conversion was due to a competing reaction, thermal decomposition of lithium aluminum hydride.

Hydrogenation of Boric Oxide in Trimethylamine.—A stainless steel shaker tube of 400-ml. capacity was charged with 12.5 g. (0.18 mole) of boric oxide, 20 g. (0.74 g.-atom) of aluminum, 10 g. (0.075 mole) of aluminum chloride, and 20 stainless steel balls. The vessel was evacuated and cooled and 50 g. (0.85 mole) of trimethylamine was introduced. Hydrogen pressure was applied, and the vessel and contents were heated to 275°. The hydrogen pressure was adjusted to 800–900 atm. These conditions were maintained for 10 hr. At the end of this time the vessel was cooled and vented. The solid residues from four similar runs were combined and heated under vacuum to 250–300°. The volatile portion was collected in a liquid nitrogen trap. Distillation of this material gave 0.98 g. of N-trimethylborazine and 4.02 g. of $[(CH_3)_2NBH_2]_2$. The residue, ~10 g., was $(CH_3)_3NBH_3$. All of these materials were identified by comparison of their B^{11} and H^1 n.m.r. and infrared spectra with authentic samples.

Anal. Calcd. for $[(CH_3)_2NBH_2]_2$: C, 40.4; H, 14.2; N, 24.6; B, 19.02. Found: C, 40.1; H, 13.3; N, 24.6; B, 17.2.

Anal. Calcd. for $(CH_3)_3NBH_3$: C, 49.4; H, 16.6. Found: C, 48.6; H, 16.1.

Similar reactions were carried out under the conditions given above with dimethylamine, pyridine, dimethylaniline, and N-methylmorpholine. In all cases an amine borane appeared to be formed as evidenced by the reduction of silver nitrate by the crude products, but the individual components were not isolated.

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Carbonate Ion Dissociation in Fused Alkali Nitrates

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The equilibrium constant K for the dissociation of carbonate ion in fused equimolar sodium–potassium nitrate solvent, according to the reaction $CO_3^{-2} \rightleftarrows CO_2 + O^{-2}$, was determined potentiometrically with an oxygen–platinum indicator electrode in conjunction with a silver–silver nitrate (1.0 M $AgNO_3$ in equimolar $(Na,K)NO_3$) reference electrode. Values of K obtained were $(3.9 \pm 0.5) \times 10^{-6}$ at 523°K. and $(5.6 \pm 0.2) \times 10^{-5}$ at 580°K. $\Delta H°$ and $\Delta S°$ for the dissociation were constant over the temperature range studied and were found to be 27.0 ± 0.1 kcal. and 27.1 ± 0.1 e.u., respectively. Values for $\Delta G°$ at 523 and 573°K. are 12.9 ± 0.1 and 11.5 ± 0.1 kcal., respectively.

Introduction

According to the Lux acid–base theory which is usually used in the description of melts containing oxyanions, a base is an oxide ion donor and an acid is an oxide ion acceptor.[1] In fused alkali nitrates, several acids have been investigated—pyrosulfate,[2] dichromate,[3] transition metal ions,[4,5] to name a few. Little has been done, however, in the characterization of bases in fused alkali nitrates. Most oxyanions are potential bases, the degree of basicity being inversely proportional to the stability of the oxyanion with respect to dissociation according to the reaction

$$MO_x^{-y} \rightleftarrows MO_{x-1}^{-y+2} + O^{-2} \qquad (1)$$

The carbonate ion displays significant basicity in a nitrate solvent. This paper is a report on the determination of the equilibrium constant for the reaction

$$CO_3^{-2} \rightleftarrows CO_2 + O^{-2} \qquad (2)$$

The method of determination consisted of the maintenance of a constant CO_2 partial pressure over the solvent in the reaction vessel and the measurement of the O^{-2} ion concentration with an oxygen–platinum electrode developed previously.[6]

Experimental

All chemicals used were reagent grade. The solvent of equimolar sodium–potassium nitrates was prepared by fusing the proper proportions of the two salts, mixing well, filtering through a fine grade fritted glass disk, and molding into slugs of about 100 g. All reagents were dried at 110° and were stored over magnesium perchlorate.

The reaction vessel and electrodes were similar to those previously described.[6] An oxygen–platinum electrode was used as the indicator electrode and a silver–silver nitrate (1.0 M $AgNO_3$ in equimolar Na,KNO_3) electrode was used as the reference electrode. The flow rates of carbon dioxide and oxygen were measured with floating ball type flow meters manufactured by Roger Gilmont Instruments, Inc.

Potential measurements were made with a Leeds and Northrup K-3 universal potentiometer. A Keithley Model 603 electrometer-amplifier was connected in series with the electrochemical cell and was used as a null indicator.

Results and Discussion

The stoichiometry of reaction 2 was verified by adsorbing on Ascarite the CO_2 gas evolved when a known

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(1) H. Lux, *Z. Elektrochem.*, **45**, 303 (1939).

(2) E. R. Duke and S. Yamamoto, *J. Am. Chem. Soc.*, **81**, 6378 (1959).

(3) F. R. Duke and M. L. Iverson, *ibid.*, **80**, 5061 (1958).

(4) F. R. Duke and W. W. Lawrence, *ibid.*, **83**, 1269 (1961).

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quantity of Na_2CO_3 was dissolved in the equimolar $(Na,K)NO_3$ solvent. To enhance the evolution of CO_2, a very weak acid, sodium dichromate, was added. This acid was sufficiently weak so that any error in the adsorption measurements due to evolution of NO_2 gas could be ignored. Within experimental error, it was observed that 1 mole of CO_2 gas was evolved per mole of carbonate added to the solvent.

The equilibrium constant for reaction 2 can be written

$$K = \frac{P_{CO_2}[O^{-2}]}{[CO_3^{-2}]}$$

or, in terms of the initial carbonate ion concentration

$$K = \frac{P_{CO_2}[O^{-2}]}{[CO_3^{-2}]_0 - [O^{-2}]} \qquad (3)$$

The electrochemical cell reaction for the cell

$$(\mathrm{Pt})\mathrm{O_2},\ \mathrm{O^{-2}}\ (\mathrm{Na,KNO_3})\ \underset{\text{glass}}{\vdots}\ \mathrm{Ag^+}\ (1.0\ M \text{ in Na,KNO}_3)\ \mathrm{Ag}$$

is

$$2Ag^+ + O^{-2} = 2Ag + {}^1/_2O_2 \qquad (4)$$

The applicability of this cell to the determination of oxide ion concentration was shown previously.[6]

The Nernst expression for the cell reaction is

$$E = E^\circ - \frac{RT}{2F} \ln \frac{P_{O_2}{}^{1/2}}{[O^{-2}]} \qquad (5)$$

The oxide ion concentration can be eliminated from eq. 5 with eq. 3 to give, after changing to common logarithms

$$E = E^\circ - \frac{2.3RT}{2F} \log \frac{P_{O_2}{}^{1/2}(P_{CO_2} + K)}{K[CO_3^{-2}]_0} \qquad (6)$$

Therefore K can be determined at temperature T by measuring the potential of the electrochemical cell at known pressures of O_2 and CO_2 and a known initial concentration of carbonate ion.

The oxygen and carbon dioxide partial pressures were varied from 0.1 to 0.9 atm. The initial carbonate ion concentration was varied from about 3×10^{-4} to $3 \times 10^{-3}\ m$. Values of K_{obsd}, calculated from observed potentials at different temperatures, are listed in Table I. Each value of K_{obsd} listed is the average of four and in some cases five measurements made at different CO_2 and O_2 pressures and different carbonate ion concentrations. From the variation of K_{obsd} with temperature the standard enthalpy change ΔH° for reaction 2 was determined from a least-squares analysis. The value of ΔH° obtained in the temperature range 523–590°K. was 27.0 ± 0.1 kcal. ΔS° for reaction 2 was calculated with this value of ΔH° and the observed values of K. ΔS° was constant over the temperature range 523–590°K. and was found to be 27.1 ± 0.1 e.u. From these constant values of ΔH° and ΔS°, values of K were calculated for the temperatures at which potential measurements were made. The values of K_{calcd} are compared with K_{obsd} in Table I.

TABLE I

COMPARISON OF THE OBSERVED AND CALCULATED VALUES OF THE CARBONATE ION DISSOCIATION CONSTANT AT DIFFERENT TEMPERATURES

Temp., °K.	E°	$K_{\text{obsd}} \times 10^5$	$K_{\text{calcd}} \times 10^5$
523	0.6421	0.39 ± 0.05	0.41
533	0.6395	0.63 ± 0.01	0.64
543	0.6370	0.96 ± 0.02	1.1
553	0.6344	1.5 ± 0.1	1.6
563	0.6319	2.3 ± 0.2	2.6
566	0.6311	2.8 ± 0.3	2.9
578	0.6281	3.9 ± 0.1	4.6
580	0.6276	5.6 ± 0.2	5.4
590	0.6250	9.1 ± 0.5	8.0

The values obtained for K appear to be too large in view of the thermal stability of alkali carbonates at these temperatures. It can be shown from available thermodynamic data that for the reaction

$$Na_2CO_3(l) \rightleftarrows Na_2O(l) + CO_2(g)$$

at 1200°K., ΔG° is approximately 40 kcal. Certainly a much larger ΔG° would be expected at 600°K., which would make K very small indeed. The magnitude of the observed value of K would indicate that the nitrate solvent provides a stabilizing environment for the products of reaction 2. Probably the O^{-2} ion offers the greatest possibilities for reaction with the solvent. One such stabilizing reaction would be the formation of the orthonitrate ion, NO_4^{-3}, according to the reaction

$$O^{-2} + NO_3^- \rightleftarrows NO_4^{-3}$$

The existence of orthonitrates was indicated by Kohlmuller,[7] who prepared stable samples of potassium orthonitrate.

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