodium nitrite and 0.5 to 1.0 grams of potassium oxalate was connected to either a gas collection bulb or a 10 cm gas IR cell depending on the type of analysis, mass spectral or infrared, to be made on the gaseous reaction products. The system was then evacuated to less than 1.0×10^{-2} torr and the reaction started by heating the reaction vessel to just above the melting point of sodium nitrite. Gases were rapidly evolved from the molten mixture as evidenced by the frothing within the reaction vessel.

The qualitative analyses of the gases evolved were made using either a CEC 21-110 high resolution mass spectrometer or a Beckman IR-5 spectrophotometer. The cooled reaction mixture was dissolved in redistilled water and analyzed by standard methods.

The gaseous products of the reaction were quantitatively analyzed using a gas train containing the following essential features and in the order given: a gas absorption tower containing a solution of sodium dithionite in 10% aqueous potassium hydroxide to remove any oxygen which might be present in the nitrogen flush gas; an anhydrous magnesium perchlorate drying tube; the reaction vessel; another drying tube; two gas absorption towers containing a solution of concentrated nitric acid in concentrated sulfuric acid to absorb the nitric oxide;[4] another drying tube; an Ascarite gas absorption tube to absorb the carbon dioxide; and, lastly, a cold trap of known volume which is immersed in liquid nitrogen in order to freeze out the nitrous oxide.

Since any oxygen present in the gas would oxidize nitric oxide to nitrogen dioxide, the assembled gas train was flushed with nitrogen for several hours to expel any oxygen which might be present. The reaction vessel containing sodium nitrite was then immersed in a molten salt bath at the desired temperature. The potassium oxalate, which had been contained in a side arm connected to the reaction vessel, was added to the molten sodium nitrite by tilting the reaction vessel and gently tapping the side arm. Although all of the weighed potassium oxalate could not be added to the reaction mixture by this procedure, this method of adding the potassium oxalate to the sodium nitrite melt was necessary in order to prevent having to open the reaction vessel to the air. Comparison of the

---

[1] Presented in part at the 158th National ACS Meeting, eNw York, September, 1969.

[2] [a] A. M. Shams El Din, A. A. El Hosary, *Electrochim. Acta*, *13*, 135 (1968). [b] J. M. Schlegel, C. A. Pitak, private communication. work done in this laboratory to be submitted for publication.

[3] [a] H. S. Swofford, P. G. McCormick, *Anal. Chem.*, *37*, 970 (1965). [b] P. G. McCormick, H. S. Swofford, *Anal. Chem.*, *41*, 149 (1969). [c] N. Coumert, M. Porthault, J. C. Merlin, *Bull. Soc. chim.*, *1967*, 332.

[4] G. C. Whitnack, C. I. Holford, E. St. C. Gantz, G. B. L. Smith, *Anal. Chem.*, *23*, 464 (1951).

carbon dioxide and carbonate ion produced to the oxalate ion added indicated that about 2% of the weighed potassium oxalate remained in the side arm or on the walls of the reaction vessel and was not oxidized. The gases produced were carried though the gas train by a continuous stream of nitrogen.

The nitric oxide trapped in the nitric acid-sulfuric acid gas absorption towers was titrated as nitrosyl hydrogen sulfate as previously described[4] with the exception of using cerium(IV) as the titrant rather than permanganate. The carbon dioxide collected in the Ascarite gas absorption tube was determined from the increase in weight of the absorption tube. The nitrous oxide frozen out in the trap was determined by evacuating the trap and a vacuum manifold of known volume and measuring the pressure developed in the system after removing the liquid nitrogen dewar and allowing the trap to warm to room temperature.

The carbonate ion produced in the reaction was determined by potentiometric titration of a solution of the cooled reaction mixture with standard hydrochloric acid. Only the carbonate-bicarbonate end point was of use because of the high concentration of unreacted nitrite ion present.

Results and Discussion

Infrared and mass spectral analyses of the gaseous reaction products showed that carbon dioxide, nitrous oxide, and nitric oxide were the only gases produced when oxalate ion was added to a sodium nitrite melt. Resolution of the mass spectrum peak at mass number 44 showed that carbon dioxide and nitrous oxide were present in nearly equal amouts. Using relative exstinction coefficients calculated from the work of Pierson, Fletcher, and Gantz,[5] quantitative evaluation of the infrared spectra of two runs showed the ratio of nitrous oxide partial pressure to carbon dioxide partial pressure to be 1.02. The mass spectrum showed a peak at mass number 28, which could be resolved into two peaks. These two peaks indicated the presence of nitrogen and carbon monixide. The relative intensities of the mass spectral peaks at a mass number of 44 and 28 were approximately 4 to 1. If one assumes nitrous oxide and carbon dioxide to be present in equal amouts, the ratio of the two intensities would be approximately 4.5 to 1, based on predetermined fragmentation patterns. Thus it may be concluded that the N_2^+ and CO^+ ions observed are due to the fragmenting of nitrous oxide and carbon dioxide. carbon monoxide being products of the reaction. The absence of carbon monoxide was further substantiated by the fact that no doublet was observed around 2100 cm^{-1} in the infrared spectra of the gaseous products. Carbonate ion was identified as a reaction product by adding freshly filtered barium hydroxide to an aqueous solution of the cooled reaction mixture and obtaining a white precipitate which evolved carbon dioxide on dissolving the precipitate in dilute hydrochloric acid.

Chemical handbooks generally list 320°C as the decomposition temperature of sodium nitrite. Since nitric oxide can be a product of the thermal decomposition of sodium nitrite, it was necessary to determine if a measurable amount of nitric oxide was produced by the decomposition of the melt under the conditions of this study. About 10.0 grams of molten sodium nitrite at 375°C was purged with nitrogen for 2 hours. The effluent gases were led through a gas analysis train similar to that described above. There was no indication that any nitric oxide or nitrous oxide was produced. By extrapolating the kinetic data of Bond and Jacobs,[6] it is estimated that less than 0.002% of the sodium nitrite would decompose in 2 hours at 375°C. It is not surprising then, that neither nitric oxide nor nitrous oxide could be detected after 2 hours. Thus it can be concluded that the nitric oxide and nitrous oxide produced when potassium oxalate is added to molten sodium nitrite comes from the reduction of nitrite ion by oxalate ion and not from thermal decomposition of the melt

From the identified products, the oxidation of oxalate ion in fused sodium nitrite may be written in general as

$$aC_2O_4^{2-}+(a+\alpha)NO_2^- = bCO_2+cCO_3^{2-}+dNO+eN_2O$$

By making use of mass balance, charge balance, and oxidation-reduction balance equations, equation (1) may be written to represent the stoichiometry of the reaction.

$$aC_2O_4^{2-}+(a+\alpha)NO_2^- = \frac{(a-\alpha)}{2}CO_2+\frac{(3a+\alpha)}{2}CO_3^{2-}+ 2\alpha NO+\frac{(a-\alpha)}{2}N_2O \qquad (1)$$

By experimentally determining any two reaction products, with the exception of the combination carbon dioxide and nitrous oxide, a and α may be determined and the amounts of the remaining two products calculated. These calculated quantities can then be compared to the experimentally determined values for verification of equation (1). Such a comparison is given in Table I for several temperatures. The good agreement between the measured amounts of nitrous oxide and carbonate ion produced and the expected amounts, as calculated from the measured amounts of nitric oxide and carbon dioxide confirms that the oxidation of oxalate ion by fused sodium nitrite follows the variable stoichiometry given by equation (1).

Oxidation of Oxalate Ion by Nitrite Ion in Molten Sodium Nitrite

	290°	335°	377°
CO_2, mmole	1.91	1.85	2.05
NO, mmole	2.96	2.60	2.69
CO_3^{2-}, mmole, obs.	8.67	8.16	9.00
CO_3^{2-}, mmole, calcd.[a]	8.69	8.15	8.97
N_2O, mmole, obs.	1.92	1.85	2.08
N_2O, mmole, calcd.[a]	1.91	1.85	2.05
N_2O/NO	1.54	1.40	1.27

[a] Based upon the CO_2 and NO measured experimentally, these are the values expected for CO_3^{2-} and N_2O.

---

[5] R. H. Pierson, A. N. Fletcher, and E. St. Gantz, *Anal. Chem.*, *28*, 1218 (1956).

[6] B. D. Bond and P. W. M. Jacobs, *J. Chem. Soc.* (*A*), *1966*, 1265.

The variable stoichiometry results from the occurrence of two different intermediate species which arise from the reduction of the nitrite ion. As shown in Table I, the ratio of the nitrous oxide produced to the nitric oxide produced decreases with increasing temperature. This variation indicates that the nitrous oxide and nitric oxide are formed by different reaction paths and not by a common path involving an intermediate such as N_3O_2. Also the path producing nitric oxide must have a higher activation energy than the path producing nitrous oxide.

It is of interest to note that in the oxidation of oxalate ion by sodium nitrite there is no nitrogen evolved whereas in the oxidation of acetate ion by molten sodium nitrite nitrogen has been observed as a reaction product by Kozlowski and Bartholomew[7] and by the present authors in unpublished work.

Although there are several reasonable reaction sequences which will lead to the stoichiometry observed, the simplest reaction sequence is given by the following equations.

$$aC_2O_4^{2-} + aNO_2^- = 2aCO_2 + aO^{2-} + aNO^- \qquad (2)$$

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

$$(a-\alpha)NO^- = \left(\frac{a-\alpha}{2}\right)N_2O + \left(\frac{a-\alpha}{2}\right)O^{2-} \qquad (4)$$

$$\left(\frac{3a+\alpha}{2}\right)CO_2 + \left(\frac{3a+\alpha}{2}\right)O^{2-} = \left(\frac{3a+\alpha}{2}\right)CO_3^{2-} \qquad (5)$$

If it is assumed then that there is no net formation of the monomeric hyponitrite ion, NO^-, and that all of the oxide ion reacts with carbon dioxide to form carbonate ion, the above reactions, when added together, give equation (1).

Although being highly speculative, the reaction path proposed above is preferable to those involving nitrogen oxides for the following reasons, other than being a simpler reaction sequence: Reactions (3) and (4) could lead to the formation of the hyponitrite type intermediates $N_2O_3^{2-}$ and $N_2O_2^{2-}$, respectively. Trace amounts of the hyponitrite ion, $N_2O_2^{2-}$, have been identified as being present when certain metals are oxidized by molten alkali metal nitrates[8] and the hyponitrite ion is known to decompose in the presence of carbon dioxide, a reaction product of this study, to yield nitrous oxide and carbonate ion. Analogously, the oxyhyponitrite ion, $N_2O_3^{2-}$, could be expected to decompose in the presence of carbon dioxide to yield nitric oxide and carbonate ion. Also, a reaction sequence involving nitrogen oxides would be contrary to the kinetic data for the oxidation of oxalate ion by nitrite ion in a nitrate melt solvent obtained in this laboratory.[2c]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

(7) T. R. Kozlowski, R. F. Bartholomew, *Inorg. Chem.*, *7*, 2247 (1968).

(8) B. J. Brough, D. H. Kerridge, *Inorg. Chem.*, *4*, 1353 (1965).