THE EFFECT OF SUBSTITUTIONAL BORON ON THE KINETICS OF THE CARBON–CARBON DIOXIDE REACTION

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Abstract—Natural graphite flakes have been doped substitutionally with boron at atomic levels of 0·2 and 1·0 per cent. The reactivity of compacted samples of these graphites and the undoped material in a dry CO/CO_2 atmosphere (ratio of 0·15) has been studied as a function of temperature (925–1050°C), carbon burn-off, CO_2 pressure, and pre-treatment in O_2. Boronation lowers the rate of carbon gasification, but does not change the activation energy for the overall reaction. Unlike the reaction in O_2, there is no evidence that retardation is caused by formation of liquid B_2O_3, which would block active sites on the graphite surface. With continuing burn-off above 10 per cent, the graphite surface area and gasification rate remain constant. Boronation does increase the order of reaction with respect to CO_2 and decrease the rate constant, k_1, in the Langmuir–Hinshelwood kinetic scheme.

1. INTRODUCTION

A study of the effect of substitutional boron on the kinetics of the carbon–oxygen reaction has recently been reported by the authors [1]. The general conclusions reached were that boron introduced substitutionally into SP-1 natural graphite lowers the activation energy of the $C-O_2$ reaction in the same manner as it has been shown [2] to lower the Fermi level. However, the decrease in activation energy was coupled with a decrease in the Arrhenius pre-exponential term, and the combined effect was inhibition of the $C-O_2$ reaction. This inhibition was attributed to physical masking of the surface by accumulated boric oxide. Removal of the boric oxide by water vapor increased the surface area of the sample, and the subsequent reaction with O_2 was faster than for undoped SP-1 graphite under the same conditions. The progressive accumulation of boric oxide during gasification resulted in a steady decrease in surface area and reaction rate with sample burn-off.

The boric oxide accumulated even when the oxidation was performed in moist O_2.

Woodley [3, 4] has investigated the reaction of boronated nuclear graphites (5% boron) with O_2 and water vapor. He found a marked inhibition of carbon gasification in both cases. He also attributes this inhibition to the presence of boric oxide species on the graphite surface. Removal of the boric oxide by leaching in boiling water increased the surface area and the gasification rate (in O_2) of Woodley's samples. Litz and Mercuri [5] studied the reactions of boron carbide (B_4C) with dry and moist air and water vapor. They concluded that there is competition between the rate of boric oxide formation and removal in the presence of water vapor. This could explain why boric oxide is not removed from the graphite surface in the moist O_2 [1] and water vapor [4] studies discussed above.

Thomas and Roscoe [6] doped single crystals of natural graphite with boron and observed a significant catalytic effect in moist

O_2. This may be due to the removal of boric oxide as volatile boric acids at the higher temperature used in their work (835°C compared with 500°–650°C in both our studies and those of Woodley) or to the lack of a porous structure in their single crystals compared with the compacted nuclear[3] and SP-1[1] graphite samples used in previous investigations.

In the present work the effect of substitutional boron on the kinetics of the carbon-CO_2 reaction is investigated, using SP-1 graphite samples at temperatures from 925 to 1050°C and CO_2 pressures from 10 to 100 Torr. The reaction was studied using CO/CO_2 gas mixtures (with a constant CO/CO_2 ratio of 0·15) to avoid transient rate effects which have previously been reported for this system[7] and were independently observed in a preliminary investigation for the present study. The authors considered it desirable to restrict the work to steady state kinetics in order to compare gasification rates on samples of varying boron content.

2. EXPERIMENTAL

2.1 The graphite samples

The preparation and analysis of the graphite samples used have been discussed in detail elsewhere[1, 8] and will not be repeated here. Suffice to say that the boron was introduced substitutionally by heating to 2500°C and tests were made to ensure that no significant amounts of interstitial boron remained. The graphite samples were compacted and machined into plates $1 \times \frac{3}{8} \times \frac{1}{16}$ in with a $\frac{1}{8}$ in hole for suspension of the samples from a microbalance. The samples studied in this work contained 0·2% and 1·0% boron (on an atom basis), as well as a specimen of the original SP-1 graphite containing less than 1 ppm boron.

2.2 The apparatus

The graphite samples were suspended by a 100 μ diameter quartz fiber from a Cahn R. G. Electrobalance with a sensitivity of 10^{-6} g. The balance was enclosed in a Pyrex vacuum system containing a double-walled quartz hang-down tube. The outer jacket of the hang-down tube was continuously evacuated by a mercury diffusion pump to minimize permeation of gaseous impurities through the walls into the high temperature region of the apparatus. The reaction system could be evacuated to 5×10^{-7} Torr by a Vac-Ion gettering pump and a two stage mercury diffusion pump. The sample suspended in the hang-down tube was heated by a resistance furnace, which produced a constant temperature zone about 4 in. in length. The temperature was controlled to ±2°C at 1000°C by a Leeds–Northrup unit.

Associated with the static reaction system was a Pyrex vacuum line for the preparation and storage of the reacting gases.

2.3 Preparation of the gases

All of the gases used were supplied in cylinders by the Matheson Company. They were Coleman Grade CO_2, C.P. grade CO and Research grade Ar. They were purified from traces of water by passing through 1 ft towers of anhydrone and P_2O_5 successively, followed by passage through 1 ft of copper turnings held at 550°C to remove O_2. The gases were further purified by condensing in cryogenic traps followed by extensive pumping. The CO and CO_2 were then allowed to expand and to mix in the volumetric ratio, $CO/CO_2 = 0·15$, and stored in 12 l. bulbs. The Ar was similarly stored in a 12 l. bulb. All these bulbs were connected to the reaction system by a common manifold.

2.4 Procedures

Before any measurements were performed on a sample, it was degassed for 10–12 hr at 2×10^{-6} Torr and 1075°C, 25°C higher than the maximum temperature used in any of the experimental runs. The samples were similarly degassed after each readjustment of the counterweights, since this step involved exposing the sample to air. Each sample was

initially burnt-off to at least 10 per cent weight loss in the standard CO/CO_2 mixture before any kinetic parameters were determined.

The rates of the carbon—CO_2 reaction were determined gravimetrically from the weight loss of the sample. A constant gas mixture ($CO/CO_2 = 0.15$) was used throughout the investigation. Activation energies were determined from Arrhenius plots of the rates at a CO_2 partial pressure of 30 Torr and temperatures between 925 and 1050°C, where the reaction rate was chemically controlled. The order of the reaction was determined in the same temperature range and CO_2 partial pressures from 10 to 100 Torr. The same data were used in the Langmuir–Hinshelwood analysis of the kinetics discussed below.

Argon BET surface areas were determined gravimetrically in the same apparatus at 77°K.

3. RESULTS AND DISCUSSION

3.1 *The effect of sample burn-off*

In the C–O_2 work reported previously[1], it was found that the SP-1 graphite samples had an initial surface area of 1.8 ± 0.2 m²/g over the initial 10 per cent burn-off in O_2. The subsequent surface area and rate of gasification (under constant reaction conditions) were independent of further burn-off up to 25 per cent for the undoped SP-1 samples, but both parameters exhibited a steady decrease with increasing burn-off in the case of the boron-doped samples.

In contrast, neither the surface area nor the rate of gasification of the boron-doped samples studied in the present work showed any evidence of a systematic decrease with increasing burn-off in the CO/CO_2 mixture. This is illustrated by the results reported in Table 1. Here the increase in surface area for the first 10 per cent burn-off in CO_2 is comparable with that produced in O_2[1], but there is no evidence of a decrease in either the rate or surface area with subsequent burn-off. In our O_2 studies, the decrease in

surface area was attributed to progressive accumulation of B_2O_3 on the surface of the graphite, which has been observed in optical work on single crystals[6] as filling the etch pits or forming a surface glaze. Treatment with water vapor decreased the sample weight

Table 1. Effect of burn-off on surface area and rate of reaction of boron doped and undoped SP-1 graphite with CO_2

Boron content	Burn-off (%)	Surface area (m²/g)	Rate* (mg/g/hr)
<1 ppm	0	1.9	—
	10	3.4	1.72
	15	3.4	1.80
1%	0	1.9	—
	10	3.6	0.50
	15	3.6	0.51
	20	3.6	0.49
	20.2	3.5†	—

*Rate determined at 1025°C, $p_{CO_2} = 30$ Torr, CO/CO_2 ratio $= 0.15$.

†Area determined after treatment in 20 Torr of water vapor at 300°C for 10 hr.

and restored the area to the 3.6 ± 0.4 m²/g range obtained for the undoped samples, with an associated increase in gasification rate. This was presumably due to the removal of the boric oxide as volatile boric acid species. In fact, a white condensate was observed in the cooler parts of the hang-down tube. In contrast, in the present work, water vapor treatment of the 1 per cent boron sample burnt-off to 20.2 per cent in the CO/CO_2 mixture caused no significant change in sample weight or area (see Table 1), and no boric acid condensate was observed in the apparatus. It is, therefore, concluded that during gasification in CO_2 there was no significant formation of B_2O_3 on the surface of the graphite.

It is surprising that the boron present in the graphite does not react, since a blank run established that amorphous boron was oxidized readily in the same temperature range (925 to 1050°C) by the CO/CO_2 mixture.

However, such effects are not unknown in boron–carbon composite materials. Woodley [4] found no significant gasification of carbon during reaction of his boronated nuclear graphites with H_2O at temperatures where undoped graphite readily reacts with H_2O. The only significant reactions he found were oxidation of the boron to B_2O_3 and its evolution as volatile boric acids. It, therefore, appears that not only does the boron inhibit the carbon gasification reactions (as discussed in the introduction); but the presence of carbon can also inhibit boron oxidation, at least in CO_2. The rates given in Table 1 show that carbon gasification in CO_2 is also inhibited by the presence of boron, as were the reactions in O_2[1, 3, 6] and H_2O[4].

It was found that the rates of carbon gasification in CO_2 were also very sensitive to prior formation of B_2O_3 on the surface of boron-doped samples during gasification in O_2. Burn-off to less than 5 per cent in O_2 of a sample containing 0·1 per cent boron was enough to suppress the C–CO_2 reaction to the point where the gasification rate was negligible over the reaction conditions studied in the present work. It was, therefore, essential that the samples used for the following kinetic studies be reacted with CO/CO_2 mixtures only, since O_2 causes B_2O_3 formation on the surface and pure CO_2 may react via a transient mode[7] with a marked increase in surface area and a consequent change in reactivity.

3.2 The effect of substitutional boron on the activation energy and order of the C–CO_2 reaction

Arrhenius plots of the rate data for three different SP-1 graphite samples, containing <1 ppm, 0·2 per cent and 1 per cent substitutional boron, are presented in Fig. 1. The rates were obtained in the temperature range 925°C–1050°C at a constant CO/CO_2 ratio (0·15), a CO_2 partial pressure of 30 Torr, and at sample burn-offs greather than 10 per cent. Each run required only a fraction of a

per-cent burn-off, and a negligible change in gas composition occurred.

Figure 1 shows that the overall activation energy of the C–CO_2 reaction is 87 ± 2 kcal/mole, independent of the boron content of the samples studied. This value is in good agreement with the results of other workers [7, 9] for the overall activation energy of the C–CO_2 reaction. For each sample, neither the value of the activation energy nor the rates of gasification are affected by additional burn-off.
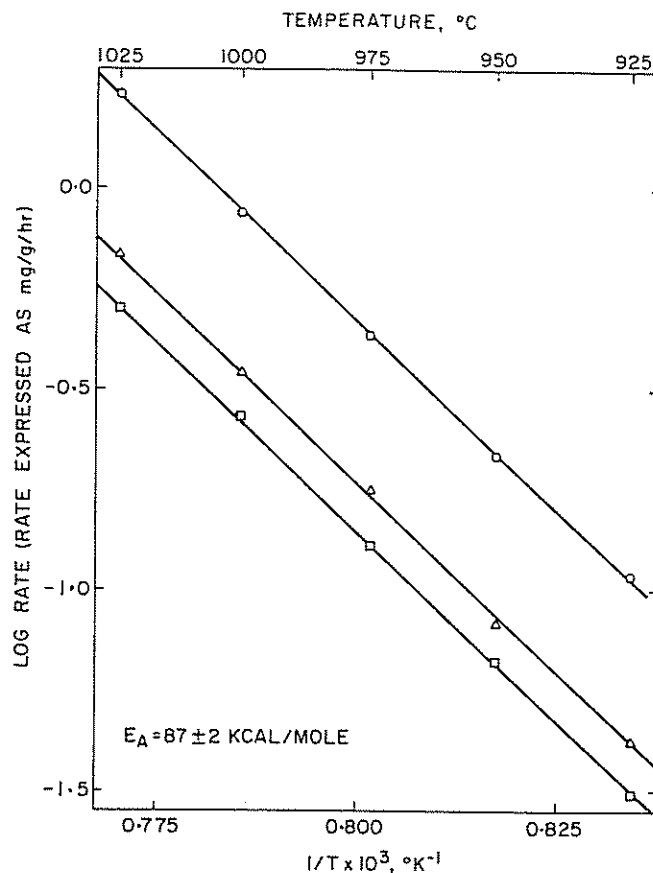

Fig. 1. Arrhenius plots for gasification of boron-doped SP-1 graphite with CO_2, CO/CO_2 ratio— $0\cdot15$, $p_{CO_2} = 30$ Torr. O, < 1 ppm B; △, $0\cdot2\%$ B; □, 1% B.

Figure 2 illustrates the effect of varying the CO_2 pressure, while maintaining the CO/CO_2 ratio constant, for reaction at 1025°C. The slope of the lines, giving the order of reaction with respect to CO_2, increases from 0·21 to 0·73 as the boron content of the graphite increases. Varying the temperature within
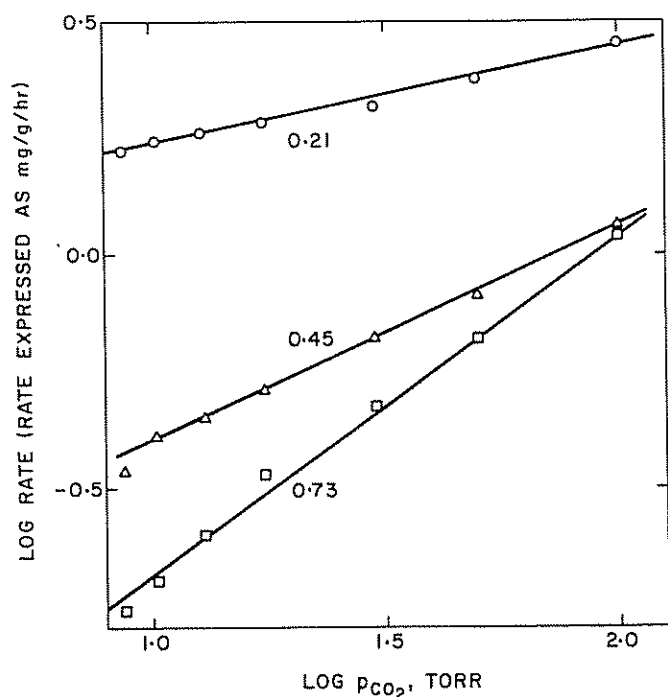
Fig. 2. Effect of varying p_{CO_2}, with a constant CO/CO_2 ratio (0·15), on the rate of gasification of boron-doped SP-1 graphites. The slope gives the apparent reaction order. O, <1 ppm B; △, 0·2% B; □, 1% B.

the 925 to 1050°C range results in only a slight random variation in these orders (within ±0·05). Similarly, the orders are not affected by additional sample burn-off. There is a tendency for the order for each sample to increase slightly at the low pressure end of the scale.

The effect of boron on the order and activation energy of the C–CO₂ reaction is in complete contrast to its effect on the C–O₂ reaction[1]. In that study, the activation energy decreased with increasing boron content, while the order was not affected by the presence of boron. This implies that since the order for the C–O₂ reaction is unchanged, the rate controlling step remains the same and rate control does not shift to another step in the mechanism. Thus the reported decrease in the pre-exponential term over-rides the decrease in activation energy, and the rate controlling step becomes even slower.

However, in the C–CO₂ reaction, the order changes with degree of boronation, while the

activation energy is not affected. The increase in order with boron content suggests that rate control shifts more towards the initial chemisorption or oxygen exchange step, which is first order with respect to CO₂. Hence, the initial step in the reaction mechanism must be sufficiently retarded to increase its influence in controlling the rate, although the overall activation energy is not significantly affected. This point will be pursued further in the following section.
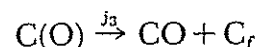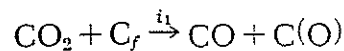
The inhibition of the C–O₂ reaction as a result of boronation was attributed to physical masking of the surface and blocking of active sites by accumulation of B₂O₃ reaction proceeds. However, there is no evidence of any accumulation of B₂O₃ on the surface in the case of the C–CO₂ reaction. Hence, the observed inhibition of the C–CO₂ reaction (Figs. 1 and 2) suggests that the decrease in the pre-exponential term is associated with a true chemical effect rather than a physical masking effect.
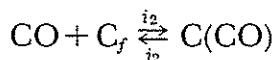
3.3 Evaluation of k_1 in the Langmuir–Hinshelwood expression

There is considerable agreement in the literature[9] that over a wide range of experimental conditions, the gasification of carbon with CO₂ follows an equation of the form
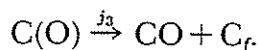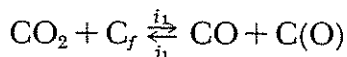
$$\text{Rate} = \frac{k_1 p_{CO_2}}{1 + k_2 p_{CO} + k_3 p_{CO_2}} \quad (1)$$

where k_1, k_2, and k_3 are rate constants or combinations of rate constants and p_{CO_2} and p_{CO} are the partial pressures of CO₂ and CO respectively. According to Walker and co-workers[9], there are two mechanisms which fit an equation of this form; they differ only in the manner in which CO retards the reaction. These are Mechanism A

$$CO_2 + C_f \xrightarrow{i_1} CO + C(O)$$

$$C(O) \xrightarrow{j_3} CO + C_f$$

$$CO + C_f \underset{j_2}{\overset{i_2}{\rightleftarrows}} C(CO)$$

and Mechanism B

$$CO_2 + C_f \underset{j_1}{\overset{i_1}{\rightleftarrows}} CO + C(O)$$

$$C(O) \overset{j_3}{\rightarrow} CO + C_f.$$

In either case, the rate constant k_1 corresponds to i_1 for the initial chemisorption or oxygen exchange step, and k_3 corresponds to the ratio i_1/j_3. If Mechanism A is operative, k_2 is equivalent to i_1/j_2; and if Mechanism B holds, k_2 corresponds to j_1/j_3.

Rearrangement of equation (1) to

$$1/\text{Rate} = 1/k_1 p_{CO_2} + k_3/k_1 + (k_2/k_1)(p_{CO}/p_{CO_2}) \tag{2}$$

shows that the constant k_1 can be evaluated from a plot of 1/Rate against $1/p_{CO_2}$ at a constant CO/CO_2 ratio. Appropriate plots are shown in Fig. 3 for two of the samples at various reaction temperatures between 925 and 1050°C. The plots show reasonable linearity. The constant k_1 can be determined from the slope of the line. The intercept corresponds to $(k_3/k_1) + (k_2/k_1)(p_{CO}/p_{CO_2})$ or since the CO/CO_2 ratio was maintained at 0·15 throughout this work, $(k_3 + 0·15k_2)/k_1$. This intercept term does not warrant a detailed discussion, since it is a complex combination of rate constants. To evaluate k_2 and k_3 individually would necessitate a further series of experiments at a number of different CO/CO_2 ratios and at several temperatures in the 925–1050°C range. The data obtained from such experiments require extensive mathematical manipulation to evaluate the individual rate constants, and the values obtained are considerably less reliable than the $k_1(i_1)$ data, which can be determined directly from the slope of the Langmuir–Hinshelwood plot.

The values determined for k_1 from Fig. 3 are plotted on an Arrhenius basis in Fig. 4. The presence of 1 per cent boron in the
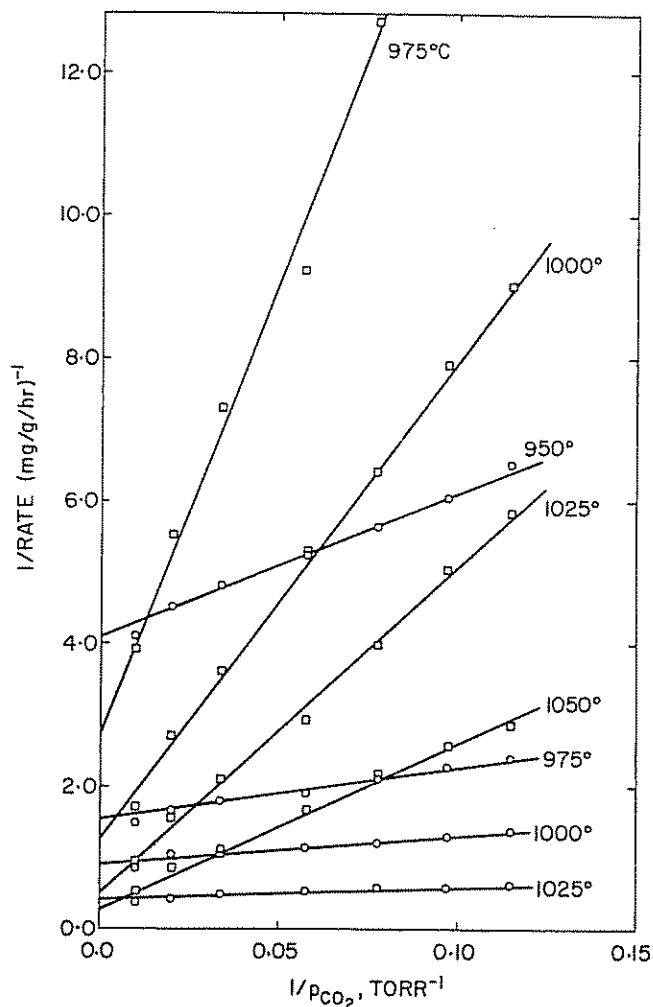

Fig. 3. Langmuir–Hinshelwood plots for boron-doped and undoped SP-1 graphite, at various temperatures. The data were obtained at a constant CO/CO_2 ratio of 0·15. O, <1 ppm B; □, 1% B.

graphite has significantly decreased the values of k_1, the rate constant for the initial chemisorption or oxygen exchange step in both Mechanism A and B. The activation energy determined from the slope of the Arrhenius plots for k_1 has also decreased, from 100 ± 5 kcal/mole for the undoped sample to 72 ± 5 kcal/mole for the 1 per cent boron sample.

Unfortunately, insufficient data were obtained to determine activation energies for k_1 on other boron-doped samples. Thus it is not possible to compare the decrease in activation energy with the lowering of the Fermi level of graphite due to boronation[2] as was done in our C–O$_2$ studies[1]. However,
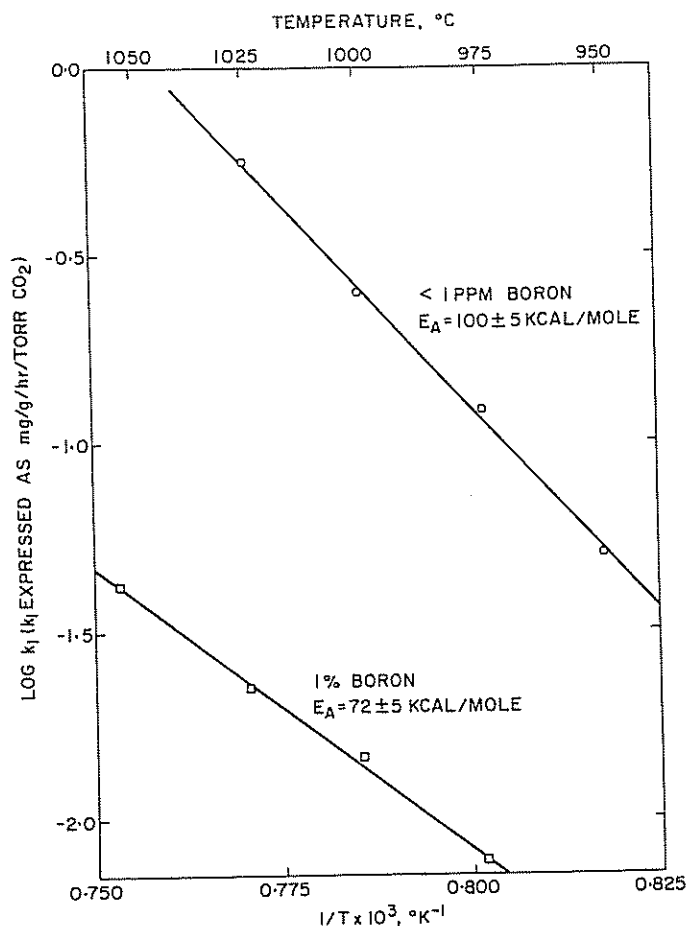
TEMPERATURE, °C

Fig. 4. Arrhenius plots of the Langmuir–Hinshelwood rate constant k_1 for boron-doped and undoped SP-1 graphite, determined at a CO/CO_2 ratio of 0·15. O, <1 ppm B; □, 1% B.

it can be concluded that substitutional boron does have a true chemical effect on the kinetics of the C–CO_2 reaction, since it influences the activation energy of at least the first step in the reaction mechanism, even though the overall activation energy is not affected. Such a phenomenon cannot be explained merely by assuming that the substitutional boron atoms present in the graphite lattice will act as lattice vacancies and increase the number of active sites, as has been suggested for the C–O_2 system [10].

The activation energy determined for the rate constant k_1 for the undoped SP-1 sample (100 kcal/mole) is rather high but is in good agreement with the values of 99 kcal/mole [11] and 103 kcal/mole [12] obtained on SP-1 graphite by earlier workers. These values were previously considered anomalous.

The observed retardation in the rate constant (k_1) values for the initial chemisorption step in the reaction mechanism can explain the increase in order of the overall reaction, reported in the preceding section. The chemisorption or oxygen exchange step is undoubtedly first order with respect to CO_2 since it involves a direct gas-surface interaction. Retardation of this step to the point where it begins to inhibit the overall reaction rate will, therefore, increase the reaction order.

The retardation of k_1 occurs despite the decrease in activation energy of this step with boronation. The inhibition must be due to an over-riding decrease in the pre-exponential term for the initial chemisorption step. Since there is no evidence of accumulated B_2O_3 on the surface during gasification in CO_2, the decrease in the pre-exponential term must be due to some chemical effect rather than physical masking of surface sites. This appears to be another example of the widely observed but little understood compensation effect, where a decrease in activation energy due to catalytic behavior is accompanied by a decrease in the pre-exponential term.

4. SUMMARY

The presence of substitutional boron in SP-1 graphite has an inhibiting effect on the C–CO_2 reaction, by retarding the initial chemisorption or oxygen exchange step. Retardation of this step, which is first order with respect to CO_2, causes it to have a greater influence in controlling the overall C–CO_2 reaction rate. This explains why the overall rate is also retarded and has an increased order, with respect to CO_2, with increased boron doping. It is surprising, however, that the presence of boron in the graphite had no apparent effect on the overall activation energy of the reaction, despite the

decrease in the activation energy for the initial step in the mechanism.

Boron-doping of graphites also retards the $C-O_2$[1, 3, 6] and $C-H_2O$[4] reactions. In fact, the only reported catalytic effect of boron-doping is in Thomas and Roscoe's [6] single crystal studies, where catalysis was observed during reaction with moist O_2 at 835°C. The more common inhibition effects in O_2 and H_2O studies have been attributed, at least in part, to the accumulation of B_2O_3 species on the surface of the graphite[1, 3, 4, 6]. However, in our studies with CO_2, there was no evidence of any B_2O_3 accumulation on the sample. Retardation in this case must be due to some chemical effect, which compensates for the decrease in the activation energy of the first step in the mechanism by also decreasing the pre-exponential term for this step. This does not mean that the previous explanation of the retardation based on surface B_2O_3 species was erroneous. In fact, it was found that prior oxidation of a boronated SP-1 sample in O_2, and hence formation of B_2O_3 on the surface, had a considerable additional retarding effect on gasification in CO_2.

In conclusion, it would appear that any further work on the kinetics of the reactions of boronated graphite should be accompanied by a parallel microscopic study of the effect of surface boron and boric acid species, if one is to distinguish between surface effects of reaction products and bulk chemical effects.

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