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THE IMPORTANCE OF ACTIVE SURFACE AREA IN THE CARBON-OXYGEN REACTION[1,2]

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Graphon, a highly graphitized carbon black, was oxidized to seven levels of burn-off between zero and 35%. The active surface area of these oxidized samples was determined by measuring the coverage of the surface with oxygen complex upon exposure of the samples to O_2 at 300° for 24 hr. After removal of the complex, the Graphon samples were subsequently treated with additional O_2. The amount of oxygen complex formed on the surface during reaction could be followed by a material balance and at the end of a run by outgassing. From these data, unoccupied active surface areas were calculated. Rate constants for O_2 depletion and product formation, calculated on the basis of unoccupied active area, were essentially constant over most of the burn-off range studied. On the other hand, rate constants, calculated on the basis of B.E.T. surface area, showed a considerable increase with burn-off.

Introduction

In the vast literature on the carbon-oxygen reaction,[3] there are literally as many different reactivities reported as there are carbon materials used. Further, the reactivity of a particular carbon material can vary with carbon burn-off.[3] These variations in reactivity have been ascribed to the fact that different carbons have, initially, different amounts of active surface areas (ASA) and that their ASA change to different extents with burn-off. The extent of ASA is thought to be a function of such properties of the carbon as crystallite size, crystallite orientation, vacancy concentration in the basal plane, and impurity concentration, type, and location.

Until recently, there was little success achieved at measuring ASA of carbon. Graham,[4] however, showed that the ASA of graphitized carbon blacks could be estimated from the low-coverage end of N_2 isotherms obtained at 78°K. The graphitized carbon blacks which he studied were found to have relatively small fractions of their total surface area (TSA) as ASA. This is attributed to the fact that the surface of graphitized carbon blacks is composed almost entirely of the basal planes of carbon crystallites.[5,6] These basal planes are not thought to be the source of strong sites, other than where they contain vacancies. Graham concluded that the strong site area in graphitized carbon blacks is primarily accounted for by the intersection of the basal plane surfaces composing the polyhedral-shaped particles.

Recently, the authors[7] have shown that the ASA of a graphitized carbon black can also be measured by exposure of the black to O_2 at 300° for a prolonged period. At this low temperature, the O_2 interacts with the carbon surface, forming carbon-oxygen complex on the strong sites and a negligible amount of gaseous CO and CO_2. Upon heating the carbon to 950°, the complex is recovered, with its volume related to the ASA of the carbon.

In this paper, the ambitious undertaking of correlating the structural properties of different carbons to their ASA will not be considered. Rather, the change in ASA with burn-off for one carbon will be measured, and these ASA will be used to calculate meaningful rate constants for the carbon-oxygen reaction (for this particular carbon).

Experimental

The carbon used in this investigation was Graphon,[4] which was produced by heat treatment of the channel black, Spheron-6, in the absence of oxidizing gases to 2800°. The original Graphon was oxidized to seven levels of burn-off between zero and 35% at a temperature of 625° and an initial O_2 pressure of 500 μ, in order to obtain samples with different ASA. The sample bed depths used in these initial treatments were sufficiently shallow to assure a uniform rate of oxidation through the bed.[3] These samples were first heated at 950°, *in vacuo*, for 3 hr. to remove essentially all of the surface complex which was present as a result of their prior oxidation. The TSA of these samples were measured by the B.E.T. method using N_2 adsorption at 78°K. The total ASA of these samples were determined from the amount of surface oxygen complex formed in 24 hr. at 300° using an initial O_2 pressure of 500 μ. The complex formed was recovered at 950° and converted to equivalent oxygen concentration. The assumption was made that the complex consists of one oxygen atom per edge carbon atom. Further, it was assumed that the edge carbon atoms lie in the (100) plane; that is, each carbon atom occupies an area of 8.3 Å.[2]

Reaction rate runs were then made at temperatures of 575, 625, and 675° and an initial O_2 pressure of 39 ± 0.5 μ, employing the reaction rate apparatus previously described.[8] At the bed depths used, the rates were not controlled by the rate of oxygen diffusion through the bed. A CEC Type 21-611 mass spectrometer was used to follow continuously, during a reaction, the concentrations of reactant and product gases. The reactor system (15.5 l.) was connected directly to the inlet leak of the mass spectrometer analyzer tube. The rate of change in pressure of the individual gases because of leakage into the mass spectrometer was negligible compared to their rate of change because of reaction. The amount of additional burn-off during the reaction rate runs was very small (in all cases less than 0.1%). Therefore, the B.E.T. and total ASA, measured prior to the reactivity runs, increased a negligible amount during a run.

Upon the completion of a reaction-rate run, the sample was heated at 950°, *in vacuo*, to recover the oxygen complex which was on the carbon surface. The agreement between the amount of oxygen complex recovered (as CO and CO_2) and the amount calculated to be on the surface from a material balance was usually within ±5%. From data on the total ASA and the ASA covered with complex, the amount of ASA unoccupied by complex could be calculated.

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(1) Based on a Ph.D. thesis submitted by N. R. Laine to the Graduate School of The Pennsylvania State University, June, 1962.

(2) This work was supported by the National Science Foundation Grant G6023 and the Atomic Energy Commission on Contract No. AT(30-1)-1710.

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(4) D. Graham, *J. Phys. Chem.*, **61**, 1310 (1957).

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Results

Variation of Total and Active Surface Area with Graphon Burn-off.—Figure 1 presents the relative change in TSA and ASA with burn-off of Graphon over the range 0–35%. The initial TSA of the Graphon was 76 m.^{2}/g.; it increased to 128 m.^{2}/g. with 35% burn-off.

Figure 2 presents typical degassing curves for the recovery of the carbon–oxygen complex formed at 300°—those for the 14.4% burn-off Graphon sample being given. From heat treatment studies above 950°, it has been found that heating to this temperature releases at least 95% of the oxygen complex formed at 300°.[7] During these studies, the maximum degassing temperature was held at 950° because of concern about annealing out of ASA on the oxidized samples at higher temperatures.[9] It is seen from Fig. 2 that almost all of the oxygen complex was recovered as CO, in line with our assumption, for the ASA calculation, that oxygen chemisorbed as atoms on the carbon.

On the original Graphon, the measured ASA constituted 0.29% of the TSA or amounted to *ca.* 0.2 m.^{2}/g. Upon oxidation to 35% burn-off, the ASA increased sharply to 3.1% of the TSA, amounting to almost 4 m.^{2}/g. That is, the ASA increased *ca.* 18-fold upon oxidation of the Graphon to 35% burn-off; whereas, the TSA increased less than twofold. Obviously, then, the Graphon samples represented an unusual material for use to examine the relative importance of total *vs.* ASA on the kinetics of the carbon–oxygen reaction.

Kinetics of the Reaction of Oxygen with the Graphon Samples.—Figure 3 presents typical reaction rate results for the reaction of O_2 at 625° with the Graphon samples—the sample previously having been oxidized to 14.4% burn-off being considered. The build-up in oxygen complex is given in units of equivalent O_2 pressure. Typically, the amount of oxygen complex increased during a reaction rate run, approaching a saturation amount. Over the temperature range 575–675° for a particular Graphon sample, the amount of complex formed at saturation decreased slightly with increasing reaction temperature. For example, for the 14.4% burn-off Graphon sample, the percentage of the total surface area occupied by complex decreased from 1.78% at 575° to 1.67% at 675°. On the other hand, the amount of complex formed at saturation coverage was markedly affected by the amount of prior burn-off which the Graphon had undergone. Table I summarizes these results for a reaction temperature of 625°. The table also includes results for the variation of unoccupied active surface area (UASA), at saturation coverage, as a function of Graphon burn-off.

Following a reactivity run, it was found that a negligible amount of the oxygen complex which was formed could be removed by degassing under high vacuum at reaction temperature. Upon raising the degassing temperature in increments, increasing amounts of the complex were removed, with removal being at least 95% complete at a degassing temperature of 950°. At each degassing temperature, the kinetics of complex release obeyed the Elovich equation,[10] in a similar manner to that found for the release of H_2 from graphite.[10] This indicates an increasing activation energy for complex removal, as the amount of coverage of the surface with complex decreased.

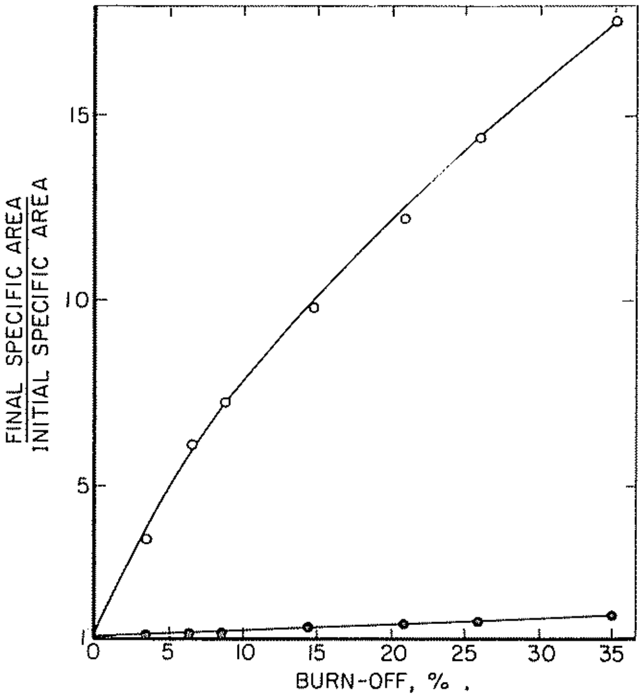

Fig. 1.—Proportional increase in total surface area (●) and active surface area (○) with amount of burn-off of Graphon in oxygen.

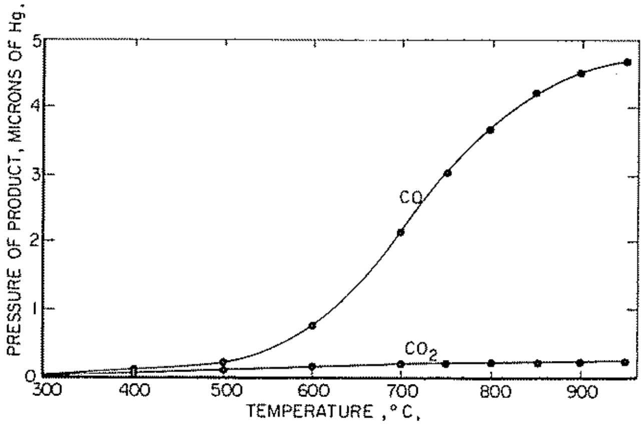

Fig. 2.—Gaseous products recovered from Graphon upon heating to 950°. Graphon (14.4% burn-off) previously saturated with oxygen complex at 300°.

TABLE I

VARIATION OF ACTIVE SURFACE AREA OCCUPIED AND UNOCCUPIED WITH COMPLEX AT SATURATION COVERAGE FOLLOWING REACTION OF GRAPHON SAMPLES WITH OXYGEN AT 625°

Burn-off (%)	Active surface area (% BET area) Occupied	Unoccupied
0	0.24	0.05
3.3	0.81	.21
6.4	1.25	.35
8.5	1.43	.42
14.4	1.74	.54
20.8	1.89	.68
25.8	1.99	.83
34.9	2.12	.99

From reactivity results, of the type shown in Fig. 3, rate constants for the disappearance of O_2 and formation of CO and CO_2 have been calculated. On the

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(10) J. P. Redmond and P. L. Walker, Jr., *J. Phys. Chem.*, **64**, 1093 (1960).

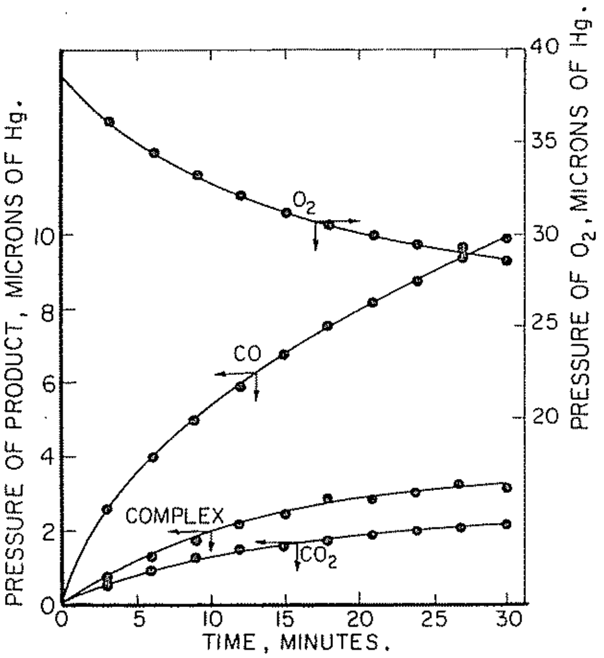

Fig. 3.—Typical reaction between Graphon (14.4% burn-off) and oxygen at 625°.

basis of TSA, the rate constants have been calculated using an equation of the form, $-\mathrm{d}P_{O_2}/\mathrm{d}t = k'_{O_2}(P_{O_2})\cdot(\mathrm{TSA})$, where $-\mathrm{d}P_{O_2}/\mathrm{d}t$ is the rate of decrease of O_2 pressure with time and (TSA) is the B.E.T. surface area for the particular Graphon sample. In all cases, a first-order dependence in O_2 pressure has been assumed. On the basis of ASA, the rate constants have been calculated using an equation of the form, $-\mathrm{d}P_{O_2}/\mathrm{d}t = k_{O_2}(P_{O_2})(\mathrm{ASA})(1 - \theta)$, where (ASA) is the active surface area for the particular Graphon sample and $(1 - \theta)$ is the fraction of the ASA which is unoccupied with complex under particular conditions of reaction time and temperature. The reasoning behind the latter equation is that the products, CO and CO_2, are being formed through an unstable oxygen complex, with the rates of their formation being retarded by the build-up of a stable oxygen complex on the active carbon surface.

Since a constant volume reactor was used in which only a small fraction (100 cc.) of the total volume (15.5 l.) was heated to the reaction temperature, the rate constants were normalized by multiplying by the ratio of the reaction temperature to room temperature in degrees absolute.[11]

Table II presents selected, typical data for the rate constants as a function of time of reaction at 625° for the Graphon sample having previously undergone a burn-off of 14.4%. Also included is the change in UASA with reaction time. The rate constants, based on TSA decreased sharply with reaction time, only beginning to level off as the amount of stable oxygen complex formed tended to saturation. In contrast, the rate constants, based on UASA, changed relatively little with reaction time. Some fluctuations were observed which, it is thought, can be primarily attributed to the fact that the surface complex concentration was determined by a difference calculation (oxygen reacted minus oxygen in the product gases) and, therefore, subject to the compounding of individual errors.

Table II

Variation of Rate Constants with Reaction Time in Oxygen for the Graphon Sample (14.4% Burn-off) at 625°

Time, min.	× 10^6, sec.$^{-1}$-m.$^{-2}$ (BET) k'_{O_2}	k'_{CO_2}	k'_{CO}	UASA % of BET	× 10^4, sec.$^{-1}$-m.$^{-2}$ (UASA) k_{O_2}	k_{CO_2}	k_{CO}
3	128.1	21.6	118.8	1.97	6.5	1.1	6.0
6	77.4	14.8	68.4	1.58	4.9	0.6	4.3
9	61.0	9.6	50.5	1.29	4.7	.8	3.9
12	48.7	9.8	46.9	1.08	4.5	.9	4.3
15	41.6	7.0	44.0	0.93	4.5	.8	4.8
18	38.5	6.6	39.8	.80	4.9	.8	5.0
21	35.0	6.3	39.7	.71	5.0	.9	5.6
24	31.1	6.3	33.0	.64	4.8	1.0	5.1
27	27.4	6.3	33.7	.60	4.5	1.1	5.6
30	25.2	5.5	33.1	.56	4.5	1 0	5.9

Table III presents selected, typical data for the rate constants as a function of prior Graphon burn-off for reaction at 625°. The rate constants were all calculated on the basis of rate data at the very end of each run. In the case of the constants based on UASA, this was the most desirable point at which to make calculations, since the amount of oxygen complex present could be more accurately determined from outgassing data than by difference calculations. The rate constants, based on TSA, increased monotonically and sharply with prior burn off given the Graphon. In contrast, the rate constants, based on UASA, were essentially constant for Graphon burn-offs between 3.3 and 34.9%. A possible explanation of why the rate constants at 0% Graphon burn-off were unmistakably higher will be considered shortly.

Table III

Variation of Rate Constants with Amount of Prior Graphon Burn-off for Reaction with Oxygen at 625°

Burn-off, %	× 10^6, sec.$^{-1}$-m.$^{-2}$ (BET) k'_{O_2}	k'_{CO_2}	k'_{CO}	k'_C	× 10^3, sec.$^{-1}$-m.$^{-2}$ (UASA) k_{O_2}	k_{CO_2}	k_{CO}	k_C
0	5.2	2.4	2.7	5.1	9.8	4.8	5.4	10.2
3.3	11.0	3.2	9.0	12.2	5.1	1.4	4.3	5.7
6.4	16.3	3.7	20.1	23.8	4.5	1.1	5.7	6.8
8.5	21.3	4.5	26.5	31.0	5.0	1.0	6.0	7.0
14.4	27.4	6.0	33.1	39.1	4.5	1.0	5.9	6.9
20.8	34.4	7.1	38.0	45.1	4.9	0.9	5.4	6.3
25.8	39.8	9.2	48.8	58.0	4.8	0.9	5.9	6.8
34.9	49.7	11.0	59.1	70.1	4.9	1.0	5.8	6.8

There has been much interest in the CO–CO_2 product ratio for the carbon–oxygen reaction.[12-17] In this study, the incremental product ratio, measured as a function of reaction time, was essentially constant. However, the product ratio was found to increase with both increase in the reaction temperature and increase in per cent Graphon burn-off. The incremental product ratios were averaged over the duration of each run, with the available values being summarized in Table IV. At 625°, the product ratio increased initially over the burn-off range 0–8.5% and then remained essentially constant for higher Graphon burn-offs. The same qualitative trend in the CO–CO_2 ratio with burn-off and reaction temperature was observed for the products recovered at the end of a run by degassing at

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(11) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, p. 59.

(12) G. Blyholder and H. Eyring, *J. Phys. Chem.*, **61**, 682 (1957).

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(14) F. Baetke, *Z. Elektrochem.*, **55**, 655 (1951).

(15) J. Arthur, *Trans. Faraday Soc.*, **47**, 164 (1951).

(16) M. Rossberg, *Z. Elektrochem.*, **60**, 952 (1956).

(17) R. J. Day, P. L. Walker, Jr., and C. C. Wright, "Industrial Carbon and Graphite," Soc. Chem. Industry, London, 1958, p. 348.

950°. However, the ratio in the degassing products was much higher than the product ratio in the primary reaction products.

TABLE IV

CO-CO_2 PRODUCT RATIOS OBSERVED AT DIFFERENT REACTION TEMPERATURES FOR GRAPHON SAMPLES OF DIFFERENT BURN-OFFS

Burn-off, %	Product ratio 575°	625°	675°
0	0.7	1.1	1.4
3.3	...	3.5	...
6.4	...	4.4	...
8.5	...	4.9	...
14.4	4.0	4.8	6.7
20.8	...	5.1	...
25.8	4.2	5.0	6.5
34.9	...	5.1	...

Discussion

It appears from adsorption studies with N_2 at 78°K. that the original sample of Graphon used in this study had a somewhat more homogeneous surface than that used by Graham in his early studies.[4] First, from low coverage adsorption studies, using the intercept method developed by Graham, our Graphon sample had the smaller ASA per unit of TSA.[9] Second, the B.E.T. area of our Graphon was 76 m.^{2}/g., compared to 82 m.^{2}/g. for Graham's sample. These results are consistent with the fact that our Graphon was heat treated to a higher temperature (2800°) than was Graham's sample (2700°). Polley, *et al.*,[18] have shown that the surface area of Spheron 6 carbon black decreases with increasing heat treatment temperature. Beebe and Young[19] have shown, from heats of adsorption studies, that the surface homogeneity of carbon black increases with increasing heat treatment temperature.

Apparently, Smith and Polley[20] were the first to recognize the potential of using carbon blacks heated to various temperatures to study reactivity and activation processes in the carbon–oxygen system. They found that the reactivity of a thermal black to air decreased sharply with increasing heat treatment temperature. They attributed this to the increase in crystallite size and the reorientation of crystallites upon heat treatment to yield a surface composed increasingly of the basal plane of the crystallites. Upon oxidation, they suggested that attack primarily occurs at the intersection of the basal plane surfaces (the location of the strong site area according to Graham[4] and others[21]), resulting in penetration into the particle and exposure of the basal plane edges. We concur with this view and conclude that in this study the exposure of the basal plane edges upon oxidation was measured by the chemisorption of oxygen on these edges at 300°. To the extent that vacancies and imperfections were originally present within the basal plane surfaces, oxidation also would be expected to increase edge concentration at these locations.[22]

Implicit in this argument is the conclusion that the edges of carbon crystallites are more reactive to oxygen than are the basal plane surfaces. Previous workers studying the interaction of oxidizing gases with a broad spectrum of carbon types, varying from purified charcoal,[23] to pyrolytic carbon,[24] to graphite single crystals,[25] have come to a similar conclusion. Possibly the high reaction rate constants found for the original Graphon sample (Table III) can be explained on this basis. That is, the reaction rate of the Graphon samples with oxygen is essentially given by the expression, $k_e(P_{O_2})\cdot(\text{ASA})(1 - \theta) + k_b(P_{O_2})(\text{TSA})$, where k_e and k_b represent the reaction rate constants for attack at the edge and basal plane carbon atoms, respectively. It can be argued that if $k_e \gg k_b$, upon some activation of the Graphon to produce a significant amount of ASA, the over-all rate can be approximated closely by the first term in the above expression. Such appears to be the case for the Graphon samples having burn-offs above 3.3%, as is seen in Table III. An estimate of k_b can then be made from the rate data for the original Graphon sample by assuming that k_e has the same value as that for the larger burn-offs. This calculation, for the three reaction temperatures, yields a value for k_e/k_b of *ca.* 2000.

The answer to the question of why edge carbon atoms are more reactive to oxygen than are basal plane carbon atoms would appear to lie with two possible factors—a geometric factor and/or an impurity factor. Regarding the geometric factor, the important point to be considered is the relative likelihood of edge *vs.* basal plane carbon atoms being able to form bonds with chemisorbed oxygen. The formation of such bonds is thought to be a required step in the conversion of oxygen to gaseous carbon oxides. From recent studies on the change in thermoelectric power of graphite upon the chemisorption of oxygen,[26] it appears that a conduction electron (π-electron) participates with an in-plane σ-electron of the carbon to form a carbon–oxygen double bond. Edge carbon atoms have unpaired σ-electrons,[27,28] which are available to form bonds with chemisorbed oxygen; basal plane carbon atoms presumably have their σ-electrons tied up in chemical bonds with adjacent carbon atoms.

Considering the impurity factor, it is known that certain impurities in small amounts can strongly catalyze the reaction of carbon with oxidizing gases.[3,29] For example, the addition of 100 p.p.m. of iron to spectroscopic graphite can increase its rate of gasification by CO_2 *ca.* 150-fold.[29] It is estimated that the total ash content of the Graphon used in this study is <100 p.p.m. However, it is known that impurities tend to diffuse to and concentrate at crystallite edges (basal plane edges in this case) during heat treatment at high temperatures. Therefore, the possibility does exist that the reactivity was higher at the edge carbon atoms in the Graphon samples because of the reaction being catalyzed by impurities concentrated at these locations.

As previously discussed at length,[3] there is consider-

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(29) J. F. Rakszawski, F. Rusinko, Jr., and P. L. Walker, Jr., "Proceedings of the Fifth Carbon Conference," Vol. II, pp. 243–250, 1963.

able disagreement as to the value of the activation energy for the carbon–oxygen reaction. As was pointed out, this is caused by, in part, the fact that different experimenters have made reactivity studies in the realm of partial diffusion control and with samples of widely different purity and crystallinity. From this study, it is clear that another factor which will invalidate the values of activation energies calculated from incomplete experimental data is the variation in UASA with temperature. For these studies, over the temperature range 575–675°, the activation energy for O_2 depletion was 36 ± 2 kcal./mole; the activation energy for carbon gasification was 44 ± 2 kcal./mole. The activation energy for carbon gasification is higher than that for oxygen consumption, since the $CO–CO_2$ product ratio increased with increasing reaction temperature—or the carbon was more efficiently gasified. Most of the studies were performed using a Graphon sample weight of 0.100 g. Sufficient runs were made, however, with 0.050-g. samples to show that the activation energies were independent of sample weight. This means that the reaction rate was solely controlled by the intrinsic chemical reactivity of the Graphon and not, in part, by the diffusion of O_2 through the bed of Graphon particles.[3]

On the basis of a uniform concentration of O_2 through the Graphon bed, the experimental reaction rates can be compared with rates predicted by the collision theory. That is, the reaction rate from collision theory can be given by $[(^1/_4 N\bar{c})(\text{UASA})\exp(-E/RT)][\zeta]$, where the terms in the first bracket represent the predicted reaction rate from simple collision theory and ζ is a steric factor (<1), suggesting that a critical orientation of the oxygen molecules on collision with the surface may be necessary for reaction to occur. Taking an activation energy of 36 kcal./mole, ζ varied from 1/56 to 1/83 for all reactivity runs, in order to make the rates calculated from collision theory agree with the experimental rates. No trend in ζ with amount of Graphon burn-off or reaction temperature was observed.

As indicated earlier, there has been controversy regarding the $CO–CO_2$ product ratio for the carbon–oxygen reaction. Particularly, the question has been asked as to whether CO and CO_2 are both primary products of the reaction. In earlier work on the Graphon–oxygen system using identical experimental conditions to those used in this study,[7] the authors have shown that CO and CO_2 are both primary reaction products. This conclusion agrees with the pioneering studies of Arthur.[15] However, Arthur further suggested that the $CO–CO_2$ primary product ratio is independent of the nature of the carbon reacted, having values of 1.6, 2.4, and 3.5 at temperatures of 575, 625, and 675°. This conclusion is based on his finding that the product ratio was the same for an artificial graphite and a coal char—two forms of carbon presumably having wide differences in crystallite size and ratios of basal plane to edge carbon atoms. As is seen from Table IV, we do not agree that the primary ratio is independent of the nature of the carbon. The ratio substantially increased over the early stages of Graphon burn-off. At each temperature, the extremes of the product ratio do encompass the values given by Arthur. Our results suggest that the product ratio might well be a function of the extent to which basal plane *vs.* edge carbon atoms participate in the reaction. Arthur's interpretation could be complicated by the fact that $POCl_3$ was used to inhibit the gas phase oxidation of CO, because as Arthur showed, $POCl_3$ also inhibited the rate of carbon consumption, perhaps by chemisorbing on active sites.[17]

DISCUSSION

J. H. ATKINS (Cabot Corporation).—Where did you obtain an area of 8.3 $Å.^2$ for an edge carbon since my calculations show an area of 6.6 $Å.^2$

F. J. VASTOLA.—This was obtained by assuming one oxygen atom interaction with one edge carbon, and that the edge carbon atoms lie in the 100 plane.

F. FARHAN (National Research Council, Ottawa).—Is it possible to decompose quantitatively the oxygen complex by heating Graphon? The obtained carbon—is it free of oxygen?

F. J. VASTOLA.—Yes.