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AN UPDATE ON THE CARBON-OXYGEN REACTION

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Abstract—Some of the pertinent literature on the C-O₂ reaction, available over the past 25 years, is considered. Fundamental, specific reaction rates are available from microscopy studies on carbons of large crystallite size, excellent crystallite alignment, and high purity. Rates are determined in a straightforward way by following recession of the active surface as a function of time. Problems of obtaining fundamental rates for gasification of carbons from measuring total active surface area and/or those fractions covered by both a stable complex and a fleeting oxygen complex during gasification are considered. Ways now appear to be available to make the necessary measurements for calculating fundamental rates using the latter approaches.

Key Words—Oxidation, gasification, surface complexes.

1. INTRODUCTION

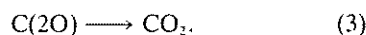
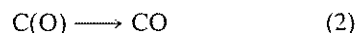
The C-O₂ reaction arguably is the most important reaction known. Voluminous amounts of research have been conducted in an attempt to elucidate the mechanism of the reaction and to obtain fundamental, specific reaction rates. One of the goals of understanding gas-carbon heterogeneous reactions is to be able to normalize (unify) experimental carbon gasification (combustion) rates. This requires a measure of the extent (fraction) of the surface which is participating in the reaction, in the case of most polycrystalline carbons. We will see that there are real problems in obtaining this measure in the case of carbons of small crystallite size and poor crystallite alignment. By contrast, as we have recently discussed[1], valuable and pertinent results have been obtained for carbons of large crystallite size, excellent crystallite alignment, and high purity. Here the use of electron microscopy on natural graphite flakes, as pioneered by Hennig[2], and light microscopy, as pioneered by Thomas[3], and the use of the "ruler" on stress recrystallized pyrolytic graphite (SRPG), as pioneered by Rodriguez and Walker[4], have permitted the direct measurement of specific reaction rates. This approach involves the following of carbon recession at the reacting (active) surface over a period of time.

This paper attempts to evaluate where we stand in our attempt to be equally successful in measuring fundamental values of the C-O₂ reactions in the case of carbons where directly following carbon recession rates is not possible. Such evaluation leads to a consideration of some of the phenomena which appear to be present when O₂ gasifies carbon under conditions of chemical rate control.

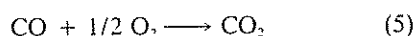
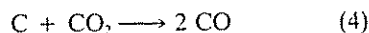
2. RESULTS AND DISCUSSION

2.1 Earlier history

When O₂ gasifies carbon, the following reactions occur



Carbon monoxide and CO₂ have been shown, from isotopic studies, both to be primary products of the reaction[5]. That is, CO and CO₂ are produced directly as gaseous products by the desorption of carbon-oxygen surface complexes. Under some circumstances, they may also be produced by the reactions



but these reactions are not necessary to produce CO and CO₂. The primary product CO/CO₂ ratio has been shown to increase exponentially with increasing temperature[6] and also to be dependent on the active surface area (ASA) available for reaction and the amount of it which is covered by a carbon-oxygen surface complex[7]. The active carbon surface is known to be terminated by different configurations of carbon atoms such as zig-zag and arm-chair sites[3] and dangling carbon atoms[8]. Product CO is thought to originate primarily from carbonyl surface groups[8]; CO₂ from lactone groups[8]. Carbon dioxide and CO are also produced from anhydride groups[9]. Note that one or two dangling carbon sites participate in the production of CO₂. Dangling carbon sites are not necessary for the production of CO.

To our knowledge, this laboratory was the first to explore the possibilities of obtaining fundamental reaction rates and reaction rate constants for the C-O₂ reaction using the concepts of total surface area (TSA) and ASA[10]. We selected a highly purified graphitized carbon black (Graphon) for our studies since we expected, on the basis of the prior studies

of Smith and Polley[11], that there would be a major difference in the proportionate increase in TSA compared to ASA as a function of extent of carbon burn-off. This proved to be correct, with TSA increasing only 40% as a result of 35% carbon burn-off, while ASA increased over 18-fold. We were thus able to distinguish clearly between the success of these two surface areas in normalizing experimental reaction rate data at seven levels of burn-off up to 35%. Reaction was conducted at temperatures between 848 and 948 K in a static reactor at a low starting O₂ pressure (about 5 Pa). A mass spectrometer was used to measure the disappearance of O₂ and the appearance of CO, CO₂, and a surface oxygen complex as a function of time. The TSA of the carbon samples was measured using N₂ at 77 K and the BET equation. The ASA was measured at each burn-off level from the amount of surface complex formed in 24 hours at 573 K, using an initial O₂ pressure of ~70 Pa. Prior to a chemisorption run, each burn-off sample was heated in high vacuo to 1223 K to remove oxygen complex formed during the preceding gasification run. Carbon gasification was negligible at 573 K; equilibrium was reached well within 24 hours. Oxygen chemisorption was assumed to be dissociative, with each oxygen atom further assumed to occupy an edge carbon atom in the (100) prismatic surface. Under these conditions each carbon atom occupies an area of 0.083 nm².

As expected, the experimental carbon gasification rates could not be normalized using the TSA. That is, TSA was composed of basal plane area and edge area, where edge area would be located at exposed crystallite edges (primarily) and at defect edges (vacancies, primarily). Reactivity was expected to be negligible at the defect-free basal plane surface. The TSA increased from 76 m²/g to 128 m²/g as carbon burn-off went from zero to 35%. Carbon reaction rates increased much more rapidly than the increase in TSA (roughly 18-fold). In an attempt to normalize reactivity data using ASA, the following expression was used for the disappearance of carbon (by gasification) with time

$$-\frac{dC}{dt} = k_a(P_{O_2})(ASA)(1 - \theta) \quad (6)$$

where ASA was measured by chemisorption of oxygen at 573 K, and θ is the fraction of this ASA occupied by surface oxygen complex at particular stages of reaction. The above equation successfully normalized reaction rates, as they increased some 18-fold as burn-off increased to 35%. Reaction rate constants (k_a) were obtained which were essentially constant over the large burn-off range.

In the context of what is to follow, it is important to recognize that this study in 1963 used low O₂ pressures to measure ASA and to conduct carbon gasification. Further, the pressure used to measure ASA was some 14-fold greater than that used for

gasification runs, which extended over about a 30-minute period. Following this study, many workers embraced the use of oxygen chemisorption at temperatures sufficiently low to make gasification negligible but sufficiently high to make O₂ physical adsorption also negligible to measure ASA of their carbons. A temperature of 573 K usually satisfied these conditions.

Once rate constants and specific reaction rates were obtained using ASA measurements, we were anxious to compare the values with those obtained using microscopy to follow gasification of carbons of large crystallite size and excellent crystallite alignment as previously described. Specific rate measured in the latter case, as rates of recession of the active surface (in units of cm/s, for example), can be converted to specific reaction rates (in units of g carbon reacting/cm² · s, for example) by knowing that the volume of carbon being gasified has a true density of ~2.268 g/cm³. As discussed previously[1], if this is done, the microscopy studies of Hennig[2], J. Baker[12], Evans *et al.*[13], Yang *et al.*[14], R. Baker *et al.*[15,16], and the "ruler" studies of Rodriguez *et al.*[4] can be compared with the specific rate of Laine *et al.*[10] (upper data point) on the Arrhenius plot, Fig. 1. Results in all cases have been normalized to an O₂ pressure of 1.3 kPa (the pressure Hennig used) assuming rates proportional to P_{O₂}⁵.

2.2 More recent history

2.2.1 Gasification of microporous carbons.

Because of the energy shortage in the 1970s and the consequent renewed interest in coal char gasification in O₂, a number of workers became interested in explaining the shape of the burn-off versus time plots of O₂ reacting with microporous carbons. Their approach was generally to derive discrete numerical models to describe pore structure transformation as the microporous carbon was gasified[17–25]. Knowing the initial pore volume of the carbon, their models permitted a calculation of change in TSA as carbon gasification and, consequently, pore volume increased in the Zone I[26] region. Variable success was achieved in attempts to normalize carbon reactivities, as a function of burn-off, using theoretically derived changes in TSA with burn-off. Some of the workers recognized the concept of ASA but simply assumed that changes in ASA were proportional to changes in TSA, for want of a better approach. The reasonable success attained in some cases suggests that for some microporous carbons of small crystallite size and poor crystallite alignment, the proportionality is not a completely unreasonable assumption. Prior to carbon burn-off, crystallite edges are already exposed in abundance. This is in contrast to the polyhedral particle of graphitized carbon black, which has just been considered, where crystallite edge area is not accessible in the original material[27]. Only on gasification are the crystallite boundaries enlarged and made accessible to the reacting gas. In this case the assumption of equal pro-

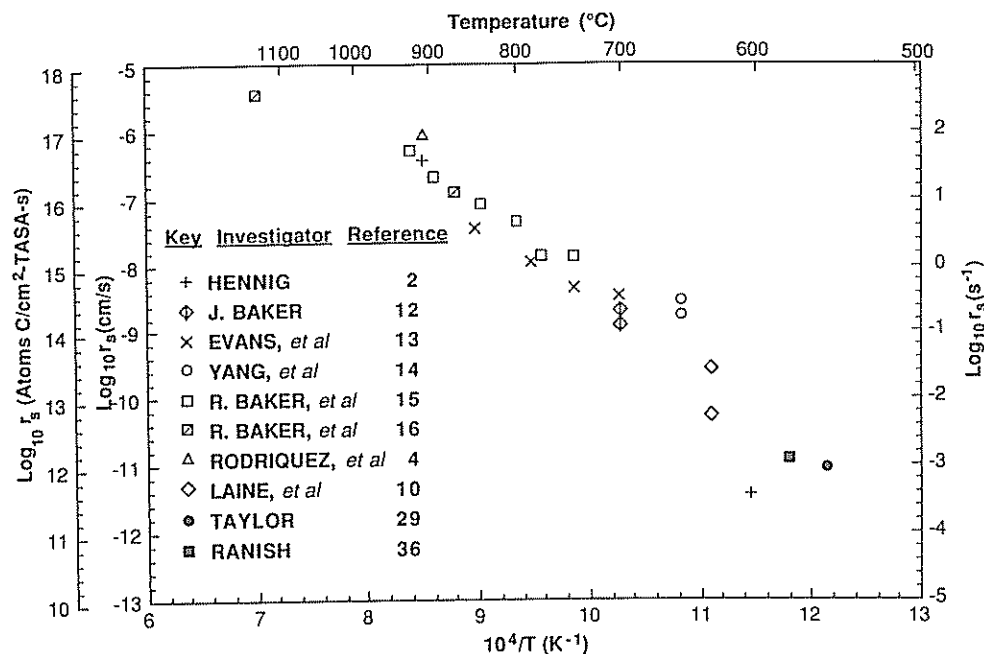


Fig. 1. Compilation of results for specific reaction rates for the C-O₂ reaction at 1.3 kPa pressure.

portionality of change in TSA and ASA would be grossly incorrect.

It is in this context that studies were conducted in this laboratory to evaluate the possibility of measuring ASA by oxygen chemisorption on a microporous carbon (char) and the success of its use in yielding meaningful specific gasification rates[28,29]. The carbon used in the study was prepared by carbonizing high-purity Saran, a copolymer of vinylidene chloride and vinyl chloride, at 1173 K as previously described[30]. The char (ground to 70 × 100 mesh) was then placed in a tube furnace and heated in N₂ to 1223 K for four hours. It was then cooled to 648 K and reacted in flowing air (0.1 MPa pressure) to the desired level of burn-off. Burn-off was followed by monitoring the CO and CO₂ produced during gasification using a gas chromatograph. Following gasification to selected burn-off levels, the char was cooled to room temperature in 0.1 MPa N₂, and TSAs were determined using N₂ adsorption at 77 K and CO₂ adsorption at 298 K. These areas were essentially in agreement, indicating negligible molecular sieving in the chars[31]. Other portions of the chars were evacuated overnight at room temperature, followed by heating to 1223 K for four hours to remove the oxygen surface complex formed during gasification as CO and CO₂ (measured by a mass spectrometer). The sample temperature was then lowered to 373 K and the carbon exposed to 0.1 MPa air for 24 hours to allow chemisorption equilibrium to be reached. The system was then evacuated at 373 K, followed again by heating to 1223 K to measure the amount of oxygen surface complex formed. It was our original thought that we could convert this amount of complex to total ASA,

using the concept generated earlier in our studies of Laine *et al.* on graphitized carbon black[10].

Figure 2 shows the reactivity plot for Saran char at 648 K out to a burn-off of ~89%. Note that at this low temperature char gasification is very slow, certainly satisfying Zone I kinetics. Under these conditions the fraction of ASA covered by oxygen complex during reaction would be expected to be high. Figure 3 shows the CO/CO₂ product ratio as a function of burn-off. The data represent four reactivity runs out to the burn-offs indicated. The ratio shows a gradual decrease as burn-off increases, from an initial value of about 0.43 to 0.30 at 72% burn-off. A CO/CO₂ ratio below one suggests that more of the fleeting oxygen complex on the surface during reaction (that complex which leads directly to gasification) is in the form of lactone groups than carbonyl groups.

Table 1 summarizes results for surface areas at various burn-off levels, calculated from N₂ physical adsorption at 77 K and from the amounts of oxygen recovered as CO and CO₂ at 1223 K following a reactivity run (initial desorption) and a chemisorption run (second desorption). To convert weight of oxygen to surface area, it was assumed that each oxygen atom occupied 0.083 nm², as previously discussed. A number of pertinent results, the possible implications of which will be considered later, should be pointed out. First, very large amounts of stable oxygen surface complex are formed during char gasification at 648 K. This is consistent with the findings of Watt and Franklin[32], Su and Perlmutter[33], and Floess *et al.*[34], who gasified a series of microporous carbons in O₂ between 573 and 725 K. Second, at high burn-offs the areas calculated to be

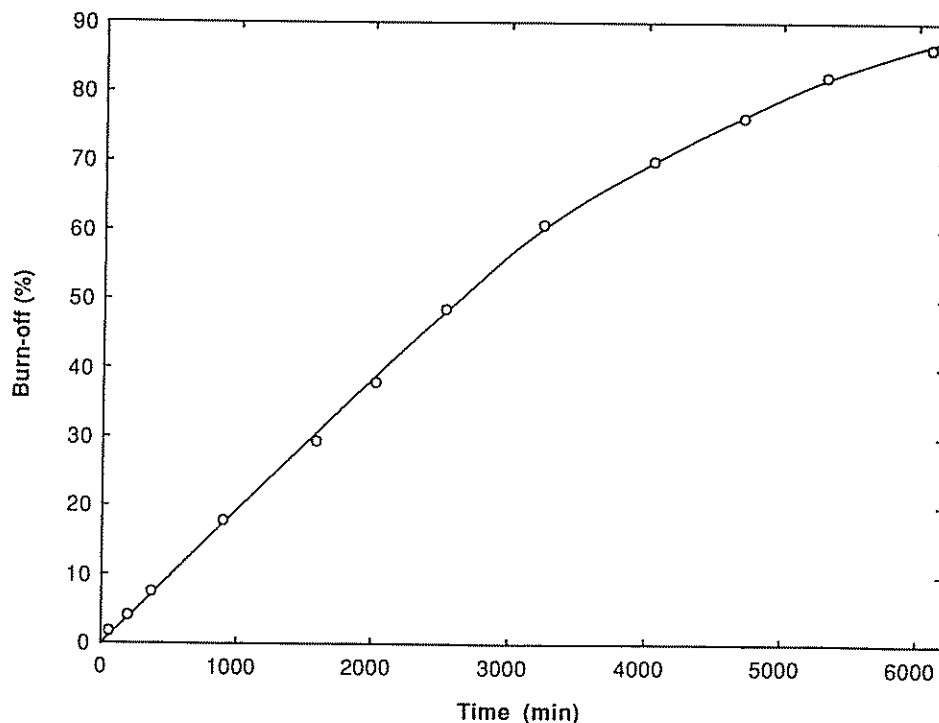


Fig. 2. Burn-off plot for Saran char at 648 K in 0.1 MPa air.

occupied by oxygen complex following gasification exceed TSA. Third, they also exceed considerably the areas occupied by oxygen complex chemisorbed at equilibrium at 373 K. It is recalled that the latter areas were assumed to be, as a result of the work of Laine *et al.* [10], the total ASA at different carbon burn-off levels.

Table 2 summarizes reactivity results normalized to initial carbon weight (g_m), reacting carbon weight (g_r), and TSA, following reaction. As expected, these parameters are not successful in normalizing reaction rates. Equation (6) cannot be tested as to its suitability for normalizing gasification rates since oxygen coverage data available in Table 1 do not permit the calculation of $(ASA)(1 - \theta)$ values—or values for the extent of ASA uncovered by oxygen complex as

a function of carbon burn-off. To obtain fundamental gasification rate constants on the basis of desorption of the fleeting oxygen complex as CO and CO₂, values for the amount of fleeting complex at the completion of gasification are needed. Neither the oxygen complex remaining after completion of the initial desorption (ASA), or the second desorption (ASA)_c is expected to represent this value. In fact, neither area successfully normalized reactivity data using the desorption equation

$$-\frac{dC}{dt} = k_d(ASA)_i = k'_d(ASA)_c \quad (7)$$

as seen in Table 2. Possible further implications of these results will be considered later.

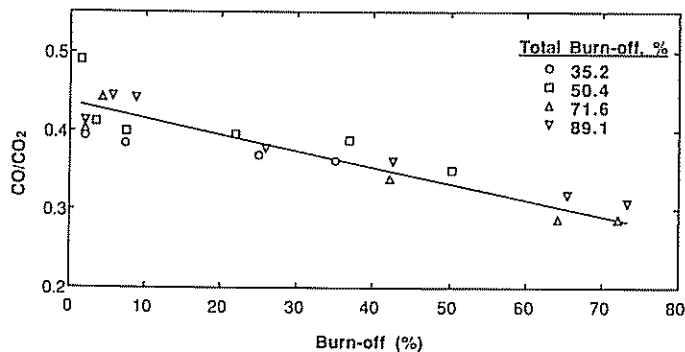


Fig. 3. CO/CO₂ product ratio resulting from gasification of Saran char at 648 K in 0.1 MPa air.

Table 1. Results of gasification of Saran char at 648 K in 0.1 MPa air

Sample Burn-off, %	TSA, m ² /g N ₂ (77 K)	Initial Desorption		Second Desorption	
		Oxygen on Char (wt %)	Oxygen Area m ² /g	Oxygen on Char (wt %)	Oxygen Area m ² /g
0	1,123	4.1	124	1.7	50.4
16.5	1,175	8.4	262	1.6	48.0
35.2	1,183	16.0	500	1.4	43.2
50.4	976	18.7	576	1.4	43.7
71.6	459	21.9	686	1.4	42.6
89.1	249	21.6	675	1.3	39.7

2.2.2 *Gasification of graphitized carbon black.* Following our gasification studies on Saran char in a flow reactor, which produced results that confused our thinking about ASA and how to measure it for the C-O₂ reaction, we decided to look at several other carbons of much different morphology. First, we returned to a graphitized carbon black (V3G), using the flow reactor[29]. Figure 4 shows the burn-off plot at 823 K in 0.1 MPa air. Reactivity again is very slow, thus obeying Zone I kinetics. Table 3 summarizes results for surface areas at various burn-off levels. As was done previously in the studies of Laine *et al.*[10], oxygen chemisorption was studied at 573 K for 24 hours at a low O₂ pressure (65 Pa) in an attempt to measure total ASA. This is termed the second desorption following a first desorption of oxygen complex at 1223 K, formed at reaction temperature. Unlike the Saran char, both the TSA and area occupied by oxygen complex increase with increasing carbon burn-off. As with Saran char, the areas occupied by oxygen following various levels of carbon burn-off markedly exceed those occupied by oxygen following chemisorption at 573 K. Thus, again the question of how to measure total ASA is raised. Table 4 summarizes attempts to normalize reactivities at different burn-offs using different parameters. These parameters again fail to normalize reactivity results. Possible implications of these results will also be considered later.

2.2.3 *Gasification of finely ground natural graphite.* Compared to the previous two carbons which have been considered, the natural graphite used here (SP-1 from Union Carbide) is of much larger crystallite size and much better crystallite alignment. It was first used in this laboratory to study the effect of oxygen chemisorption on the thermoelectric power of graphite[35]. It has a mean particle diameter of about 30 μm and a thickness of about 0.5 μm. That is, the ground particles are thin flakes. The larger

dimension of the flake is primarily basal plane (surfaces), and the thin dimension (edges) is primarily prismatic surface. Studies were conducted in a flow system at different temperatures and O₂ pressures[36]. Unlike the system used by Taylor[28], this system enabled us to conduct studies over a broad range of pressures at 0.1 MPa and above.

It was clear from the studies of Taylor, just discussed, that chemisorption at 573 K did not permit the determination of total ASA. To determine fundamental, specific reaction rates at least one of two pieces of information was needed. One piece was the product of total ASA (TASA) and the fraction of it uncovered by complex, or TASA (1 - θ). The other piece was the product of total ASA and the fraction of it covered by a fleeting complex, designated by θ', or TASA (θ'). It is the fleeting complex which is undergoing decomposition resulting in carbon gasification to CO and CO₂. At the instant a gasification run is completed, it was thought that the total complex on the surface should equal the sum of the stable complex and the fleeting complex. It was the aim of our research on SP-1 graphite to measure the amount of fleeting complex at the completion of a run, or TASA (θ'). Then converting this amount of complex to ASA reacting, we could calculate a fundamental, specific reaction rate.

Our approach was to react SP-1 graphite to a fixed level of burn-off (about 20%) at a constant temperature (850 K) in different pressures of O₂ 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 oxygen complex should increase with increasing O₂ pressure. With the aim of preserving the total complex on the surface at the completion of a gasification run, the O₂ pressure was maintained while the carbon sample was cooled to room temperature. We expected that this procedure

Table 2. Various reactivities of Saran char at 648 K in 0.1 MPa air

Sample Burn-off, %	g/g _{int} *s x 10 ⁶	g/g _r *s x 10 ⁶	g/m ² TSA*s x 10 ⁹	g/m ² (ASA) _r *s x 10 ⁸	g/m ² (ASA) _c *s x 10 ⁹
16.5	3.1	3.7	3.1	1.4	0.77
35.2	3.1	4.7	4.0	0.94	1.0
50.4	3.1	6.2	6.3	1.1	1.4
71.6	1.8	6.3	14	0.92	1.5
89.1	0.7	6.6	27	1.0	1.7

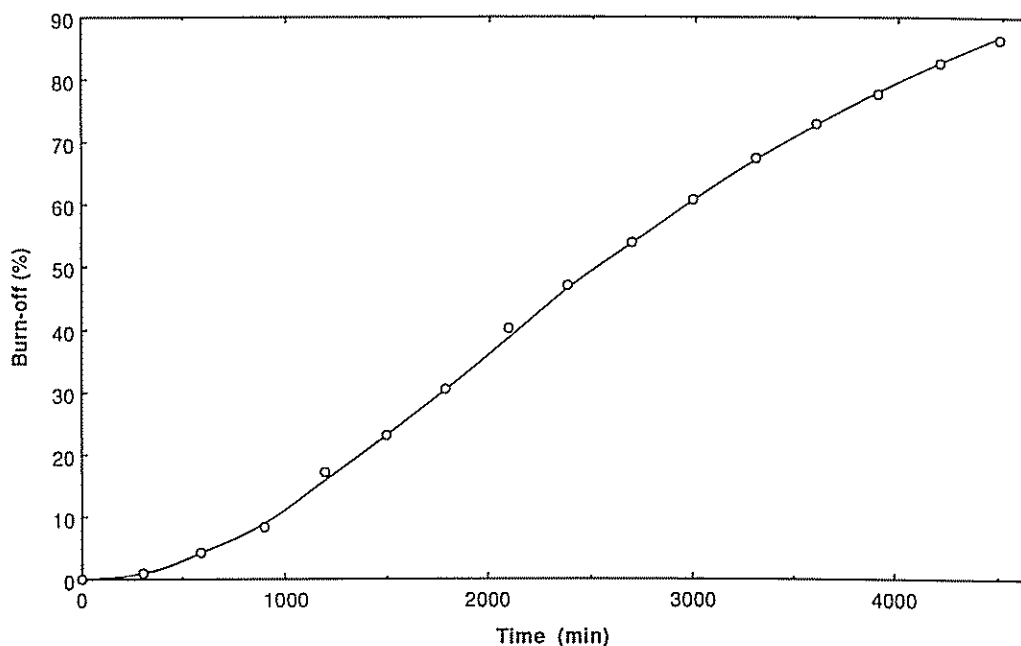


Fig. 4. Burn-off plot for V3G at 823 K in 0.1 MPa air.

would realize, on the one hand, negligible loss of fleeting oxygen complex and, on the other hand, negligible further addition of complex—either fleeting or stable. Only then was O_2 pumped from the reactor, followed by in-situ heating of the sample to 1223 K to recover the total complex as CO and CO_2 .

Results are summarized in Figure 5. Reactivities at 20% burn-off at 850 K are plotted against the total surface oxide (both stable and fleeting) recovered at the completion of each run. The linear plot shows two important features. First, there is a finite intercept of $5.5 \mu\text{mol O/gC}$ at negligible (zero) gasification rate. This is interpreted as the amount of stable oxygen complex existing at completion of the gasification runs; that is, this amount is independent of reacting O_2 pressure. Second, there is a constant proportionality between gasification rate and amount of fleeting complex remaining which yields a fundamental, specific rate constant of 0.043 s^{-1} at 850 K. Assuming that the oxygen complex occupies 0.083 nm^2 per O atom, Table 5 summarizes results for the areas occupied. These areas are to be compared with that occupied by complex following a chemisorption experiment at 573 K in 0.1 MPa O_2 (that is, $0.13 \text{ m}^2/\text{g}$) and the TSA of the 20% burn-off sample (that is, $3.6 \text{ m}^2/\text{g}$).

3. PRESENT THOUGHTS ABOUT THE CARBON-OXYGEN REACTION

It is clear that fundamental, specific reaction rates for the C- O_2 reaction (and, indeed, other carbon gasification reactions) can be obtained using the combination of graphites of high purity, large crystallite size, and high crystallite alignment with microscopy or the "ruler." Purified natural graphite flakes of large particle size and SRPG qualify for such studies. Not only do these graphites enable the following of the recession of the active surface as gasification proceeds, but they also allow gasification to be conducted at higher temperatures where build-up of oxygen surface complex is minimized. This is because these graphites contain negligible internal porosity, meaning that reaction occurs almost entirely at the exterior surface of the sample. Thus, Zone I kinetics are operative to much higher temperatures, before the transition region between Zones I and II comes into play.

By comparison, obtaining fundamental results for the C- O_2 reaction using carbons of small crystallite size and poor crystallite alignment and/or small particle size is seen to be more difficult. Here there is a need to measure an ASA to normalize reactivity results. As is seen, there can be uncertainty as to

Table 3. Results of gasification of V3G at 823 K in 0.1 MPa air

Sample Burn-off, %	TSA, m^2/g N_2 (77 K)	Initial Desorption		Second Desorption	
		Oxygen on Char (wt %)	Oxygen Area m^2/g	Oxygen on Char (wt %)	Oxygen Area m^2/g
0	63	---	---	---	---
6	65	0.23	7.1	0.03	1.0
20	86	0.34	10.5	0.10	3.0
60	112	0.96	29.2	0.29	8.9

Table 4. Various reactivities of V3G at 823 K in 0.1 MPa air

Sample Burn-off, %	$g/Gr^*s \times 10^6$	$g/Gr^*s \times 10^6$	$g/m^2 TSA^*s \times 10^8$	$g/m^2(ASA)_r^*s \times 10^7$	$g/m^2(ASA)_c^*s \times 10^6$
6	2.5	2.7	4.2	3.8	2.7
20	4.6	5.7	6.6	5.4	1.9
60	4.3	10.7	9.6	3.7	1.2

how to do this. In preceding studies by Laine *et al.*[10], the existence of active sites on carbon surfaces were confirmed and their importance in the C-O₂ reaction shown. Indeed, workers have appreciated for a long time that the total carbon surface is composed of a combination of "weak" sites and "strong" sites. They know that graphite crystals exhibit large differences in surface energies in their different crystallographic directions[37]: about 0.11 J/m² in the basal plane and 5 J/m² in the prismatic planes. Thus, it would be expected that large differences would exist in the rates of interaction of gases when exposed to the basal plane surface as compared to the edge or prismatic surfaces.

The Laine approach was predicated on the assumption that the total ASA involved in the C-O₂ reaction could be measured by exposing the carbon to O₂ at low enough temperatures, where gasification rates were insignificant, for sufficiently long periods of time. In the Laine *et al.* study conducted at very low O₂ pressures, the amount of complex formed at 573 K at equilibrium did exceed the complex formed during reaction between 748 and 848 K. In retrospect, this experimental finding (expectation) was assured by conducting the gasification reaction at very low pressures (about 5 Pa) for short periods of time and the 573 K chemisorption at much higher pressures (about 70 Pa) for a much longer time (24 hours). Under these gasification conditions, negli-

gible fleeting oxygen complex would exist on the surface during reaction and only a small fraction of ASA would be covered by stable complex.

Our studies on microporous carbons, graphitized carbon black, and finely ground SP-1 graphite conducted at much higher O₂ pressures than those used by Laine *et al.* (20 kPa to 3.5 MPa) show that the number of sites chemisorbing oxygen during gasification can exceed significantly the number of sites which chemisorb oxygen in the absence of gasification at low temperatures. Thus, the Laine approach[10] is not of general applicability. In retrospect, why might the amount of oxygen chemisorption during gasification exceed that during low temperature chemisorption studies? At least five possibilities come to mind:

1. We know from extensive studies on oxygen chemisorption that there is a distribution of adsorption sites on which adsorption can occur[38,39]. Whether chemisorption occurs at a particular temperature depends on site activity and O₂ pressure. Indeed, there are some sites on graphitized carbon black which can chemisorb oxygen at 195 K[38]. Thus, at selected chemisorption temperatures all high-energy sites which are active at higher gasification temperatures might not be active for chemisorption.

2. Gasification instantaneously produces nascent (very active) carbon sites; that is, sites which contain an unpaired electron[40]. Some of these sites will tend to rehybridize rapidly to less active sites by forming in-plane σ pairs[41]. Alternatively, depending on the O₂ pressure, some fraction of those will undergo collisions with O₂ and the formation of an oxygen complex prior to rehybridization.

3. Spill-over of oxygen atoms from the prismatic surfaces (crystallite edges) to the basal planes may occur at gasification temperatures but not at lower chemisorption temperatures. Several conditions are necessary: sufficiently rapid rates of diffusion of oxygen atoms and chemisorption of O atoms on defect-free parts of the basal plane. Isotopic studies indicate that oxygen complexes on carbon are more or less mobile, depending on the sites on which chemisorption occurs[42]. For example, at 553 K some O¹⁶ complex was first added to the carbon followed by the addition of some O¹⁸ complex. Upon desorbing the complex in temperature steps up to 1153 K, the ratio of O¹⁶ to O¹⁸ in the product CO and CO₂ was the same at each desorption temperature starting at 673 K. In other words, the last oxygen on was not the first to be desorbed, as would be expected if the oxygen complex was immobile on sites of a priori

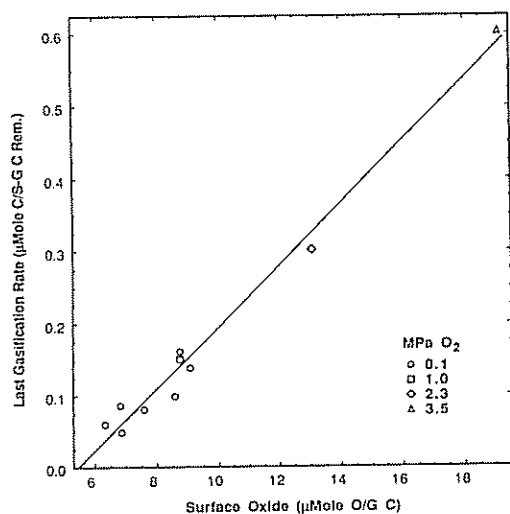


Fig. 5. Relationship between gasification rate of SP-1 graphite at 850 K and 20% burn-off and amount of oxygen complex present on the surface. Gasification conducted at O₂ pressures between 0.1 and 3.5 MPa.

Table 5. Surface areas occupied by oxygen complex following gasification of SP-1 graphite to 20% burn-off at 850 K

Reacting O ₂ Pressure MPa	Areas, m ² /g Occupied by		
	Stable Complex	Fleeting Complex	Total Complex
0.1	0.27	0.11	0.38
1.0	0.27	0.16	0.43
2.3	0.27	0.37	0.64
3.5	0.27	0.67	0.94

heterogeneity. Measurable diffusion of stable complex on the surface was at least occurring at temperatures of 673 K and above.

Theoretical molecular orbital calculations by Bennett *et al.*[43] and Hayns[44] show clearly that oxygen atoms can chemisorb on the defect-free basal plane of graphite. Hayns estimated a bonding energy of 171 kJ/mole at a mid C—C bond distance 0.125 nm above the surface and an activation energy of about 46 kJ/mole for migration across the defect-free basal plane surface. Yang and Wong[14] confirm experimentally the diffusion of O atoms across the basal plane of graphite at 923 K.

4. At gasification temperatures, oxygen atoms are able to penetrate between basal planes (intercalate), yielding a graphitic oxide. Experimental evidence does not support this possibility. Intercalation shifts (001) x-ray diffraction peaks to lower angle (2θ) values or higher d -spacings. To the contrary, x-ray diffraction studies on Saran char show that the (002) diffraction peak shifts to a slightly higher angle as char burn-off proceeds[29].

5. Following carbon gasification, heating to 1223 K not only removes oxygen surface complex as CO and CO₂ but also converts some of the carbon sites to less active sites. For example, some dangling carbon sites could be converted to nondangling sites in zig-zag or arm-chair configurations[45]. The result could be reduced oxygen complex formation when chemisorption is subsequently conducted at 573 K. In fact, Taylor[29] confirmed the annealing out of active sites as a result of staged desorption up to 1223 K of Saran chars following their gasification at 648 K in 0.1 MPa air. Following each staged desorption (six temperatures were used) in a high-vacuum apparatus, a Laine-type gasification run was conducted at 684 K, in situ, starting with an O₂ pressure of about 5 Pa. The initial rate of decrease in O₂ pressure went through maxima with increasing desorption temperature for all three char samples of different burn-off studied.

Recently, Kelemen and Freund[46] conducted studies which are pertinent to our present discussion. Using Auger electron spectroscopy, photoelectron spectroscopy, and low-energy electron diffraction, they followed the chemisorption of oxygen on the edge surface and basal plane surface of SRPG. Using the Laine condition for chemisorption (that is, 573 K), they followed the uptake of oxygen up to an O₂ exposure of 8×10^{10} Langmuirs (or about 10^7 Pa · s).

This is to be compared with the Laine conditions of 70 Pa O₂ for 24 hours, or 0.6×10^7 Pa · s. At the end of their exposure, they report roughly one oxygen atom per three carbon atoms on the edge surface. Considering that for the main oxygen functional groups expected to be on the surface (that is, carbonyl, lactone, and anhydride), the O/C ratios would be 1.0, 1.0, and 1.5, this experimental ratio means that no more than one third of the edge ASA is covered using the Laine conditions. By contrast, the basal surface of the SRPG, after the 573 K chemisorption, had an O/C ratio one order of magnitude less than that found at the edge surface. Kelemen and Freund attribute this low level of activity to a small concentration of defects at which oxygen would dissociatively chemisorb.

Kelemen and Freund also determined the reactive adsorption coefficient (a collision efficiency) for the chemisorption of oxygen on edge surface as a function of coverage ($\theta = 1$ for a coverage of roughly one oxygen to three carbons). The coefficient dropped from about 10^{-3} as $\theta \rightarrow 0$ to 10^{-12} as $\theta \rightarrow 1.0$. Assuming a Boltzmann distribution of energies at 573 K, they estimate a barrier to chemisorption of 54 kJ/mole at $\theta = 0.2$, increasing to 134 kJ/mole at $\theta = 0.9$. They attribute this to induced heterogeneity[47] at the edge surface. From our previous discussion, it could also be due to a priori heterogeneity[47]. Kelemen and Freund also measured thermal stabilities of the oxygen chemisorbed on the edge surface under ultra-high vacuum at 573 K. At very low oxygen coverages, CO formation energies exceeded 334 kJ/mole; it decreased to 242 kJ/mole at the highest oxygen coverage produced at 300 K. Thus, it is clear that the stable oxygen complex formed during carbon gasification should not be considered as an inhibitor or retarder of gasification, as was originally suggested by Laine *et al.*[10]. Rather, a build-up in stable oxygen complex is required at low gasification temperatures (like those considered here) to decrease the activation energy required for desorption of the next oxygen complex formed to CO and CO₂ reaction products—thus realizing a measurable gasification rate. Obviously, as reaction temperature increases the amount of stable complex needed before measurable gasification proceeds will decrease until finally θ will approach zero. This rationale is analogous to that used by Boudart in describing heterogeneous catalysis[47]. He concludes that catalyzed reactions of commercial interest are possible in part because the catalyst surface is dirty enough

(that is, covered by sufficient chemisorbed species) to assure rapid desorption of reaction products.

Su and Perlmuter[33] suggest that low-temperature char gasification in O_2 involves not only desorption of a fleeting complex (that is, complex formed once θ is high enough to make its desorption rapid) but also direct involvement of the stable complex. They suggest that the complex, which is stable in vacuo at gasification temperatures, is removed from the surface at some rate as a result of gas-phase O_2 molecules colliding with it. It would be a kind of sputtering where energetic impinging gaseous species remove surface layers[48]. However, we are not aware that direct experimental confirmation of the suggestion of Su and Perlmuter exists.

It is clear from the foregoing that low-temperature oxygen chemisorption cannot be relied on to measure total ASA of carbons. It thus becomes of interest to consider other possible approaches. One such approach is the use of physical adsorption. Graham suggested the use of physical adsorption at very low relative pressures to measure the strong site area of graphitized carbon blacks[49]. His reasoning was that at very low relative pressures (or at low surface coverages), the adsorption isotherm would exhibit linearity on a homogeneous surface (for example, an ideal basal plane of carbon). But if the surface also contained some high-energy sites (for example, edge sites of carbon), the isotherm would deviate from linearity as zero pressure is approached. Extrapolation of the linear portion of the isotherm to zero pressure would yield an intercept on the ordinate which would represent the amount of adsorbate (or surface area) occupying strong sites. This approach was used in our laboratory to determine the increase in strong site area of Graphon as a result of gasification in O_2 at 873 K[50]. Following gasification, the samples were outgassed at 1173 K for 12 hours to remove oxygen complex formed during gasification. Physical adsorption was conducted at low pressures of N_2 at 77.8 K. Figure 6 presents the isotherms. It is seen that the intercepts on the ordinate increase sharply with burn-off. The strong site area increases from about 1.3% of TSA on the original Graphon to 18% of TSA for the sample gasified to 37% burn-off.

These results can be used to estimate the strong site area on V3G (used by Taylor) following 20% burn-off in O_2 . It is estimated that the strong site area consists of 10% of TSA ($86 \text{ m}^2/\text{g}$), or about $8.6 \text{ m}^2/\text{g}$. This is to be compared with the estimated areas covered by oxygen complex following gasification at 823 K and subsequent chemisorption at 573 K (that is, 10.5 and $3.0 \text{ m}^2/\text{g}$, respectively, as seen in Table 3). The value obtained from physical adsorption does not appear to be unreasonable, but it is lower than the area estimated to be occupied by oxygen complex following reaction. There are at least two possible reasons for this discrepancy. First, it was assumed that the oxygen complex (carbonyl) on edge, active sites occupied an area of 0.083 nm^2 per

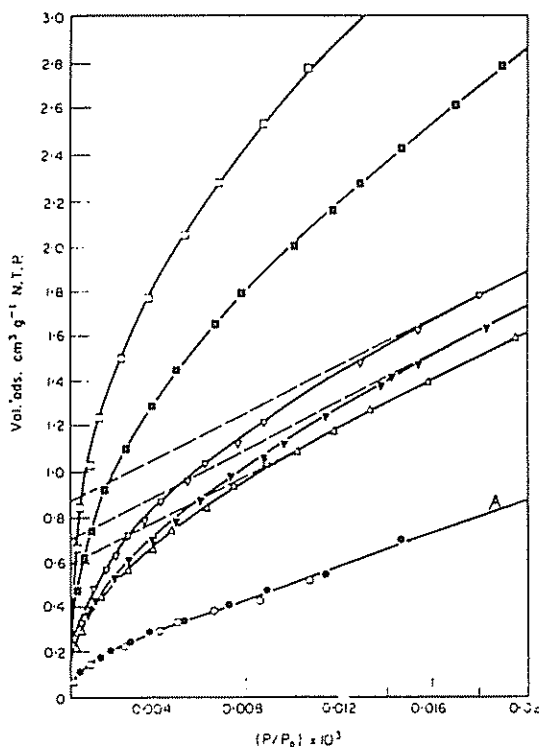


Fig. 6. Nitrogen isotherms at 77.8 K on Graphon samples of different burn-offs: \square , 37%; \blacksquare , 24%; ∇ , 6.5%; \blacktriangledown , 4.5%; \triangle , 1.6%; \circ and \bullet , unoxidized[50].

oxygen atom. This is the value for zig-zag sites. The value would be 0.071 nm^2 for carbonyl oxygen on arm-chair sites. The value, per oxygen atom, for a lactone group would also be expected to range between ~ 0.07 and 0.08 nm^2 . However, for an anhydride group, which involves three oxygen atoms per two carbon atoms, the area occupied by an oxygen atom would only be $\sim 0.05 \text{ nm}^2$. Therefore, the area occupied by the oxygen complex on the edge sites of V3G at the completion of the run to 20% burn-off could range from a high of $10.5 \text{ m}^2/\text{g}$ to a low of $6.3 \text{ m}^2/\text{g}$, depending on the amount of each functional group which was present. Second, some of the oxygen complex may have spilled over onto the defect-free part of the basal plane during gasification and be chemisorbed. This would represent additional area not picked up by the strong site physical adsorption technique.

Using the strong site areas for the graphitized carbon blacks taken to 20% burn-off, as measured by physical adsorption, for TASA, specific reaction rates for the Laine *et al.* results[10] and Taylor results[29] can be recalculated. Values are shown in Fig. 1, with the lower data point of Laine *et al.* being the rate normalized by physical adsorption results.

More recently, the approach of Thomy and Duval[51] has been used to estimate the strong site area of SP-1 graphite before and after gasification to $\sim 20\%$ burn-off. Following gasification, the samples were outgassed at 1073 K. This method is based on the

experimental fact that sharp, essentially vertical rises are observed in isotherms for Kr physical adsorption at 77 K on carbons containing a large fraction of their surface as defect-free basal plane. For Kr this vertical rise occurs at a relative pressure of $\sim 2.8 \times 10^{-4}$ for adsorption in the first layer. The Thomy and Duval approach is based on a comparison of the height of the rise for exfoliated graphite, which has essentially all of its surface as basal plane, to that of the carbon being studied. Both isotherms are normalized by plotting θ (amount of Kr adsorbed per monolayer amount of Kr) versus relative pressure. The higher the fraction of the total surface which is defect-free basal plane surface, the higher the vertical rise. Using this approach, it is estimated that the as-received SP-1 and the sample reacted to $\sim 20\%$ burn-off have 20 and 44% of their total area, respectively, as strong site area. Or, the specific edge areas of these samples are 0.52 and 1.58 m²/g, respectively. This strong site area for the graphite burned off to 20% can be used to normalize the rate data of Ranish at 850 K, as shown in Fig. 1. From a least-squares calculation, the best straight line through the data points in Fig. 1 is given by $r_s = 1.50 \times 10^{28} \exp(-3.128 \times 10^4/T)$ atoms C/cm² TASA · s. The data point of R. Baker *et al.*[16] has been omitted from this calculation because it probably was under some diffusion control at the high temperature used. The activation energy for the reaction is 260.1 kJ/mole.

The strong site area estimated from Kr adsorption for the 20% burn-off SP-1 sample can be compared with areas which are estimated to be covered by oxygen complex following gasification. As seen from Table 5, they range from 0.38 to 0.94 m²/g as O₂ pressure used in the reaction increases from 0.1 to 3.5 MPa. A value of 0.083 nm² per oxygen atom is assumed for this calculation; and, as just discussed, this value could be too high.

Knowledge of the total strong site area (or TASA) is not needed to obtain meaningful specific reaction rate constants for carbon gasification as opposed to meaningful specific reaction rates. The latter rates are used only if one is going to compare results for carbons of small and randomly oriented crystallites with those obtained by microscopy on carbons of large crystallite size. What is needed to obtain a specific reaction rate constant is the area associated with the fleeting oxygen complex. It is this area which is undergoing gasification. As shown by Ranish[36], if this value is available along with an experimental gasification rate, both at the same extent of carbon burn-off, meaningful specific reaction rate constants can be obtained. Ranish obtained information on the amount of fleeting (unstable) complex by reacting at a constant temperature but over a range of O₂ pressures. More recently, Radovic and coworkers have measured the amount of unstable complex (and, thus, the reactive surface area) for the C-CO₂ reaction, using transient kinetics[52]. Undoubtedly, results of this approach will be forthcoming shortly for the C-O₂ reaction.

4. SUMMARY AND CONCLUSIONS

Trigonally bonded carbons have active (strong) sites at edges of basal planes of the crystallites and at edges of defects within the basal plane. Active sites are points attacked by O₂, leading to carbon gasification with production of CO and CO₂. The availability of carbons of large crystallite size, high crystallite alignment, and high purity has made it possible to obtain fundamental, specific gasification rates by following active area recession rates. During gasification of carbons at lower temperatures, a significant amount of oxygen complex builds up on the surface of active sites, concurrently with production of gas phase CO and CO₂. This total complex consists of some complex which is stable at gasification conditions and some which is fleeting (unstable), leading continuously to gas phase products. It is shown that knowledge of the amount of fleeting complex permits the determination of fundamental specific gasification rate constants.

Problems and possibilities for determining total ASA of carbons as a function of carbon burn-off have been considered. Low-temperature oxygen chemisorption is shown to be unreliable for this purpose. Physical adsorption appears to have possibilities which should be explored in more detail. In principle, knowledge of total ASA and total oxygen complex existing at any instant (burn-off) of gasification would permit the calculation of the fraction of ASA uncovered. However, such calculation assumes that oxygen atom spill-over and chemisorption on defect-free parts of the basal plane do not occur during gasification. As discussed, this assumption need not necessarily be true.

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