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Energy Systems Group, Canoga Park, California 91304

Graphite Oxidation in Sodium Carbonate/Sodium Sulfate Melts

GARY B. DUNKS,* D. STELMAN, and S. J. YOSIM

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The oxidation of spectroscopic grade graphite in sodium carbonate/sodium sulfate melts using oxidizing (air and oxygen) or inert (argon and nitrogen) sparge was investigated between 900 and 1000 °C. The oxidation rate increased with increasing graphite surface area, increasing melt temperature, and increasing oxygen concentration. The rate, in oxidizing atmospheres, at 900 °C was faster in pure sodium carbonate than in pure sodium sulfate with the maximum rate observed in mixed melts. At 950 °C the oxidation rate was virtually equal in the two pure melts, and at 982 °C the rate was faster in pure sodium sulfate. In melts containing sodium sulfate, the rate-determining step was apparently the same for reactions conducted in oxidizing and inert atmospheres, with sodium sulfate acting as a catalyst in the former and a reagent in the latter. Sequences of reactions are proposed for the oxidation of graphite in pure sodium carbonate, pure sodium sulfate, and mixed melts.

Introduction

The oxidation of carbon in the presence of sodium carbonate has been studied under a variety of experimental conditions.[1-4] The effect of sodium carbonate is to lower the ignition temperature or onset of weight loss of carbon by 150–175 °C,[1,2] thus acting as a rather efficient catalyst for the oxidation. The mode of the catalytic effect is probably the formation of sodium peroxide,[2,4] which then participates in an oxidation–reduction cycle, with sodium oxide, oxygen, carbon, carbon monoxide, and carbon dioxide. Consistent with electrochemical studies, which have shown that peroxide ion is formed directly from molten alkali carbonates and oxygen,[5] the sequence of reactions for the oxidation of graphite in molten sodium carbonate given by eq 1–5 was proposed.[4] The sum

$$Na_2CO_3 + {}^1/_2O_2 \rightleftarrows Na_2O_2 + CO_2 \tag{1}$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \tag{2}$$

$$Na_2O + {}^1/_2O_2 \rightarrow Na_2O_2 \tag{3}$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \tag{4}$$

$$Na_2O + CO_2 \rightleftarrows Na_2CO_3 \tag{5}$$

of the sequence is represented by eq 6.

$$C + O_2 \rightarrow CO_2 \tag{6}$$

The addition of sodium sulfate to sodium carbonate melts increased the rate of carbon oxidation even further.[3,6] The overall process of carbon oxidation in the absence of oxygen in sodium carbonate melts containing sodium sulfate was represented by eq 7.[6] In the presence of oxygen, the sulfide

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \tag{7}$$

ion produced was rapidly reoxidized to sulfate ion (eq 8), thus completing a cycle in which sulfate ion acted as a catalyst.

$$Na_2S + 2O_2 \rightarrow Na_2SO_4 \tag{8}$$

We report now the results of more extensive studies of the oxidation of carbon in the form of spectroscopic grade graphite in sodium carbonate/sodium sulfate melts employing both oxidizing and nonoxidizing atmospheres.

Experimental Section

The graphite used in all of the experiments was spectroscopic grade SP2-Z powder (Union Carbide Corp.) with the following properties determined by UCC. The graphite (>80% graphitic) was prepared from petroleum coke with use of a proprietary binder and heat-treated at 3000 °C. The total ash content was <2 ppm; impurities present were iron (0.3 ppm), magnesium (0.2 ppm), and silicon (0.4 ppm). Prior to use, the graphite was sieved with use of 80-mesh (0.0180-cm) and 100-mesh (0.0150-cm) screens. All of the experiments were performed with use of the −80 +100 mesh fraction, which had a specific surface area of 1.01 m^2/g (BET, nitrogen, or krypton adsorption measured by Micromeritics Instrument Corp., Norcross, Ga. 30071).

The air (300 ppm of CO_2), oxygen, nitrogen, argon, and carbon dioxide contained <10 ppm of water vapor and were obtained from Airco. The calibration gases were obtained from and analyzed by Airco.

The sodium carbonate was Baker anhydrous reagent grade (99.5%). Impurities were as follows: nitrogen compounds as N, 0.001%; phosphate (PO_4), 0.001%; silica (SiO_2), 0.005%; sulfur as SO_4, 0.003%, iron, 5 ppm.

The sodium sulfate was Baker Analyzed Reagent grade (99.2%). Impurities were as follows: insoluble matter, 0.004%; chloride (Cl), 0.005%; phosphate (PO_4), <0.001%; divalent cations, <0.005%; potassium, 0.004%; nitrogen compounds as N, 3 ppm; arsenic, <0.3 ppm; heavy metals as Pb, 3 ppm; iron, <3 ppm.

The experiments were performed in a large laboratory-scale reactor and/or a smaller reactor with approximately the same relative configurations. The reactors and analytical procedures were described previously in detail.[4]

The large reactor was charged with 5448 g of sodium carbonate, which provided a quiescent melt bed approximately 15 cm deep. To this melt was added sodium sulfate to provide melt of the desired composition. The small reactor was charged with 125 g of sodium carbonate and sodium sulfate in various compositions, which provided a quiescent melt bed approximately 4 cm deep. Melts that contained sodium carbonate were sparged with CO_2 for approximately 10 min prior to each experiment to convert Na_2O (from melt decomposition) and NaOH (from absorbed moisture) to Na_2CO_3. The melt was then sparged with N_2 at a superficial velocity of 30.5 cm/s (77.8 and 6.8 L/min (STP) for the larger and smaller reactors, respectively) with the analytical instruments in operation until the concentration of CO_2 in the reactor and sample lines was reduced to the background level. Pure sodium sulfate melts were not treated with CO_2 but were sparged with argon just prior to use.

The inert gas (nitrogen or argon) flow was stopped, and a preweighed sample of graphite was quickly charged to the melt and the appropriate sparge gas flow started (30.5 cm/s), which marked $t = 0$. Throughout the experiment, the composition of the exhaust gas was monitored by IR (CO_2 and CO) each 0.5 min and by GC (CO_2, CO, N_2, O_2, etc.) each (approximately) 8 min. These analytical data, together with the melt temperature, time, and sparge gas flow rate, were gathered, partially reduced, and stored on magnetic tape by a Hewlett-Packard Model 3052-A Data Acquisition System. The data could be recalled and plotted with use of a Hewlett-Packard Model 9872-A Plotter.

Analysis of certain melts subsequent to the oxidation experiment was accomplished by allowing the entire melt to cool and solidify under an argon atmosphere. Sulfate was determined by dissolving a weighed sample, acidifying to eliminate interference by carbonate, sulfide, sulfite, and thiosulfate, and precipitating with barium chloride. Sulfide was determined by precipitation with cadmium carbonate. The sulfide content of the precipitate was determined by adding iodine solution and titrating the excess iodine with thiosulfate. Sulfite and thiosulfate

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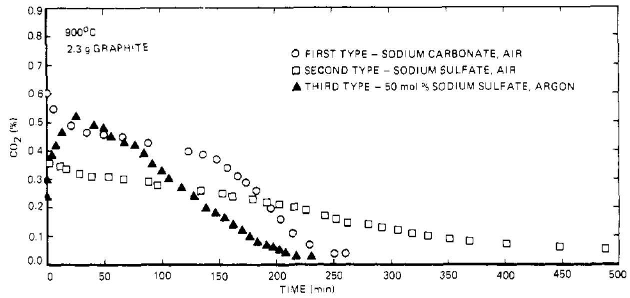

Figure 1. Three general shapes of exhaust gas carbon dioxide concentration vs. time curves.

were determined by titrating an aliquot of the solution subsequent to the cadmium sulfide precipitation with iodine. A second aliquot was treated with excess formaldehyde to remove sulfite as inert hydroxysulfonate and again titrated with iodine to determine thiosulfate. The difference between the first and second iodine titrations determined the sulfite content. Total sulfur was determined by aqueous bromine oxidation followed by precipitation of barium sulfate. Carbonate was determined by acidification of an aliquot and absorption of the resultant carbon dioxide by Ascarite.

Results

The course of the oxidation of graphite in sodium carbonate/sodium sulfate melts was followed by monitoring the concentrations of volatile products in the reaction off-gas. The major product, regardless of the experimental conditions employed, was carbon dioxide. Low concentrations of carbon monoxide (<0.03%) were observed when the melt contained a significant quantity of graphite and reduced oxidant concentration. This situation occurred at the beginning of each experiment and at the conclusion of certain experiments in which graphite was in excess relative to the available oxidant. In both cases, the carbon monoxide observed probably arose from the reaction of graphite with carbon dioxide according to eq 9. The carbon monoxide accounted for <1% of the

$$CO_2 + C \rightleftharpoons 2CO \qquad (9)$$

graphite charged in all experiments, and therefore, its contribution to the exhaust gas was ignored. With the exception of trace amounts of sulfur dioxide detected near the beginning of some experiments conducted in melts that contained sodium sulfate, no sulfur-containing gases were observed.

The integral of the plot of the carbon dioxide concentration in the exhaust gas vs. the reaction time of an experiment should represent the quantity of graphite charged to the melt. The integrals of the curves from experiments conducted with air or oxygen in pure sodium carbonate melts tended to be high (≤5%) even after corrections were made for the carbon dioxide in the air (300 ppm). The integrals of curves from experiments conducted in melts that contained sodium sulfate tended to be low (by as much as 20%), especially those conducted in pure sodium sulfate melts with argon. These results indicate that carbon dioxide was evolved from sodium carbonate melts in excess of that produced by graphite oxidation and that carbon was retained by melts that contained sodium sulfate.

The shapes of the carbon dioxide concentration vs. reaction time curves were of three general types as illustrated in Figure 1. The transitions from one curve shape to another were gradual and varied with the experimental conditions. The first type consisted of an initial, relatively flat portion, which then decreased rapidly to the background carbon dioxide concentration. This shape was typical of experiments conducted in sodium carbonate melts at 900 °C using air with high graphite surface areas (>1 m^2/mol of melt) and suggests that early in the experiment when the graphite surface area was high the rate was dependent on a nearly constant concentration of oxidant. As the graphite surface area decreased, a point was reached at which the melt contained sufficient oxidant to saturate the graphite surface remaining, which then became rate controlling. The two regions of the curve have been termed the oxidant limited region and the graphite surface area limited region.[3,4] The second type of curve observed decreased steadily with time. This curve shape was typical of experiments conducted in sodium carbonate melts at 900 °C using air with low initial graphite surface areas (<1 m^2/mol of melt) and in sodium sulfate melts at 900 °C using air with initial graphite surface areas <5 m^2/mol of melt. This curve shape suggests that the melts contained sufficient oxidant such that the graphite surface area was rate limiting throughout the experiment. The third type of curve observed increased early in the experiment to a maximum and then decreased with time. This curve shape was typical of experiments conducted at melt temperatures >900 °C using air for all melt compositions, for experiments conducted in sodium sulfate melts at 900 °C using air at graphite surface areas >5 m^2/mol of melt, and for all experiments conducted using argon. This curve shape suggests that the oxidant concentrations in the melts increased with time early in the experiments to a point where there was sufficient oxidant to saturate the graphite surface, which then became rate controlling. The oxidation rates described in this paper are defined as the instantaneous carbon dioxide concentrations in the exhaust gas at the time when 50% of the graphite had been consumed ($t_{1/2}$).

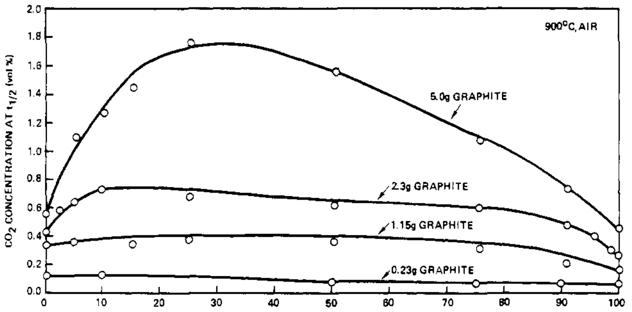

Figure 2. Effect of melt composition on the rate (CO_2 concentration at the time when 50% of the graphite had been consumed) of graphite oxidation (small reactor).

Effect of Melt Composition. The effect of melt composition on the oxidation rates for four graphite loading levels, with use of air at 900 °C, is shown in Figure 2. The oxidation rate for the highest graphite loading studied (5.0 g, 5.05 m^2) increased rapidly as the sodium sulfate concentration of the melt was increased from 0 to approximately 25 mol % and then decreased as the composition of the melt approached pure sodium sulfate. The oxidation rates for the lower graphite loadings showed increasingly less dependence on the melt composition. The rate enhancement in mixed melts as compared to the rate in pure sodium carbonate melts was approximately 10% for 0.23 g (0.232 m^2), 18% for 1.15 g (1.16 m^2), 88% for 2.3 g (2.32 m^2), and 207% for 5.0 g (5.05 m^2).

The effect of the melt composition on the oxidation rate of reactions performed at 900 °C using argon, compared to similar reactions conducted with air, is shown in Table I. The results obtained with the employment of identical 2.3-g graphite loadings in the small reactor show that, as the sodium sulfate concentration of the melt was increased from approximately 15 to 90 mol % sodium sulfate, the oxidation rate remained virtually constant and then decreased as the melt composition approached pure sodium sulfate. Thus, the oxidation rate for experiments conducted using argon exhibited a lower dependence on melt composition than that of similar experiments conducted with air. The dramatic increase in the oxidation rate in melts that contained 10 mol % sodium carbonate over the rate in pure sodium sulfate melts (Table I)

Table I. Effect of Melt Composition on the Rate of Graphite Oxidation at 900 °C in Air and Argon[a]

sodium sulfate concn, mol %	reacn rate[b] air	reacn rate[b] argon	sodium sulfate concn, mol %	reacn rate[b] air	reacn rate[b] argon
0.0	0.40		50.0	0.63	0.40
10.0	0.73	0.47	90.0	0.48	0.39
15.0		0.41	100.0	0.22	0.16
25.0	0.69	0.40			

[a] Charged with 2.3 g of graphite, small reactor. [b] Instantaneous carbon dioxide concentration (vol %) of the exhaust gas after 50% of the graphite had been consumed.

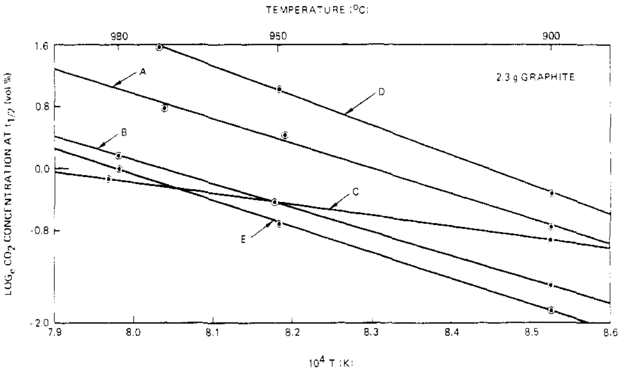

Figure 3. Temperature dependence of graphite oxidation (small reactor): (A) 10 mol % sodium sulfate, argon, slope = -3.22×10^4, E_a = 268 kJ/mol; (B) pure sodium sulfate, air, slope = -3.09×10^4, E_a = 255 kJ/mol; (C) pure sodium carbonate, air, slope = -1.41×10^4, E_a = 117 kJ/mol; (D) 10 mol % sodium sulfate, air, slope = -3.83×10^4, E_a = 318 kJ/mol; (E) pure sodium sulfate, argon, slope = -3.36×10^4, E_a = 280 kJ/mol.

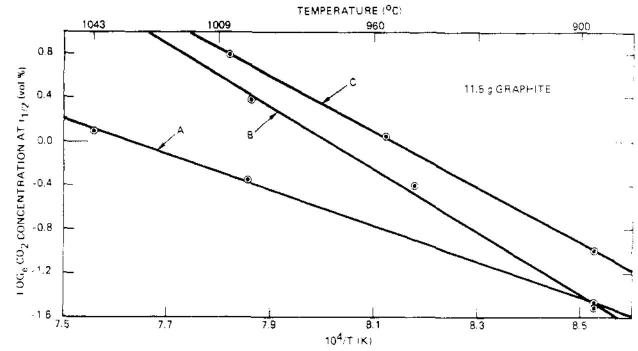

Figure 4. Temperature dependence of graphite oxidation (large reactor): (A) pure sodium carbonate, air, slope = -1.63×10^4, E_a = 134 kJ/mol; (B) 10 mol % sodium sulfate, argon, slope = -2.86×10^4, E_a = 239 kJ/mol; (C) 10 mol % sodium sulfate, air, slope = -2.53×10^4, E_a = 209 kJ/mol.

Table II. Oxygen Dependence of the Rate of Graphite Oxidation in Sodium Carbonate/Sodium Sulfate Melts at 900 °C

amt of graphite charged, g	sodium sulfate concn, mol %	rate[a] air	rate[a] oxygen	oxygen dependence[b]
2.3[c]	0	0.40	0.86	0.49
2.3[c]	10.0	0.73	1.03	0.22
2.3[c]	100	0.22	0.26	0.11
11.5[d]	0	0.23	0.51	0.51
11.5[d]	0.92	0.37	0.56	0.27
11.5[d]	10.0	0.37	0.51	0.21
115[d]	0	0.66	1.35	0.45
115[d]	0.92	1.95	2.40	0.13
115[d]	10.0	2.40	3.10	0.16

[a] Instantaneous carbon dioxide concentration when 50% of the graphite had been consumed in the presence of air or oxygen. [b] Slope of the log (rate) vs. log (oxygen concentration) plot. [c] Small reactor. [d] Large reactor.

clearly indicates that sodium carbonate played a significant role in the process even in inert atmospheres. Moreover, the fact that the oxidation rate with argon was relatively independent of melt composition while the rate with air decreased (from 15 to 90 mol % sodium sulfate) suggests that oxygen reacted with sodium carbonate (or its decomposition products) to produce an active oxidant.

Temperature Dependence. The dependence of the rate of graphite oxidation on melt temperature for various melt compositions is shown in Figure 3 (small reactor) and Figure 4 (large reactor).

The temperature dependences determined for graphite oxidations conducted in melts that contained 10 mol % sodium sulfate using air in the large reactor and small reactor corresponded to apparent energies of activation (E_a) of 209 and 318 kJ/mol, respectively. Energies of activation determined in similar experiments using argon in the large reactor and small reactor were 239 and 268 kJ/mol, respectively. The large difference in the apparent energies of activation for the experiments conducted with air in the two reactors may have been due to localized heating in the small reactor. The experiments conducted in the large reactor were done with 11.5 g of graphite (0.23 m^2/mol of melt), while the experiments done in the small reactor were conducted with 2.3 g of graphite (2.03 m^2/mol of melt). Thus in the small reactor, with less melt relative to the graphite present (to dissipate the heat from the exothermic reaction), the surface of the graphite may have become significantly hotter than the temperature of the bulk melt. The E_a for the argon experiment conducted in the small reactor would be expected to be relatively free from localized temperature effects since that process is endothermic. Since the values of E_a for the air and argon experiments in the large reactor were similar and are comparable to the argon value determined in the small reactor, it was assumed that the energy of activation determined in the small reactor with air in 10 mol % sodium sulfate melt was high. The energies of activation determined in pure sodium sulfate melts with air and argon in the small reactor were 255 and 280 kJ/mol, respectively. The energies of activation determined in pure sodium carbonate melts in the large reactor and small reactor with air were 134 and 117 kJ/mol, respectively. The large difference between the E_a values determined in sodium sulfate containing melts relative to those determined in pure sodium carbonate melt allows the conclusion that different rate-controlling steps were operating in the two systems. In addition, the similarity of the E_a values determined in 10 mol % sodium sulfate melts as compared to those found in pure sodium sulfate melts suggests that the rate-controlling process in the two melt compositions containing sodium sulfate was the same. Finally, in mixed melts the E_a values determined in argon were comparable to those determined in air, which suggests that the rate-determining step was the same whether or not oxygen was present. Inspection of Figure 3 shows that, for identical graphite loadings at sufficiently high temperature (>950 °C), the oxidation of graphite in pure sodium sulfate melt with air was faster than in pure sodium carbonate melt.

Oxygen Dependence. The oxygen dependences of the rate of graphite oxidation in sodium carbonate/sodium sulfate melts at 900 °C are presented in Table II. In pure sodium carbonate melts, the oxygen dependence was approximately half-order. In sodium sulfate containing melts, the oxygen dependence was less than in sodium carbonate melts and tended to decrease as the sodium sulfate concentration increased.

Carbon Dioxide Dependence. The introduction of carbon dioxide to the air sparge gas was found to slightly decrease

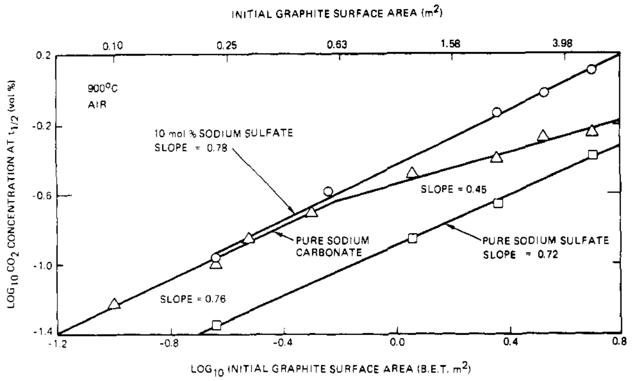

Figure 5. Graphite surface area dependence of graphite oxidation (small reactor).

Table III. Graphite Oxidation Rate Dependence on Graphite Surface Area as a Function of Melt Composition[a]

melt compn, mol % sulfate	rate dependence[b] (order)	melt compn, mol % sulfate	rate dependence[b] (order)
0	0.76,[c] 0.45[d]	75	0.90
10	0.78	90	0.84
25	1.03	100	0.72
50	0.99		

[a] Based on data presented in Figures 2 and 5 (small reactor, air, 900 °C). [b] Slope of log (rate) vs. log (graphite surface area). [c] Graphite surface area *limited* region. [d] Oxidant *limited* region.

the rate of graphite oxidation in pure sodium carbonate melts (−0.12 order).[4] This is consistent with the proposed process (eq 1–5) in which carbon dioxide is a product and/or consumes chemical species that are involved in the rate-determining step. Both of these possibilities slow the rate of oxidation. No similar experiments were conducted in melts that contained sodium sulfate.

Graphite Surface Area Dependence. The dependences of the graphite oxidation rate on graphite surface area in pure sodium carbonate melt, sodium carbonate melt that contained 10 mol % sodium sulfate, and pure sodium sulfate melt at 900 °C with air are shown in Figure 5. In pure sodium carbonate, the slope of the log (rate) vs. log (surface area) plot was 0.76 at surface areas <0.6 m² and 0.45 at surface areas >0.6 m². In 10 mol % sodium sulfate and pure sodium sulfate melts, the plots were linear throughout the range of graphite areas studied with slopes of 0.78 and 0.72, respectively. The rate dependence on the graphite surface area varied with the composition of the melt (Table III) and was actually first-order only between 25 and 50 mol % sodium sulfate. The graphite surface area dependence determined in 0.92 mol % sodium sulfate melt (large reactor) at 900 °C with argon sparge was 0.72 (Figure 6).

Effect of Sodium Sulfide. Literature reports indicate that the reduction of sulfate by hydrogen, carbon monoxide, and various carbonaceous materials is catalyzed by sulfide.[7,8] To determine if such catalysis was operating under the present conditions, two experiments were conducted (small reactor) in which identical samples of graphite (2.3 g) were oxidized at 900 °C with argon in pure sodium sulfate melt and in sodium sulfate that initially contained 4 mol % sodium sulfate (produced in situ with carbon monoxide). Each experiment was terminated after 100 min by removing the entire reactor from the furnace and allowing the melt to cool. The frozen melts were dissolved in water, and the graphite that remained in each was isolated. The results shown in Table IV indicate that under virtually identical conditions, graphite was oxidized approximately twice as fast in the sulfide-containing melt as in initially pure sodium sulfate melt. The results also showed that more graphite was consumed than was indicated by integration of the carbon dioxide curves. In a subsequent experiment that was allowed to proceed to completion, conducted in pure sodium sulfate melt, the integral of the carbon dioxide vs. time curve corresponded to only 1.85 g of carbon. The melt was allowed to cool in situ under a stream of argon and removed from the reactor tube nearly intact. The frozen melt was analyzed and found to contain 0.18 g of unreacted graphite and 1.82 wt % sodium carbonate (0.26 g of carbon). Thus, the total quantity of carbon found by analysis of the products account for 99.5% of the graphite charged. The melt also contained sodium sulfide (4.64%), sodium sulfite (1.21 wt %), and sodium thiosulfate (0.76 wt %). The quantity of carbon consumed by the reaction (2.12 g, 0.177 mol) was in fair agreement with the sodium sulfate consumed (10.5 g, 0.074 mol) if the 2:1 stoichiometry of eq 7 is assumed. The relatively large quantity of graphite that remained in the reactor at the end of the experiment (~8% of the graphite charged) was typical of experiments conducted in melts that contained high concentrations of sodium sulfate. One possible explanation is that graphite ($\rho \cong 2$ g/cm³), is more buoyant in melts containing high sodium sulfate concentrations (sodium sulfate $\rho = 2.6517$ g/cm³ and sodium carboante $\rho = 1.9530$ g/cm³ at 900 °C[9]) and may tend to splash up on the walls of the reactor and remain unreacted.

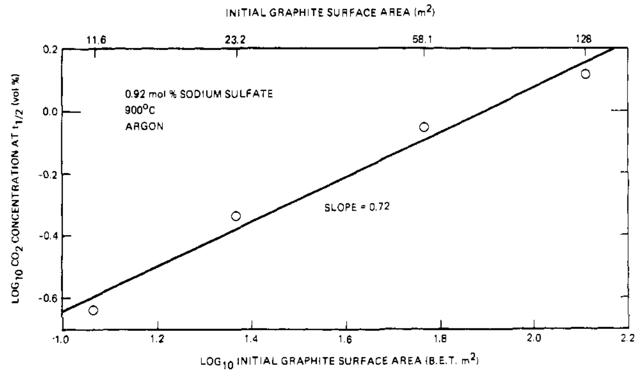

Figure 6. Graphite surface area dependence in the presence of argon (large reactor).

Table IV. Effect of Sodium Sulfide[a]

init sulfide concn, mol %	amt of graphite, g			CO_2 integral, g of C	% diff
	charged	recovered	consumed[b]		
0	2.3011	1.8581	0.4430	0.36	18.7
3.91	2.3007	1.3943	0.9064	0.76	16.2

[a] Conditions: sodium sulfate melt, 900 °C, argon, small reactor. [b] First 100 min.

Initial Graphite Oxidation Rate. The carbon dioxide production from graphite oxidation in pure sodium sulfate melt with argon was relatively low for more than 30 min, which suggests that the direct reaction of sodium sulfate with graphite is very slow (Figure 7). With sodium sulfide initially present, the carbon dioxide evolution began at low concentration and increased rapidly over the first 25 min of the experiment. Similarly, with sodium carbonate initially present, the carbon dioxide concentration of the exhaust gas increased to a max-

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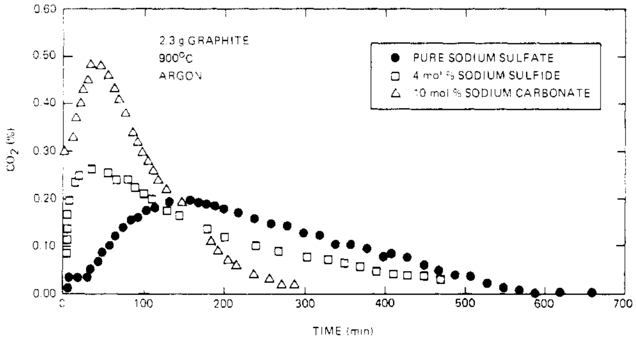

Figure 7. Effect of sodium sulfide and sodium carbonate on the rate of graphite oxidation (small reactor).

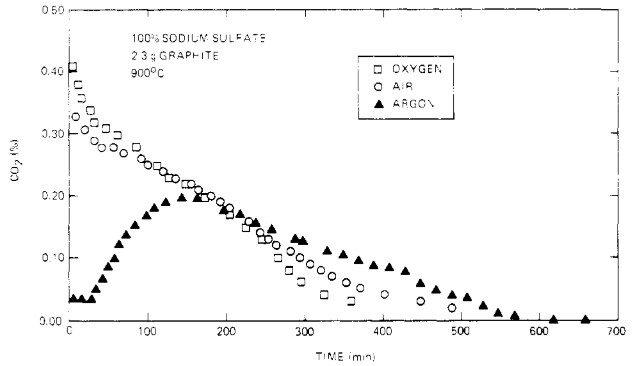

Figure 8. Comparison of the rates of graphite oxidation in air, oxygen, or argon (small reactor).

imum over the first 30 min of the experiment (Figure 7). In experiments conducted in pure sodium sulfate melts using air or oxygen, the carbon dioxide evolution began at a relatively high level (Figure 8). The time required for the carbon dioxide evolution to maximize in the exhaust gas was as follows (melt composition, sparge gas): carbonate, air or oxygen ≅ sulfate, oxygen > sulfate, air > sulfate/sulfide, argon ≅ sulfate/sulfide/carbonate, argon > sulfate/carbonate, argon >> sulfate, argon. It is unlikely that the direct reaction of oxygen with graphite is significant in molten sodium carbonate since it has been shown by other studies that the rate of graphite oxidation in the absence of catalysts is much slower than the rate of oxidation when the graphite is doped with sodium carbonate.[2] Similarly, in pure sodium sulfate melts, the oxidation rate was only slightly faster in oxygen than in argon, which suggests that the direct reaction of graphite with oxygen was not significant. A more likely explanation for the almost instantaneous evolution of carbon dioxide as the oxygen-containing sparge gas was begun is that the melt contained a species that reacts rapidly with oxygen to produce a very reactive oxidizing agent. By analogy to the above discussion, the results indicate that in the absence of oxygen (i.e., argon), both sodium sulfide and sodium carbonate may react with sodium sulfate melt to produce an active oxidizing species.

Discussion

The reaction rate dependencies for graphite oxidation conducted in pure sodium carbonate, 10 mol % sodium sulfate, and pure sodium sulfate melts are summarized in Table V.

Some constraints placed on possible mechanisms by the experimental results discussed above are as follows:

(1) Graphite oxidation in pure sodium carbonate melts operates in both the oxidant *limited* regime and the graphite surface area *limited* regime. The oxidation rates in sodium sulfate melts tended toward the graphite surface area *limited* regime for all graphite loadings studied. This suggests that the concentration of oxidant was higher at the graphite surface in the sodium sulfate containing melts.

Table V. Summary of Results

regime	graphite surface area dependence[a] large reactor	graphite surface area dependence[a] small reactor	temp dependence[b] (E_a), kJ/mol large reactor	temp dependence[b] (E_a), kJ/mol small reactor	oxygen dependence[c,d] large reactor	oxygen dependence[c,d] small reactor
	Pure Sodium Carbonate Melt					
oxidant ltd, air	0.37	0.45	147	117	0.48[e]	0.49
graphite surface area ltd, air	0.98	0.76	134	105	0.42	0.51
90.0 Mol % Sodium Carbonate/10.0 Mol % Sodium Sulfate Melt						
air	0.86	0.78	209	318[g]	0.19[e]	0.22
argon	0.85[f]		239	268	h	h
	Pure Sodium Sulfate Melt					
air		0.72		255		0.11
argon				280	h	h

[a] Slope of log (rate) vs. log (area). [b] Slope of ln (rate) vs. $1/T$ (−1.987). [c] Slope of log (rate) vs. log (P_{O_2}). [d] 21% O_2 (air) and 99.6% O_2. [e] Average value. [f] 0.92 mol % sodium sulfate. [g] Possibly high value. [h] Not applicable.

(2) The apparent energies of activation for graphite oxidation in pure sodium carbonate melts as compared to those determined in melts that contained sodium sulfate were significantly less, which indicates that a different rate-determining step was operating in the two systems.

(3) The apparent energies of activation for reactions conducted in 10.0 mol % sodium sulfate melt and in 100 mol % sodium sulfate melt were similar, which suggests that the same rate-determining step may operate in both melts.

(4) The apparent energies of activation for reactions conducted in sodium sulfate containing melts in argon and air were similar; thus the rate-determining step probably does not involve oxygen.

(5) The oxidation rate of graphite with air in pure sodium carbonate melt at 900 °C was much faster than the rate in similar reactions in argon. This suggests that oxygen was involved in the rate-determining step of the reactions conducted in pure sodium carbonate melts.

(6) Sodium sulfide and sodium carbonate individually and in concert increased the rate of oxidation in sodium sulfate melts with argon.

(7) A slight decrease in the rate of oxidation of graphite was observed in sodium carbonate melt as the carbon dioxide concentration of the air sparge gas was increased.

Sodium Carbonate–Oxidizing Sparge Gas. A sequence of reactions (eq 1–5) was proposed[4] for graphite oxidation in pure sodium carbonate melts with air that is consistent with the constraints above and with the results of thermogravimetric[2] and electrochemical[5] studies in the literature. Thus in the early stages of the experiment when the graphite surface area was high, the rate-controlling step was the formation of oxidant (e.g., sodium peroxide, eq 1 or 3). Equations 1 and 3 are both consistent with the half-order oxygen dependence determined experimentally. As the available graphite surface area decreased during the experiment, a point was reached at which the melt contained sufficient sodium peroxide to react with all of the graphite surface area available, which became rate-limiting (i.e., the rate approached first order in graphite surface area (eq 2)). An increase in carbon dioxide pressure would increase the rate of the backward reaction of eq 1 and increase the rate of the forward reaction of eq 5, the effect being to decrease the overall rate of the process.

Sodium Carbonate/Sodium Sulfate–Oxidizing Sparge Gas. The direct reaction of graphite with sodium sulfate (eq 7) is slow as evidenced by the rate of carbon dioxide production over the first 30 min of experiments conducted in pure sodium sulfate melts using argon (e.g., Figure 7). The dramatic initial rate increase observed in the experiment conducted in sodium sulfate melt that contained 10 mol % sodium carbonate as compared to the experiment conducted in pure sodium sulfate, both using argon (Figure 7), suggests that sodium carbonate reacts directly with sodium sulfate or its decomposition products to produce the oxidant. The overall process (eq 10)

$$Na_2SO_4 + Na_2CO_3 \rightarrow CO_2 + Na_2O_2 + Na_2SO_3 \tag{10}$$

would not readily proceed in the absence of species capable of continuously removing the products. A careful rate study of the thermal decomposition of sodium carbonate in the presence of sodium sulfate may determine the extent of their interaction. Such a study was not done; however, support for such interaction was provided by the observation that the background concentration of carbon dioxide in the exhaust gas from sodium carbonate/sodium sulfate mixed melts was always slightly higher than that from sodium carbonate alone. The difference was approximately within the range of experimental error, and thus no definite conclusion could be made.

In the presence of air and graphite, the sodium sulfite produced by the reaction of sodium carbonate and sodium sulfate could disproportionate, be oxidized to sodium sulfate, or be reduced by graphite according to eq 11, 12, and 13,

$$4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S \tag{11}$$

$$Na_2SO_3 + {}^1/_2O_2 \rightarrow Na_2SO_4 \tag{12}$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \tag{13}$$

respectively. The reduction of sodium sulfite (eq 13) is faster than the reduction of sodium sulfate and possibly faster than disproportionation at low concentrations.[10] Thus, it is reasonable to assume that both the sodium peroxide and sodium sulfite produced by the reaction of sodium carbonate with sodium sulfate may react with graphite. The overall sequence of reactions that appears to best represent the results of this study for the oxidation of graphite using air or oxygen in sodium carbonate/sodium sulfate mixed melts is represented by eq 2, 4, 5, 8, 10, 13, and 14. The sum of the sequence is

$$Na_2CO_3 + Na_2SO_4 \rightarrow CO_2 + Na_2O_2 + Na_2SO_3 \tag{10}$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \tag{2}$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \tag{4}$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \tag{13}$$

$$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2 \tag{14}$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \tag{5}$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4 \tag{8}$$

represented by eq 6. The rate-determining step of the proposed sequence is the oxidation of graphite by sodium sulfite (eq 13), and the rate is limited by the available graphite surface area. Clearly, the reactions involving oxygen (eq 1 and 3) in the sequence proposed for graphite oxidation in pure sodium carbonate may also operate in the mixed-melt system. Therefore, as the ratio of carbonate to sulfate in the melt increased, it would be expected that the reactions of oxygen with sodium carbonate (eq 1) and sodium oxide (eq 3), both of which produce sodium peroxide, would become increasingly important. Indeed, the oxygen dependence shows such a trend (Table II) and the increased concentration of sodium peroxide may explain why the rate of graphite oxidation increased as the concentration of sodium carbonate in the melt increased from ~0 to ~80 mol % (Figure 2).

Sodium Sulfate–Oxidizing Sparge Gas. In pure sodium sulfate melts with air or oxygen, the rate of graphite oxidation in the first few minutes of the experiment showed a marked increase over the rate in a comparable experiment conducted with argon (Figure 8). If it is assumed that oxygen did not react directly with graphite (as discussed above), then this result suggests that oxygen interacted with sodium sulfate melts to increase the oxidizing capability of the melt very early in the experiment. A possible reaction of oxygen with sodium sulfate is represented by eq 15. The thermal decomposition

$$Na_2SO_4 + {}^1/_2O_2 \rightleftarrows SO_3 + Na_2O_2 \tag{15}$$

of the sulfur trioxide produced to form sulfur dioxide and oxygen (eq 16) may compete favorably with the reverse re-

$$SO_3 \rightleftarrows SO_2 + {}^1/_2O_2 \tag{16}$$

action of eq 15, the net effect being the oxygen-catalyzed decomposition of sodium sulfate as represented by eq 17.

$$Na_2SO_4 \rightleftarrows SO_2 + Na_2O_2 \tag{17}$$

Thus, while oxygen is required to initiate the rapid decomposition of sodium sulfate, it plays no part in the subsequent reactions, which involve graphite. The overall process proposed for the oxidation of graphite in pure sodium sulfate melt using air or oxygen is represented by eq 2, 4, 8, 13, 14, 17, and 18,

$$Na_2SO_4 \rightleftarrows SO_2 + Na_2O_2 \tag{17}$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \tag{2}$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \tag{4}$$

$$SO_2 + Na_2O \rightarrow Na_2SO_3 \tag{18}$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \tag{13}$$

$$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2 \tag{14}$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4 \tag{8}$$

the sum being represented by eq 6. Thus, sodium sulfate acted as a catalyst under these conditions.

Sodium Sulfate–Inert Sparge Gas. The rate of oxidation of graphite in pure sodium sulfate melts using argon was shown to be strongly accelerated in the first minutes of the experiments by sodium carbonate or sodium sulfide (Figure 7). The direct reaction of graphite with sodium carbonate in inert atmospheres is very slow, and clearly sodium sulfide cannot react with graphite to produce carbon dioxide. Therefore, the rate enhancement produced by carbonate and/or sulfide must involve sodium sulfate. A possible interaction between sodium sulfate and sodium carbonate was discussed above (eq 13). A possible sodium sulfide catalyzed thermal decomposition of sodium sulfate is represented by eq 19 and 20 in which the

$$Na_2SO_4 + Na_2S \rightarrow Na_2S_2O_3 + Na_2O \tag{19}$$

$$Na_2S_2O_3 \rightarrow SO_2 + {}^1/_2O_2 + Na_2S \tag{20}$$

net process is represented by eq 17. The direct reaction of sodium sulfate with sodium sulfide has been postulated by several authors;[11] however, an analysis by Fotiev of the thermodynamics indicated that no reaction could occur below 1473 K.[11] A later report suggests that the calculations of Fotiev were in error.[7] The reactions represented by eq 19 and 20 account not only for the increase in the carbon dioxide evolution during the first 100 min of the graphite oxidation under these conditions (which parallels the production of so-

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(10) A. A. Fotiev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **9**, 107 (1960).

(11) A. A. Fotiev, *J. Appl. Chem. USSR* (*Engl. Transl.*), **35**, 2307 (1962), and references therein.

dium sulfide) and the dramatic rate increase observed in melts that initially contained sodium sulfide but also a source of sodium thiosulfate, which was found in the melt subsequent to a similar experiment. A sequence of reactions that is consistent with the results of this study for the oxidation of graphite in pure sodium sulfate using argon is represented by eq 2, 4, 13, 14, 17, and 18. The overall process is represented by eq 7. Sodium sulfate is consumed under these conditions.

$$Na_2SO_4 \rightleftarrows SO_2 + Na_2O_2 \tag{17}$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \tag{2}$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \tag{4}$$

$$SO_2 + Na_2O \rightarrow Na_2SO_3 \tag{18}$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \tag{13}$$

$$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2 \tag{14}$$

Sodium Carbonate/Sodium Sulfate–Inert Sparge Gas. In sodium carbonate/sodium sulfate mixed melts with argon, a sequence of reactions proposed for the oxidation of graphite may be represented by eq 2, 4, 5, 10, 13, and 14, in which the overall process is represented by eq 7.

$$Na_2SO_4 + Na_2CO_3 \rightarrow CO_2 + Na_2SO_3 + Na_2O_2 \tag{10}$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \tag{2}$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \tag{4}$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \tag{13}$$

$$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2 \tag{14}$$

$$Na_2O + CO_2 \rightleftarrows Na_2CO_3 \tag{5}$$

There are other reactions possible between the species discussed, and indeed, there may be other species involved in these complex systems. Even though the reaction sequences presented are consistent with the data presently available, they may not be the only sequences capable of explaining the results.

To understand more about the chemistry of graphite oxidation in sodium carbonate/sodium sulfate mixed melts, it will be necessary to determine how the concentrations of the ionic species in the melt change with variations in the reaction conditions and how they relate to the reaction rate. Such studies are presently under way.

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Registry No. Graphite, 7782-42-5; Na_2SO_4, 7757-82-6; Na_2CO_3, 497-19-8; Na_2S, 1313-82-2.

Contribution from the Department of Chemistry,
Auburn University, Auburn University, Alabama 36849

Some Observations on the Solution Chemistry of Molybdenum(II) Trifluoroacetate

THOMAS R. WEBB* and TENG-YUAN DONG

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Solutions of molybdenum(II) trifluoroacetate in pyridine have been shown to contain not the axial bis(pyridine) adduct known in the solid state but a species with both bidentate and monodentate carboxylate ligands. Ring opening and closing proceed with an apparent free energy barrier (ΔG^*) of ca. 13 kcal/mol. Evidence is presented for dissociative control of this process.

Introduction

Some years ago, Cotton[1] established that binuclear molybdenum(II) carboxylates such as molybdenum trifluoroacetate form axially symmetrical adducts with pyridine and other Lewis bases. Recently, Andersen[2,3] has described two additional reactions: the formation of binuclear complexes containing equatorial bases (with certain phosphines) and the formation of monuclear complexes (with isocyanides). Cotton[4] has reported the structures of two equatorial adducts.

We have begun[5] to investigate the solution chemistry of binuclear molybenum(II) complexes in order to establish the species present in solution and the mechanisms by which these complexes react. We report here the behavior of molybdenum(II) trifluoroacetate in pyridine-containing solutions. Our results indicate that this complex rearranges from the axial adduct to an equatorial adduct in the presence of excess pyridine. A ring opening–closing process occurs in solution; we report a ^{19}F NMR study of the process.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 580 recording spectrophotometer. Electronic spectra were measured on a Cary 17 spectrophotometer. NMR spectra (^{19}F, 84.67 MHz) were recorded on a Varian EM-390 spectrophotometer; temperatures were calibrated in terms of the chemical shifts of methanol and ethylene glycol samples.[6] Conductivities were measured at room temperature with a Beckman RC-18A bridge. Pyridine, toluene, and benzene were redistilled (pyridine from KOH pellets) and stored over 4A molecular sieves in dark bottles. Molybdenum trifluoroacetate was prepared by literature methods[7] and characterized spectroscopically.

Table I. Data for Solutions of Molybdenum Trifluoroacetate in Pyridine

infrared,[a] cm^{-1}	1713 (br), 1617, 1611
NMR,[b] ppm	−70.5, −73.3
equiv conduct,[c,d] $\Omega^{-1}\ mol^{-1}\ cm^2$ [e,d]	<1.5
Raman,[e] cm^{-1}	343
electronic,[f] nm	502

[a] Thin-film spectrum; 1750–1300-cm^{-1} region. [b] ^{19}F, negative shifts upfield from $CFCl_3$; $T = -30$ °C. [c] Measured on 0.0050 M solutions of $Mo_2(O_2CCF_3)_4$ at room temperature (ca. 23 °C); a value of 30.6 $\Omega^{-1}\ mol^{-1}\ cm^2$ was measured for Et_4NClO_4 under identical conditions. [d] Measurements were complicated by slow air oxidation of the dilute solutions employed. Solutions and cells were purged with argon before measurements were made; a 50% increase in conductivity was noted over a 1-h period. In the presence of air, conductivity increased by more than a factor of 3. [e] Mo–Mo stretching vibration from ref 1. [f] Calculated from data in ref 6.

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