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THE REACTION OF SULFUR DIOXIDE WITH GRAPHITE^(a)

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THE REACTION OF SULFUR DIOXIDE WITH GRAPHITE

INTRODUCTION

Reactions of oxides of sulfur are of increasing interest due to the need for basic data for air pollution studies. Previously studies have been conducted on the reactions of sulfur dioxide with various types of carbon.^(1,2) C. W. Siller⁽²⁾ reviewed the early literature and studied the reaction of SO_2 with anthracite coal. More recently,⁽³⁾ a study of chemisorption of SO_2 on activated carbon has been completed.

For several years, studies at Hanford have been conducted on the oxidation of moderator grade nuclear graphite by O_2 , H_2O , and CO_2 . The present study determines the rate of graphite removal by exposure to small partial pressures of sulfur dioxide carried by a helium gas stream. The effect of added carbon monoxide and added carbon dioxide on the weight loss rates is also determined.

EXPERIMENTAL

Thermal Studies

Small samples of TSX graphite were exposed to He/SO_2 mixtures in the apparatus shown in Figure 1. The possible effects of added CO or CO_2 were determined by pre-mixing the desired gas combination in a gas cylinder. The samples were heated to the reaction temperature in flowing helium then the test gas was turned on. The temperature was controlled to $\pm 3^\circ\text{C}$. The flow rate was approximately $400 \text{ cm}^3/\text{minute}$.

The gases used were helium, grade A from the Bureau of Mines, CP grade CO (minimum purity 99.5%) and Colman grade CO_2 (minimum purity 99.99%) from

the Matheson Company. The gases were used without further purification.

The graphite was in the form of small cylinders 1 inch long by 0.43 inch in diameter. TSX is a nuclear grade graphite, manufactured by the National Carbon Company. Typical ash content is less than 10 ppm. The density is 1.70 g/cm^3 .

Analysis

The progress of the reaction was followed by an infrared analysis of the products and by determining the loss of weight to a sample.

The effluent gas was passed through a gas cell with a 1 meter path length and analyzed semiquantitatively on a Perkin Elmer Model 237-G Spectrophotometer. Calibrations were made by preparing known mixtures containing CO_2 , CO, COS, CS_2 , and SO_2 in He and analyzing. The Beer-Lambert Law was assumed to be valid for all gases in the concentration range of interest. The limit of detection for the gases was as follows: $\text{SO}_2 = 20 \text{ ppm}$, CO = 500 ppm, $\text{CO}_2 = 20 \text{ ppm}$, COS = 10 ppm, and $\text{CS}_2 = 20 \text{ ppm}$. Sulfur was observed qualitatively by visual detection as a deposit on the quartz tube downstream from the furnace.

Weight loss rates were determined by comparing the weight of the graphite sample before and after an oxidation treatment. The rates are expressed as grams of graphite lost per gram of the graphite sample per hour.

RESULTS

Thermal Oxidation

The reaction of SO_2 with graphite yields a variety of products depending upon the reaction conditions. Earlier work by Siller⁽²⁾ outlined a large number of possible reactions which might occur in the reaction of SO_2 with

carbon materials. The gaseous products observed in this study include CO, CO₂, COS, and CS₂. In addition solid sulfur was plated out on the cooler surfaces downstream from the reaction zone. Table I is a summary of the products detected under a variety of initial conditions including inlet gas concentrations of (1) 1% SO₂ in helium, (2) 1% SO₂, 1% CO in helium, and (3) 1% SO₂, 1% CO₂ in helium. The temperature was also varied covering the temperature range from 700-1040°C. Studies include heating the gas in the absence of a graphite sample as well as with the sample in place.

The graphite oxidation rate was primarily determined by the loss of weight from the graphite sample.

The effect of SO₂ concentration on the rate is shown in Figure 2, which plots log rate vs. log SO₂(ppm). It will be noted from the figure that the apparent order of the reaction increases with increasing temperature. Such behavior is consistent with the following Langmuir type equation:

$$R = \frac{k_1 P_{SO_2}}{1 + k_2 P_{SO_2}} \quad (1)$$

in which the rate is inhibited by the adsorption of the reactant.

The magnitude of k_2 must decrease with increasing temperature to account for the apparent change in order. The rate constants of equation (1) have been evaluated from the data of Figure 2 from a plot of $1/R$ vs. $1/P_{SO_2}$. The rate constants thus determined for a variety of temperatures were then plotted on a standard Arrhenius plot to obtain the Arrhenius parameters.

The calculated temperature dependence for the overall reaction is shown in Figure 3 as a plot of log rate vs. $1/T$. The lines are calculated from equation (1) with:

$$k_1 = 4.39 \times 10^{-2} e^{-5.12 \times 10^3/RT} (\text{hr} - \text{mm of H}_g)^{-1} \quad (2)$$

$$k_2 = 4.28 \times 10^{-5} e^{2.87 \times 10^4/RT} (\text{mm of H}_g)^{-1} \quad (3)$$

Both CO and CO₂ were added to the inlet gas stream in order to determine the possible effect of product gases on the reaction rate. Figure 4 is a plot of log rate vs. 1/T for the three different inlet gas combinations: (1) 10,000 ppm SO₂, (2) 10,000 ppm SO₂ plus 10,000 ppm CO₂, and (3) 10,000 ppm SO₂ plus 10,000 ppm CO. Carbon monoxide, when added to the inlet gas at a concentration of approximately 1%, decreases the weight loss rate by about 40%. The addition of carbon dioxide, which is not observed as a product of the C + SO₂ reaction in the absence of added CO, does not appear to effect the weight loss rate. However, at 1000°C CO₂ itself reacts with graphite to produce CO at a rate of about 1/10 that observed. Therefore, a small inhibition by the CO₂ could be offset by the CO₂-graphite reaction.

DISCUSSION

In a system involving the species C, O, and S a number of different reactions can be postulated. Insight into the most probable reactions is obtained by observing the gaseous products and solid sulfur obtained under various experimental conditions.

Sulfur dioxide in the absence of graphite was observed to be thermally stable in the temperatures range investigated here, 700-1040°C. When graphite is added to the system a trace of product CO is observed at 900°C, solid sulfur first appears with the graphite at 1,000°C, and COS and CS₂ are additional products observed at 1040°C.

The addition of CO to the SO₂ inlet gas, while reducing the apparent graphite weight loss rate (Figure 4), enhances the rate of formation of COS, CO₂ and solid sulfur as shown in Table I. In the absence of graphite CO₂ is first detected at 1000°C. However, in the presence of graphite CO₂ and COS are observed at 700°C, solid sulfur at 800°C, and finally CS₂ at 1040°C.

The addition of CO₂ to the inlet gas has little effect on the weight loss rate (see Figure 4) as well as the rate of product formation. The data indicate that perhaps a small retardation of formation of CO, COS, CS₂ and solid sulfur occurs.

This system is kinetically very complicated due to the many possible products, gaseous, solid, and absorbed, and consideration must be given to both heterogeneous and gas phase processes. However, it does seem useful to make a few comments on possible mechanisms for the reaction.

Initially, particularly at low temperature, the products are carbon monoxide and sulfur. By analogy with the mechanism of the CO₂-graphite, the following mechanism seems possible.

At the highest temperature studied, CO₂ and COS also are produced. These products, however, appear to be due to secondary processes involving the product CO since they are formed at a much faster rate and at lower temperatures when CO is added to the inlet stream. This secondary process appears to be a surface catalyzed process since the products are formed only when the carbon sample is present. A possible path for formation of

the CO_2 and COS follows:

The CO also reduces the rate of weight loss from the sample. This, however, may be explained in terms of a competition for the activated SO_2 or other oxidizing species forming CO_2 .

Carbon disulfide is observed only at the highest temperatures studied and may arise as the disproportionation of COS by the reaction.

or as a reaction of sulfur with the carbon sample

Both of these reactions are thermodynamically capable of producing CS_2 in the concentration observed.

CONCLUSIONS

The primary products in the system $\text{C/SO}_2/\text{He}$ appear to be CO and solid sulfur, in the temperature range of 700-1040°C. Secondary products COS, CO_2 , and CS_2 are observed at high temperatures or when CO is added to the inlet gas. It is suggested that the CO competes with the graphite for the activated SO_2 . This process requires a graphite surface to be significant.

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TABLE I
INFRARED GAS ANALYSIS IN THE SYSTEM C/SO₂/CO/CO₂/He

Reactant Gas - 10,000 ppm SO ₂	10,000 ppm SO ₂ /10,000 ppm CO		10,000 ppm SO ₂ /10,000 ppm CO ₂	
T°C	No C	With C	No C	With C
700	N.R. ^a	N.R.	N.R.	CO ₂ -35 COS-90
800	N.R.	N.R.	N.R.	CO ₂ -385 COS-160 S ₂ -Trace
900	N.R.	CO-Trace	N.R.	CO ₂ -725 COS-210 S ₂
1000	N.R.	CO-650 ^c S ₂ ^b -Trace	CO ₂ -125	CO ₂ -990 COS-265 CS ₂ - 5 S ₂
1040	N.R.	CO-2300 CO ₂ - 25 COS- 50 CS ₂ - 80 S ₂	CO ₂ -135	CO ₂ -1760 COS-385 CS ₂ - 70 S ₂
				N.R.
				CO-1975 COS- 35 CS ₂ - 35 S ₂

^a N.R., No Reaction Detected

^b Solid sulfur appearing on the cooler quartz downstream from the graphite.

^c Concentrations in ppm.

APPARATUS FOR STUDYING THE C + SO₂ REACTION

FIGURE 1
Apparatus for Studying the C + SO₂ Reaction

PRESSURE DEPENDENCE OF THE C + SO₂ REACTION

SAMPLE NUMBER 201-491B

SA-2000-466 (R-65)
AEC-RL RICHLAND, WASH.

RATE g/g/HR

FIGURE 2

Pressure Dependence of the C + SO₂ Reaction

FIG. 3
TEMPERATURE DEPENDENCE OF C + SO₂ REACTION

RATE
G/G/HR

SAMPLE # 204-491 B

SEMI-LOGARITHMIC
358-71
KEUFFEL & ESSER CO.
MADE IN U.S.A.
3 CYCLES X 70 DIVISIONS

RATE
g/g/hr

KE
SEMI-LOGARITHMIC 358-71
KEUFFEL & ESSER CO. MADE IN U.S.A.
3 CYCLES X 70 DIVISIONS

10⁻²

10⁻³

10⁻⁴

Sa # 201-491-A

10,000 ppm CO + 10,000 ppm SO₂

10,000 ppm CO₂ + 10,000 ppm SO₂

10,000 ppm SO₂

LINEAR "LEAST SQUARES" LINES

Fig. 4 Effect of Added CO and CO₂
on the C + SO₂ Reaction

TEMPERATURE, °C

1050 1000 950 900 850 800 750 700

1/T °K × 10³

.78 .80 .82 .84 .86 .88 .90 .92 .94 .96 .98 1.00 1.02 1.04 1.06