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HIGH PRESSURE STUDIES OF THE CARBON-OXYGEN REACTION

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Abstract—The reaction of highly crystalline graphite flakes at O_2 pressures between 0.1–6.4 MPa and temperatures between 733–842 K is followed. The global activation energy for the reaction is 204 ± 4 kJ/mole and is independent of carbon burnoff and O_2 pressure. The order of the reaction decreases from 0.83 to 0.51 as reaction temperature increases from 733 to 842 K. The results are considered on the basis of the known existence of stable and fleeting oxygen complexes on the carbon surface and the possible existence of nascent carbon active sites during carbon gasification.

Key Words—Oxidation, gasification, surface complexes, reaction order.

1. INTRODUCTION

The C–O_2 reaction arguably is the most important reaction known. Voluminous amounts of research have been conducted in an attempt to elucidate the mechanism of the reaction and to obtain fundamental rate constants. In drawing attention to the obtrusiveness of this reaction Thomas[1] said in 1970, "It has so far defied all efforts to unify it with the other gasification reactions. We proceed well into the area of theoretical, if not experimental, uncertainty. This reaction is of rabbinical complexity." Fortunately, since 1970, excellent progress has been made in understanding the general framework of the reaction[2]. This understanding has been aided by the availability of high-purity graphite single crystals and stress recrystallized pyrolytic graphite[3,4]. The complexity of the reaction is understandable since it involves dissociative oxygen chemisorption, oxygen surface diffusion, and desorption of surface oxygen complexes[2]. Understanding of these steps, individually, is made difficult because of the combination of *a priori* and induced surface heterogeneity[5]. Understanding the global result of these steps as they occur simultaneously presents still greater difficulty.

It is now generally accepted that all carbons have a fraction of their total surface area comprised of active sites[6]. It is on these sites, which exist at the edges of the basal plane of graphite, where activated chemisorption of oxygen first proceeds. The oxygen complex formed under steady-state conditions during carbon gasification is known to consist of two broad types—a stable complex not directly undergoing desorption, and a fleeting complex resulting in carbon gasification. The fraction of the total active surface area (TASA) occupied by these two complexes depends upon the temperature and O_2 pressure at which the reaction is conducted.

This study has been extended to high O_2 pressures (up to 6.4 MPa) for at least two reasons. First, surprisingly little kinetic data are available for the C–O_2 reaction above 0.1 MPa pressure. Second, as pressure increases, the amount of fleeting oxygen complex participating in carbon gasification increases. This enables the measurement of this complex even though one works with a highly crystalline graphite of low surface area.

2. EXPERIMENTAL

2.1 *Reactants*

The carbon used was spectroscopic purity SP-1 natural graphite powder from Union Carbide Corp. It is comprised of flakes having diameters in the range 1–200 μm. The BET surface area (Kr, 0.195 nm^2, 77 K) is 1.8 m^2/g. Typical flake diameter and thickness are 30 and 0.5 μm, respectively. Microscopic examination of the powder after various periods of oxidation reveal very few crystallite boundaries within the flakes and negligible basal plane pitting. The flakes do, however, exhibit extensive terracing in the basal plane. Estimates for the active area, (100) and (110) prismatic surfaces, range from 3% of the total area (based on simple unroughened average geometry) to 30% of the total area (based on the height of isotherm steps using Kr at 77K and the Thomy and Duval method[7,8]). Total impurity content of the graphite is guaranteed to be under 1 ppm. The only impurities detected in the lot used were 0.1-ppm Fe, 0.1-ppm Mg, and 0.2-ppm Si.

The O_2 was used as received. It had <3-ppm H_2O, <0.5-ppm total hydrocarbons, and >99.99% O_2.

2.2 *Apparatus*

Apparatus details are given elsewhere[9]. Basically, the apparatus consists of a gas mixing system, a furnace, and a monitoring system for pressure, flow rate, CO, and CO_2 concentrations. Product gas concentrations were determined by nondispersive infra-

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red analyzers. Flow rate was determined by a thermal type mass flowmeter. Pressure was determined by a strain gauge-type pressure transducer. The furnace had three independent heat zones and was double jacketed. A flowing ultra high-purity Ar atmosphere was maintained between the jackets for desorption experiments. For reactivity experiments, high-purity oxygen was maintained between the jackets. The sample was contained in a boat of high-purity (>99.99%) alumina in the central heat zone. A microcomputer controlled the furnace temperatures and recorded the data. Instantaneous gasification rates were determined from the total gas flow and the product concentrations. Instantaneous sample weight was calculated from the initial weight and the integrated gasification rate. Calculated final sample weights agreed with gravimetrically determined final sample weights to within 0.5%.

Calculations show that, at reaction conditions used, negligible concentration gradients of O_2 existed through the graphite bed[9]. Since the C–O_2 reaction is very exothermic, the sample temperature will be higher than the surrounding gas temperature. The difference in temperature (ΔT) will be determined by the CO/CO_2 product ratio, the gasification rate, and the heat transport mechanism. For all of the runs conducted in this study, it is estimated that the maximum ΔT is 1.0 K, which is equivalent to the measured rate being about 2.5% higher than the true rate[9].

2.3 *Procedure*

The graphite was first burned off to about 17% so that the specific total active surface area would remain essentially invariant during the subsequent reactivity measurements, as previously observed[10–12]. After this initial burnoff, a linear program thermal desorption (LPTD) run was performed in flowing high-purity Ar at 5 K/min to 1234 K. The sample was held at maximum temperature for 4 h before cooling down in Ar to reaction temperature.

Each isobaric reactivity run consisted of a number of measurements at selected temperatures. Data were recorded at each temperature until steady-state conditions were observed, but in all cases data were recorded for at least ten residence times after the temperature had stabilized. Steady-state concentrations were typically observed before one residence time had passed once the temperature was stable. Residence times were dominated by the hot pressurized sample chamber volume and ranged from about 0.3 min at 0.2 MPa to 13 min at 5 MPa at 673 K and 0.7 standard liter per minute (slpm). Gasification rates were found to be essentially independent of the flow rates used in this study, that is between 0.2 and 0.7 slpm.

For each isobaric series, the temperatures were selected in stepwise increasing order, with final replicate determinations at some or all of the lower temperatures. This was done in order to check for changes in surface activity which may have occurred during the isobaric series. Stepwise increases were used in order to avoid the sample-gas temperature lag associated with faster continual temperature increases. The first isobaric series and the last isobaric series were performed after a LPTD at low pressures in order to check for overall changes in surface activity which may have occurred between the isobaric series.

3. RESULTS

Isobaric runs were made at nine pressures between 0.1 and 6.4 MPa. Arrhenius plots for selected runs at 1.0 and 6.4 MPa are given in Fig. 1. No significant changes in rates were seen in the ascending and descending temperature series at each pressure. Rates are expressed as μmoles C lost per gram C remaining per second, where the g C remaining is approximated by the average weight of carbon during the isobaric series. Some error is thus introduced for series in which a significant burnoff occurred but not enough to affect the interpretation of the results or an estimation of the Arrhenius parameters. The activation energy for the nine isobaric runs was 204 ± 4 kJ/mole, with no significant effect of reaction pressure or carbon burnoff on activation energy seen.

Results could be combined in an order plot (Fig. 2). This order plot uses data extrapolated from the Arrhenius plots for the two extreme temperatures and the average temperature investigated during the experiments. The order plot also gives the least-square fits for the seven more reproducible higher pressure data points. The ± value after the order estimate is the estimate of the standard deviation.

4. DISCUSSION

It is now recognized that under steady-state carbon gasification conditions there exist two broad types of oxygen complexes on the carbon active sites[6]. One is a stable complex which does not directly lead to carbon gasification. The other is a fleeting complex. The complexes form by dissociative chemisorption of O_2 on to carbon active sites. If the fraction of the active sites covered by the fleeting complex is θ_f, the rate of carbon gasification is proportional to the product of θ_f and a rate constant. At a particular temperature, the order of reaction depends upon the relationship between the change of θ_f and the change in pressure of the reacting gas. At one extreme, if θ_f approaches one throughout the range of pressure change investigated, the reaction will be zero order. At the other extreme, if θ_f is small, the change in θ_f will be directly proportional to the change in pressure; and the reaction will be first order. At intermediate values of θ_f, the order of the reaction will vary from zero to one.

It is apparent that at a particular temperature, where the values of the rate constants for the formation and conversion of the surface-oxygen complex (by gasification) are fixed, the pressure of the reacting gas can affect θ_f and, hence, the order of the reaction.

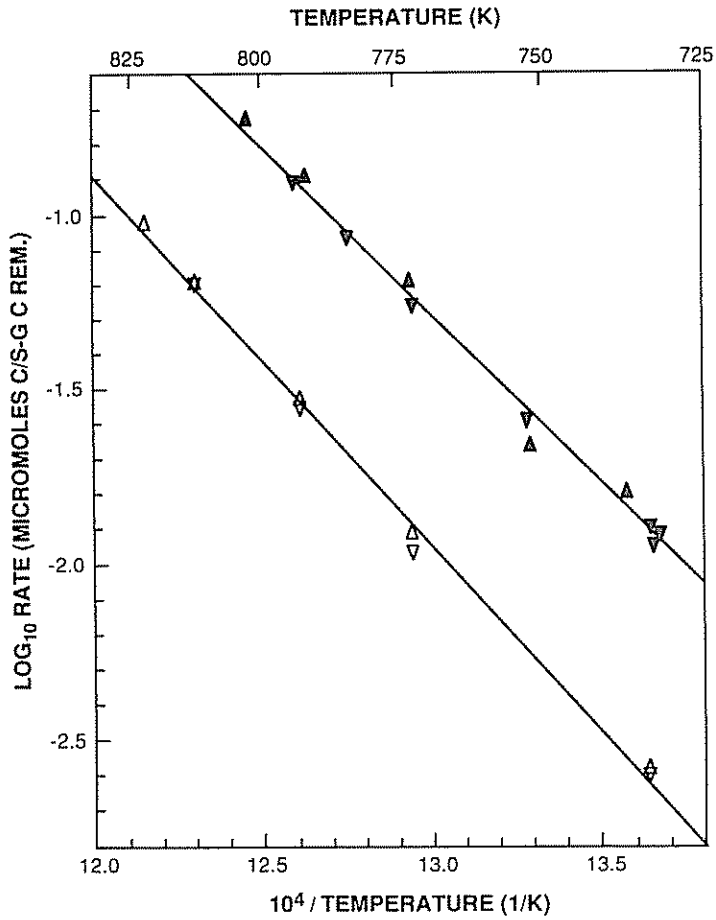

Fig. 1. Arrhenius plots for isobaric runs at 1.0-MPa O_2 (open symbols) and 6.4-MPa O_2 (closed symbols). Ascending (Δ,▲) and descending (▽,▼) temperatures.

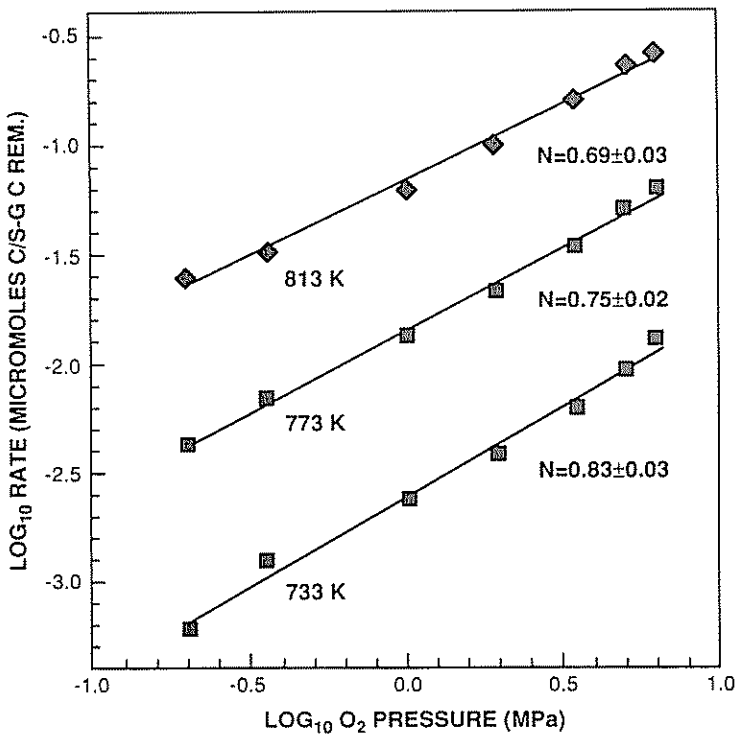

Fig. 2. Carbon reactivity as a function of O_2 pressure.

For example, at sufficiently higher pressures, θ_f approaches one and the reaction order approaches zero. Reaction temperature can also affect the order of a reaction. Since the rate constant for the conversion (or desorption) of the surface-oxygen complex has a considerably higher activation energy than the rate constant for the formation of the complex[13,14], the reaction order should decrease with decreasing temperature and ultimately become zero order at sufficiently low temperature. It was our intention in this study to achieve a zero-order reaction by working at elevated pressures (up to 6.4 MPa or 64 atm) and low gasification temperatures, but this result was not achieved. Unexpectedly, as seen in Fig. 2, the reaction order increased with decreasing reaction temperature when the order was calculated over the pressure range 0.2–6.4 MPa. It was not possible to conduct the reaction at higher temperatures and remain in the Zone I region of chemical reaction control due to mass and heat transport effects on the reactions[15]. Apparatus design limited our going to significantly higher pressures.

It is desirable to look more deeply into what we know about the mechanism of the C–O_2 reaction. It has been shown, by using O_2^{18-18} and O_2^{18-18}, that CO and CO_2 are both primary products of the reaction[16]. It has further been shown that the variation of the product ratio, CO/CO_2, with temperature is given by $A\exp(-E/RT)$, where E equals 27 kJ/mole and is independent of both the specific active surface area (ASA) and the fraction of this area covered by oxygen complex[17]. On the other hand, the pre-exponential factor A, increases with increasing ASA and decreasing surface oxide coverage[17]. Carbon monoxide is thought to be derived, primarily, from oxygen complexes existing as carbonyl groups on zigzag (100) and armchair (110) carbon sites; CO_2 is thought to be derived, primarily, from lactone[18] and anhydride[19,20] groups on dangling carbon sites. It is obvious that with increasing reaction temperature, and constant ASA and its coverage, oxygen becomes increasingly more efficient at gasification of carbon atoms. This fact, in part, determines the magnitude of the overall activation energy measured experimentally for the C–O_2 reaction.

Extensive studies have been conducted on the kinetics of oxygen chemisorption on carbon surfaces, for example by Bansal *et al.*[13]. For runs at constant temperature and constant O_2 pressure, plots of the extent of oxygen chemisorbed versus log (time) show linear regions broken by sharp changes in slope. Abrupt changes in slope occur at equal values of oxygen chemisorbed at different adsorption temperatures. Such kinetics are associated with the Elovich equation[21] and is attributed to *a priori* and/or induced heterogeneity[5]. *A priori* heterogeneity is attributed to the active surface area being terminated by different configurations of carbon atoms. Sharp changes in slope of the so-called Elovich plots are attributed to the presence of different sets of sites on which activation energies for oxygen chemisorption differ widely. Induced heterogeneity is thought to occur if chemisorption of oxygen results in a significant change in the Fermi level (or work function) in the solid. If the chemisorption of oxygen on graphite resulted in the participation and localization of a mobile π-electron, for example, the Fermi level would be lowered. In fact, such an effect has been found for the chemisorption of oxygen on the graphite used in this study[22]. That is, increasing oxygen chemisorption progressively reduced the negative absolute thermoelectric power of the graphite, eventually converting it to a positive value. Induced heterogeneity is expected to result in a linear increase in activation energy for adsorption (E_a) and a linear decrease in heat of adsorption (q) with increasing coverage (θ). It is also expected to result in a linear decrease in activation energy for desorption (E_d) with increasing coverage.

We recently reported on additional studies with SP-1 graphite which shed further light on the connection between gasification rate and O_2 pressure[2]. Our approach was to react the graphite to a fixed level of burnoff (about 20%) at essentially a constant temperature (837–851 K) in different pressures of O_2 ranging from 0.1 to 3.5 MPa. The rationale was that at the completion of each reactivity run the amount of stable oxygen complex should be the same but the amount of fleeting complex should increase with increasing O_2 pressure. Results are summarized in Fig. 3. Reactivities at 20% burnoff are plotted against the total surface oxide (both stable and fleeting) recovered at the completion of each run by heating to 1234 K. The linear plot shows two important features. First, there is a finite intercept at 5.5-μmole O/gC at a negligible (zero) gasification rate. This is interpreted as the amount of stable oxygen complex existing at the completion of the gasification runs; this amount is independent of O_2 pressure. Second, there is a constant proportionality between gasification rate and the amount of fleeting complex remaining.

The question is immediately raised as to why there is this direct proportionality between gasification rate (desorption of a surface oxygen complex) and amount of fleeting complex on the surface. As has just been discussed, for desorption involving induced and/or *a priori* heterogeneity, as described by the Elovich equation, the rate of desorption increases exponentially with increasing θ. Direct proportionality between desorption rate and θ_f would only be expected if E_d is independent of θ_f. Studies by Kelemen and Freund[23] confirm experimentally, however, that this independence does not exist for desorption of oxygen from graphite. Using Auger electron spectroscopy, photoelectron spectroscopy, and low-energy electron diffraction, they measured thermal stabilities of the oxygen chemisorbed on the edge surface of stress recrystallized pyrolytic graphite at 573 K. At very low oxygen coverages, CO formation energies exceeded 334 kJ/mole; it decreased to 243 kJ/mole at maximum oxygen coverage achieved at 300 K.

A possible answer to the apparent inconsistency

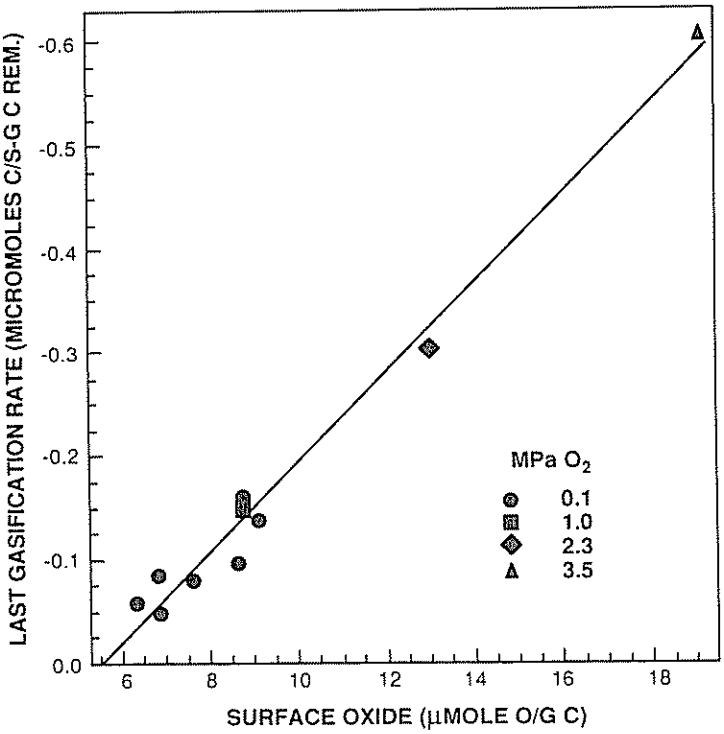

Fig. 3. Relationship between last gasification rates at 844 K and 20% burnoff and amount of oxygen complex present on the surface. Gasification conducted at O_2 pressures between 0.1 and 3.5 MPa.

appears to evolve from a paper by Long and Sykes written some years ago[24]. They say that the heat generated through the dissociative chemisorption of O_2 onto the carbon surface contributes to overcoming the activation energy required for the subsequent desorption of the carbon–oxygen complex. But in the presence of induced and/or *a priori* heterogeneity, the heat of chemisorption (q) decreases linearly with increasing θ. Therefore, the activation energy for desorption as a function of θ will be given by

$$E_{d,\theta} = E_{d,0} - \alpha\theta - \beta(q_{a,0} - \delta\theta),$$

where $E_{d,0}$ is the activation energy for desorption as $\theta \rightarrow 0$; $q_{a,0}$ is the heat of oxygen chemisorption as $\theta \rightarrow 0$.

Since $\alpha\theta$ increases with increasing θ and $\beta(q_{a,0} - \delta\theta)$ decreases with increasing θ, the change in $E_{d,\theta}$ with changing θ will be modulated and could, in principle, approach $E_{d,0}$ in magnitude. Thus, even though E_d, in the absence of continuing gasification, will decrease as θ increases (as shown by Kelemen and Freund), in the presence of continuing gasification E_d need not change as θ changes. It means that E measured for the $C–O_2$ reaction (204 kJ/mole in this study) should be less than E_d measured experimentally at comparable θ values.

The independence of E_d of θ_f is a necessary but not a sufficient condition for the gasification rate to be directly proportional to θ_f. As discussed earlier, Phillips *et al.* find that the CO/CO_2 product ratio is given by $A\exp(-E/RT)$ and that the pre-exponential term A decreases with increasing θ. That is, the higher the coverage of active sites with complex, the less efficient the complex is at removing carbon atoms in the desorption (gasification) step. The production of a CO_2 molecule requires two oxygen atoms, the production of a CO molecule requires one oxygen atom. Therefore again the question is raised as to why Fig. 3 exhibits a linear plot.

Several more pieces of important information can be extracted from Fig. 3. The first is that θ_f is $\sim P^{0.51}$. Then since the desorption (gasification) rate $d\theta_f/dt$ is $\sim\theta_f$, $d\theta_f/dt$ is also $\sim P^{0.51}$. Thus over the temperature range 733 K to ~844 K, the order of the reaction decreased monotonically from 0.83 to 0.51. The question is again raised as to why the order is decreasing with increasing gasification temperature when straightforward elementary kinetics suggests that it should be the opposite. As will be seen shortly, perhaps the reason is that the gasification event instantaneously produces a nascent active site[2]. The nascent carbon site can be characterized as one having an unpaired σ electron and/or a geometric configuration of high energy. In the case of the former sites, they will rehybridize at some rate, following the gasification event, to less active sites by forming in-plane σ pairs[25]. In the case of the latter sites, they will anneal to sites of lower energy via surface diffusion of carbon atoms—for example, a dangling site transforming to a site in the (100) or (110) surface[20]. Depending upon the O_2 pressure and the rate constants for these conversions, O_2 will undergo collisions with some fraction of the nascent sites resulting in the for-

mation of an oxygen complex, before their conversion to less active sites occurs.

The simplest set of reactions embodying a nascent site concept is given below

$$C + \tfrac{1}{2}O_2 \xrightarrow{k_a} C(O), \quad (1)$$

$$C^* + \tfrac{1}{2}O_2 \xrightarrow{k_b} C(O), \quad (2)$$

$$C(O) \xrightarrow{k_c} CO + C^*, \quad (3)$$

$$C^* \xrightarrow{k_d} C. \quad (4)$$

Reactions (1) and (2) are not written in rigorous form to make the mathematics more tractable. Although accuracy is lost, the general features of these steps are preserved. A nascent site, C*, is created during the gasification step, reaction (3). For simplicity, only CO is considered as a product, and both regular and nascent active sites are assumed to form the same kind of surface oxide. The total active surface is thus comprised of regular bare sites C, nascent bare sites C*, and covered sites C(O).

The assumption of steady-state values of these parts of the TASA results in an expression for the fraction of covered sites, θ, given below:

$$\theta = \frac{k_d P^{1/2} + k_b P}{k_c k_d / k_a + (k_c + k_d) P^{1/2} + k_b P}. \quad (5)$$

Since the gasification rate is proportional to θ, the dependences of the rate are also given by eqn (5). The form of eqn (5) is very similar to that of the Nagle–Strickland-Constable rate equation[26], except that $P^{1/2}$ replaced P. This is expected since the Nagle–Strickland-Constable model assumes one site per O_2 adsorbed versus two sites per O_2 adsorbed in equations (1) and (2). Nagle and Strickland-Constable, like us, assume that a more reactive site for oxygen chemisorption is being thermally converted, at some rate, to a less active site.

One limiting case of eqn (5) results for low values of θ when k_c/k_a is very large. Under these conditions, eqn (5) simplifies to yield $\theta \simeq (k_d/k_c k_d)(k_d P^{1/2} + k_b P)$. For low coverages then, the order will be between 0.5 and 1.0 depending on the relative importance of nascent-site deactivation and nascent-site adsorption with higher pressures favoring higher orders. Since site deactivation is expected to have a higher E than nascent-site adsorption, the order will decrease from 1 to 0.5 as the temperature is increased. If the temperature increases to the point where k_d is comparable to k_c, then

$$\theta \simeq \frac{k_d P^{1/2}}{k_c k_d / k_a + (k_c + k_d) P^{1/2}}, \quad (6)$$

and the order will vary between 0 and 0.5, with higher pressures favoring the lower order. The order behavior predicted from a nascent-site concept thus agrees, qualitatively, with that observed experimentally.

Upon completion of the oral presentation of a recent paper on the C–O_2 reaction by Radovic *et al.*[27], an interesting question was asked about the fleeting complex (Radovic *et al.*[27] call it reactive surface area). Following gasification of a Saran char to different burnoffs in flowing O_2 at 823 K, the fleeting complex was recovered upon switching to a pure Ar stream at reaction temperature. The question raised by L. Bonnetain was: "In the case of combustion with O_2, have you observed the same CO/CO_2 ratio during the desorption stage as that observed during the combustion?" Radovic reported that the CO/CO_2 ratio of the combustion products in 0.001-MPa O_2 was about 1.2 and stayed relatively constant over the entire burnoff range. In contrast, the CO/CO_2 ratio of the total gas collected following desorption was about 6.0 and again was relatively constant over the entire burnoff range. Unfortunately, Radovic *et al.* had no information on instantaneous values of the CO/CO_2 ratio as θ_f went from an initial value at the end of the combustion run to zero. Radovic attributed the lower ratio found during reaction to the fact that higher surface coverage is maintained under steady-state combustion conditions than during desorption conditions when θ_f ultimately goes to zero. He suggests that the more oxygen complex on the surface the greater the probability of CO_2 desorption.

Some of our results allow at least a qualitative comparison of the CO/CO_2 ratio obtained following desorption of the fleeting complex and that measured during gasification. For gasification in 0.1- and 2.3-MPa O_2 at 840 K, the CO/CO_2 ratios over wide burnoff ranges were 0.84 and 0.46, respectively. These ratios were essentially independent of O_2 flow rate in the reactor over a wide range and thus secondary reactions were minimal. Upon LPTD runs to 1234 K, the total surface oxide collected (stable plus fleeting) was 7.0 and 13.0 μmoles/g following reaction at 0.1- and 2.3-MPa O_2, respectively. The CO/CO_2 ratio of the gas collected following LPTD runs decreased from 6.3 to 3.3 as reaction pressure increased from 0.1 to 2.3 MPa. Since most of the oxygen complex recovered following gasification at 0.1 MPa is derived from the stable complex (5.5 μmoles/g compared to a total of 7.0 μmoles/g), the CO/CO_2 ratio derived from the stable complex, is approximated as that derived from the total complex for the gasification run at 0.1 MPa. It can then be estimated, knowing the weights of stable and fleeting complex recovered following gasification at 2.3 MPa, that the CO/CO_2 ratio for the fleeting complex is equal to or greater than 1.1. This is to be compared with a CO/CO_2 ratio of 0.46 during gasification. Thus we find, as did Radovic *et al.*[27], that the CO/CO_2 ratio obtained following desorption of the fleeting complex exceeds that produced during combustion (gasification).

These results emphasize, as we discussed earlier, that steady-state carbon gasification in O_2 is a dynamic process. Desorption of CO and CO_2 in the ab-

sence of continuing carbon gasification is a different phenomenon than desorption in the presence of gasification. In the former case, the integrated amounts of CO and CO_2 recovered following desorption are obviously not set (predetermined) by the nature of the complex existing just when carbon gasification is terminated. Rather the nature of the complex appears to be changing as desorption proceeds and θ_f goes to zero. This can probably be attributed, at least in part, to significant surface mobility of oxygen on both the basal and prismatic surfaces of the carbon[2,28–30]. Induced and *a priori* heterogeneity also will contribute to this phenomenon. The instantaneous CO/CO_2 ratio produced will be a function of the value of θ_f at which it is being produced.

5. SUMMARY AND CONCLUSIONS

Under steady-state conditions for the gasification of carbon in O_2, there exists on the carbon surfaces two broad oxygen complexes—a stable complex which cannot be removed from the surface at reaction temperature and a fleeting complex θ_f, which is continuously desorbing to gaseous reaction products CO and CO_2. Gasification rates are found to be directly proportional to the amount of fleeting complex existing under steady-state conditions. Considerations are given, such as *a priori* and induced heterogeneity[5] and variation of CO/CO_2 product ratio with θ_f[17], as to why a direct proportionality might not be expected. Over the pressure range 0.1–6.4-MPa O_2, the order of the reaction is found to decrease with increasing reaction temperatures between 733–842 K. Reasons are given, pro and con, as to why this result should or should not be found. To support the finding, the concept of nascent active site production, following a desorption (gasification) event, is invoked.

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