

KINETICS OF OXYGEN INTERACTION WITH GRAPHON BETWEEN 450 AND 675°C*

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Abstract—Graphon, a highly graphitized carbon black, was first oxidized to eight levels of burn-off between 0 and 35% to introduce varying amounts of active surface area. Following the cleaning of the activated samples by heating at 950°C in a vacuum of 10^{-6} torr, chemisorption of oxygen between 300–625°C was studied. At a low O_2 pressure, i.e. 0.5 torr, the saturation amount of oxygen adsorbed sharply increased at temperatures above 400°C, suggesting the presence of at least two types of active sites. The kinetics of the reactivity of O_2 with the Graphon samples was studied between 450–675°C. From the kinetics, the number of the more active sites could be determined. For the Graphon sample of maximum burn-off, the area occupied by these sites is $3.5 \text{ m}^2/\text{g}$ or about 3% of the total surface. This value agrees closely with that obtained from low pressure O_2 chemisorption results at 300°C. The rate of oxygen interaction on the more active sites (I) is given by $k_{0_2}(I)p_{O_2} \text{TAS}(I)[1-\theta(I)]^2$, where $k_{0_2}(I) = 1.6 \times 10^{-5} \exp(-29,000/RT) \text{ cm sec}^{-1}$.

1. INTRODUCTION

THE REACTION of carbon with O_2 produces gaseous carbon oxides and surface oxygen complexes. The first step in the reaction is the chemisorption of oxygen on the carbon surface to form these surface oxides. The gaseous products are formed by the decomposition of the surface oxygen compounds. It is generally assumed that the reaction takes place on certain selected portions of the surface known as active sites. The reactivity of a given sample is determined by the extent and the reactivity of these active sites. Three methods have been reported in the literature for measuring the total active sites on Graphon surfaces. GRAHAM⁽¹⁾ and GRIFFITHS *et al.*⁽²⁾ used the low coverage end of N_2 adsorption isotherms, measured at 78°K, to estimate total active sites. HEALY *et al.*⁽³⁾ measured water adsorption on Graphon samples containing surface oxides. They reasoned, first, that the oxides covered active sites and, second, that water would only adsorb on the fraction of surface covered by oxygen. LAINE and co-

workers⁽⁴⁻⁶⁾ measured the amount of oxygen chemisorbed at 300°C when exposed to O_2 for 24 hr. For Graphon samples activated by prior oxidation to burn-off levels between 0 and 35%, the total active area ranged from 1.1 to 18% of the BET surface by the method of GRIFFITHS *et al.*, while the method of LAINE *et al.* gave values of 0.3–3.2% of the BET surface. The latter values were shown to be an index to the reactivity of the activated Graphon surface toward O_2 at higher temperatures.

The reactivity of carbons decreases as stable oxides accumulate on their surfaces. These surface oxides can be removed by thermal decomposition at temperatures in excess of their formation temperature. Removal of the oxides will restore the original reactivity to the surface. At present, little is known about the exact nature of these surface oxides. WALKER *et al.*⁽⁷⁾ have shown that the decrease in reactivity as these oxides accumulate on the active sites cannot be attributed to an increase in activation energy for chemisorption with surface coverage. Other authors^(4-6,8,9) have attributed the decrease in reactivity to coverage of active sites by the surface oxygen. In the latter case, only those sites not covered with oxygen remain available for reaction. For purposes of

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discussion and calculations, it is frequently assumed that there is one oxygen atom per carbon site in the surface oxide structure.^(4-6,9-11)

2. EXPERIMENTAL

The carbon used in this work was Graphon, a highly graphitized form of the carbon black, Spheron 6. Adsorption and reactivity runs were made on samples activated by carbon burn-off at 625°C and an initial O₂ pressure of 500 millitorr. Residual surface oxides resulting from this activation were removed by heating for 3 hr at 950°C in a vacuum of 10⁻⁵ torr. Oxygen chemisorption at temperatures between 300 and 625°C from initial O₂ pressures of either 0.5 or 700 torr was used to estimate the total number of active sites on the activated samples. The surface oxides formed during chemisorption were decomposed by heating at 950°C for 3 hr and the resulting gaseous carbon oxides converted to an equivalent number of oxygen atoms. It was assumed that each oxygen atom occupied one site on the (10 $\bar{1}$ 0) plane of the Graphon surface.⁽⁴⁻⁷⁾

The reaction rates were monitored by analyzing the composition of the gas phase in a static reactor, similar to that previously described.^(5,6) The partial pressures of O₂, CO and CO₂ were measured with a CEC Type 21-611 mass spectrometer. For fast reaction rates, these partial pressures were measured continuously by connecting the reactor directly to the mass spectrometer, while for slower reactions the analysis was performed on aliquot portions of the gases withdrawn at periodic intervals. The amount of oxygen remaining on the surface at any time during the reaction was calculated by an oxygen material balance.

Assuming one oxygen atom per surface site, and knowing the total number of active sites (TAS) on the sample, it was possible to determine the number of available active sites (AAS) for reaction.

The range of reaction conditions considered was extended by using data obtained by LAINE⁽⁴⁾ on activated Graphon samples following an experimental procedure similar to that described here. It will be clearly indicated when LAINE's data are being used. The total range of conditions encompassed eight sample burn-off levels between 0 and 35%, reacting at temperatures ranging from 450 to 675°C with initial O₂ pressures of 6.2-72.8

millitorr. The O₂ used in all cases was Matheson 99+ grade, that had been dried by immersion in liquid N₂ prior to charging into the reactor.

3. RESULTS AND DISCUSSION

3.1 General reaction

Figure 1 illustrates a typical O₂-Graphon reaction at 550°C on an 18.5% burn-off sample. The curves depict the consumption of O₂, the production of gaseous products, and the build-up of oxides on the Graphon surface. The surface oxygen, C(O), is represented as an equivalent pressure of oxygen atoms. In general, as the reaction at any temperature progressed the rate of oxygen consumption and the rates of gaseous product and total surface oxide formations decreased. The initial rates of all reactions increased with increasing temperature, pressure, and prior sample burn-off. The rate of O₂ consumption only exhibited first order behavior after some significant reaction period. This is illustrated in Fig. 2 for the reaction shown in Fig. 1. The attainment of first order behavior in O₂ consumption coincides closely with the point where the rate of total surface oxide formation becomes very small.

3.2 Total active sites

Active surface areas of activated Graphon samples have been reported by LAINE *et al.*⁽⁴⁻⁷⁾ They used chemisorption results obtained from a 24 hr exposure at 300°C to 0.5 torr initial O₂ pressure in a static reactor. The active areas determined from their data were found to be an index to the reactivity of the sample at higher temperatures. It was concluded that total active surface area had been measured by their technique.

A study of the amount of oxygen that could be chemisorbed on similar Graphon samples was undertaken to verify these conclusions. Results are presented in Table 1. They show the amount of oxygen chemisorbed at different temperatures and initial O₂ pressures for four burn-off levels of Graphon. The results in each series are presented in the order that the data were taken; LAINE's values are included for comparison.

The data in series A and B show the variation in surface coverage as the temperature of chemisorption was changed. In both series, initial O₂ pressures of 0.5 torr and an exposure time of 24 hr

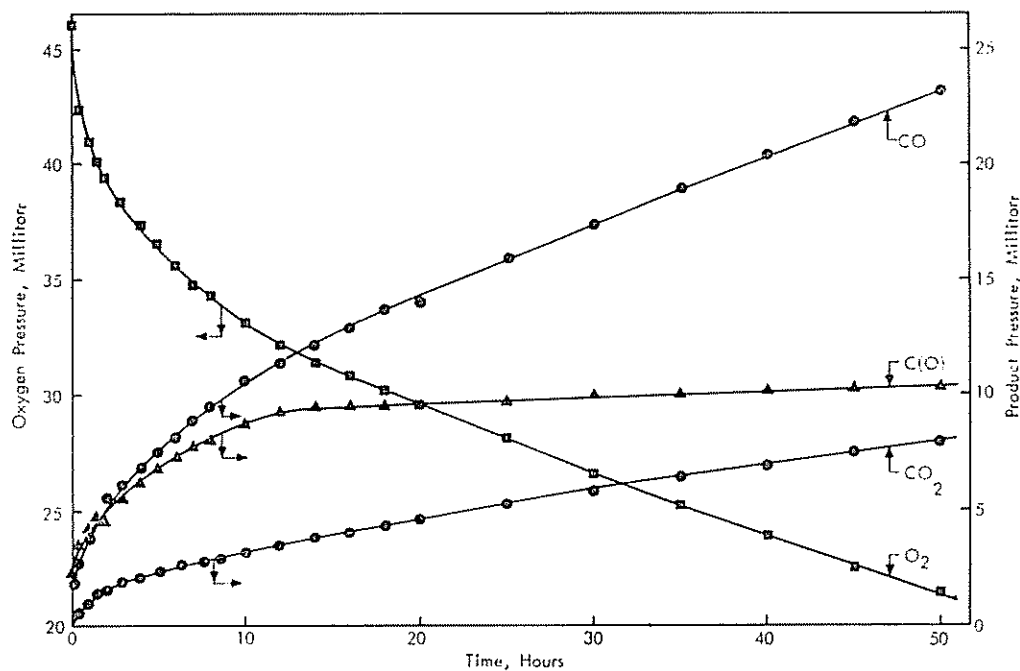


FIG. 1. Reaction of O_2 with Graphon at $550^\circ C$. 0.1 g sample having 18.5% previous burn-off.

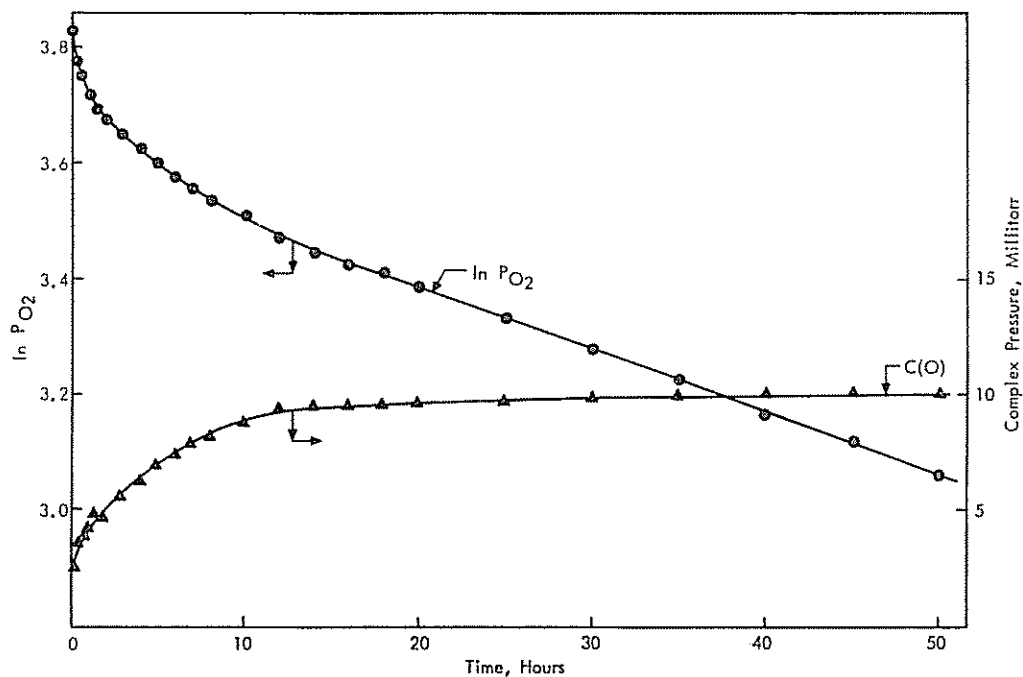


FIG. 2. Reaction of O_2 with Graphon at $550^\circ C$ showing lack of first order behavior in O_2 pressure and build-up of surface oxygen complex. 0.1 g sample having 18.5% previous burn-off.

TABLE 1. OXYGEN CHEMISORPTION CAPACITY OF ACTIVATED GRAPHON

T(°C)	Capacity ^a	Ratio ^b	T(°C)	Capacity ^a	Ratio ^b
(A) 2.9% Burn-off ^c			(B) 19.9% Burn-off ^c		
300 ^d	16.6	—	300 ^d	54.4	—
400	18.6	1.12	300	55.3	1.02
450	27.6	1.66	500	120.1	2.20
500	44.2	2.66	300	60.5	1.11
300	16.8	1.01	550	180.6	3.32
500	49.1	2.95	300 ^e	112.0	2.05
(C) 7.7% Burn-off ^c			(D) 18.5% Burn-off ^c		
300 ^d	30.9	—	300 ^d	52.0	—
625	100.1	3.24	625	167.8	3.22

(a) Capacity in micromoles O per gram of Graphon.

(b) Measured value/LAINE's value.⁽¹⁾

(c) Initial O₂ pressure, 0.5 torr.

(d) After LAINE.⁽¹⁾

(e) Initial O₂ pressure, 700 torr.

were used at each temperature. For the 2.9% burn-off samples, the amount chemisorbed increased only slightly between 300–400°C and then increased sharply above 400°C. Gasification becomes significant at 500°C, so the trend was not pursued to higher temperatures. The 300°C value for this series, measured after the first chemisorption at 500°C, showed that the larger chemisorption at 500°C was not caused by significant additional activation of the Graphon. Series B also confirms that the larger chemisorption at 500°C was not caused by sample activation. For the last run in Series B, chemisorption was measured at 300°C, with an initial O₂ pressure of 700 torr, for 24 hr. Twice as much coverage was attained upon increasing the initial pressure by about three orders of magnitude.

Coverages C and D were attained during the oxidation of Graphon at 625°C up to burn-offs of 7.7 and 18.5%, respectively. Initial O₂ pressures of 0.5 torr in a 12.4 l. system were used; a sufficient number of charges of O₂ were consumed to produce the desired level of burn-off.

The results show that the amount of surface oxide formed in a 24 hr period increased both with increasing temperature and pressure over the ranges studied. It can be concluded that chemisorption performed under the conditions proposed by LAINE⁽⁴⁾ did not measure the total active surface areas of activated Graphon samples. The agree-

ment between the values obtained from this study with those reported by LAINE, both for 24 h chemisorption from 0.5 torr O₂ pressure at 300°C, indicates that our activated samples were very similar.

3.3 Surface oxides

The surface oxides have been considered by authors in the past to be thermally stable at their formation temperatures. However, in the more recent literature evidence has been presented to show that at least a portion of the surface oxides can be thermally removed at their formation temperatures.^(8,9,11,12) The stability of the surface oxides at their formation temperature was investigated. The method used was to make a reactivity run in the usual manner. After the reaction had proceeded for a sufficient length of time to accumulate a reasonable quantity of oxide on the surface, the reaction gases were removed; and the build-up of gaseous products at the reaction temperature in the absence of O₂ was followed. Results are presented in Fig. 3. The curves depict the observed pressures of CO, CO₂, and the amount of oxygen removed from the surface as an equivalent pressure of oxygen atoms. The data shown were obtained from an 18.5% burn-off Graphon sample, before significant coverage of active sites by oxygen occurred. Before each determination, the sample was outgassed for 3 hr at 950°C and then cooled to reaction temperature under 10⁻⁵ torr pressure. Measurements were made at temperatures of 450 and 550°C at initial pressures ranging between 20 and 73 millitorr. The rate of O₂ consumption per unit of average O₂ pressure during the initial time periods was constant—that is, first order in O₂ pressure. This in turn means that the rates of both oxygen chemisorption and carbon gasification were first order in O₂ pressure.

As surface oxides form, the amount of active surface available for reaction decreases. If one assumes that the reaction continues to be first order in O₂ pressure and that the deviation from apparent first order behavior is caused by a decrease in the available active sites, then the rate of O₂ depletion can be written as:

$$-R_{O_2} = k_{O_2}(p_{O_2})f(\text{AAS}) \quad (1)$$

The term $f(\text{AAS})$ represents some function of the

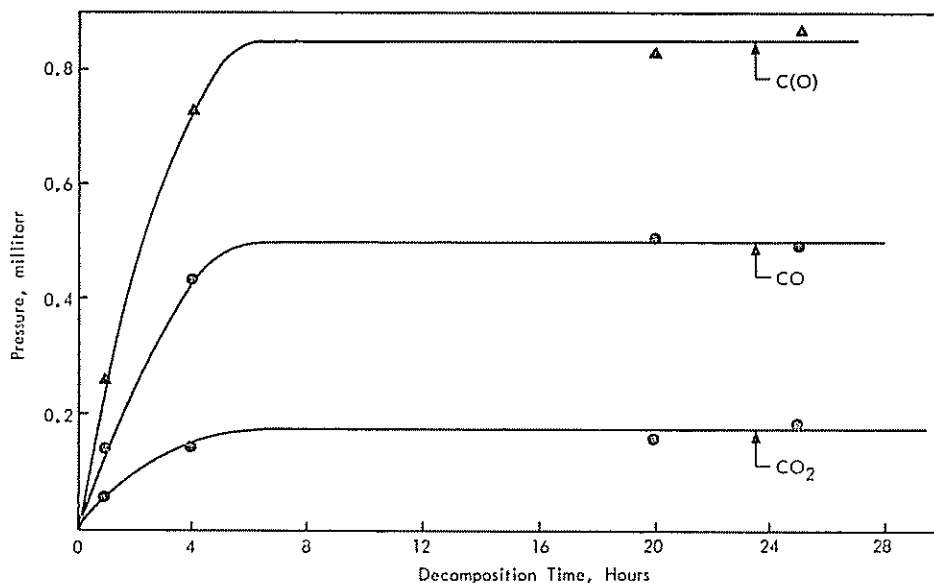


FIG. 3. Decomposition of surface oxide as CO and CO₂ at 550°C following reactivity run in O₂ at the same temperature.

available active site area, AAS. To describe the rate of reaction, one must know the manner in which $f(\text{AAS})$ changes as oxides accumulate on active sites.

To evaluate the form of the function $f(\text{AAS})$, one can consider some possible methods of interaction between O₂ and the active sites on the Graphon surface. The probable distribution of the oxygen on the surface for each of the cases considered here has been discussed by TRAPNELL.⁽¹⁴⁾ The three cases to be considered are:

1. Molecular adsorption where O₂ reacts with only one surface site

$$f(\text{AAS}) = \text{TAS}(1-\theta)$$

TAS is the total number of active sites available at zero surface coverage, and $\text{TAS}(1-\theta)$ is the number of uncovered sites.

2. Dissociative adsorption of O₂ on two adjacent surface sites where the two atoms each form an immobile surface oxide

$$\begin{aligned} f(\text{AAS}) &= \text{TAS}(1-\theta) \frac{Z}{Z-\theta} (1-\theta) = \\ &= \text{TAS} \frac{Z}{Z-\theta} (1-\theta)^2 \end{aligned}$$

Z is the nearest neighbor number and $(1-\theta)Z/(Z-\theta)$ is the probability that if one site is vacant, its neighbor is also vacant. $f(\text{AAS})$ is the number of adjacent site pairs that are available for reaction.

3. Dissociative adsorption of O₂ on two adjacent sites where the two atoms each form a mobile surface oxide

$$f(\text{AAS}) = \text{TAS}(1-\theta)(1-\theta) = \text{TAS}(1-\theta)^2$$

$(1-\theta)$ is the probability that if one site is vacant, its neighbor is also vacant. As in case (2), $f(\text{AAS})$ is the number of adjacent site pairs that are available for reaction.

The rate constant, k_{O_2} , could be evaluated from the integrated form of equation (1). The expression cannot be integrated directly, but the integration can be approximated by considering, individually, small reaction increments. The reaction increments are chosen small enough so that during any increment the change in surface coverage is small. That is, $f(\text{AAS})$ for any reaction increment can be considered constant. From the integration of equation (1) over the n^{th} reaction increment, one can evaluate the apparent rate constant k_{An} , for that increment:

$$k_{\text{An}} = \frac{\ln(p_{\text{O}_2})_1 - \ln(p_{\text{O}_2})_2}{t_2 - t_1} \quad (2)$$

$(p_{O_2})_1$ and $(p_{O_2})_2$ are the O_2 pressures at times t_1 and t_2 , respectively. The reaction increment begins at time t_1 and ends at time t_2 .

The apparent rate constants for each increment are related to each other and to the rate constant per unit of available active sites by

$$k_{O_2} = \frac{k_{A1}}{f(AAS)_1} = \frac{k_{A2}}{f(AAS)_2} = \dots = \frac{k_{An}}{f(AAS)_n} \quad (3)$$

where the subscripts refer to the number of the particular reaction increment and $f(AAS)_n$ is the average value of $f(AAS)$ for that increment. If one compares any reaction increment to the first reaction increment, the following relationship is obtained:

$$\frac{k_{An}}{k_{A1}} = \frac{f(AAS)_n}{f(AAS)_1} \quad (4)$$

The ratio of apparent rate constants is experimentally observable; and, thus, this expression can be used to evaluate the ratio of surface terms. To do this, the surface terms for the various modes of interaction of O_2 with surface sites are substituted for $f(AAS)$. Making the further substitution that θ may be written as CAS/TAS, where CAS is the number of surface sites covered by the oxides, one can rearrange equation (4) into a form that permits the calculation of the total number of active sites, TAS, as a function of the average number of sites covered and the observed ratio of k_{An} to k_{A1} . The expression for each mode of interaction is given below; the symbols are as previously defined.

Case 1: Molecular adsorption

$$TAS = (CAS)_n (1 - k_{An}/k_{A1})^{-1}$$

Case 2: Dissociative, immobile adsorption

$$TAS = (CAS)_n \frac{2Z - \frac{k_{An}}{k_{A1}} + 4Z \left(\frac{k_{An}}{k_{A1}} \right) (Z-1) + \left(\frac{k_{An}}{k_{A1}} \right)^2}{2Z \left(1 - \frac{k_{An}}{k_{A1}} \right)}$$

Case 3: Dissociative, mobile adsorption

$$TAS = (CAS)_n (1 - \sqrt{k_{An}/k_{A1}})^{-1}$$

To test these relationships, TAS is calculated for each reaction increment from the experimental data. The proper expression will yield a

value of TAS that is constant over the entire range of surface coverage observed for each level of burn-off. A summary of the incremental TAS values calculated from selected reactivity runs for each of the cases considered is presented elsewhere.⁽¹⁵⁾ For Case 2, values were calculated for Z equal to 2 and 3. As Z increases, the value of the probability term for Case 2 approaches that for Case 3 as the limiting value for any fraction of surface covered. Because of this limiting relation, calculations were not performed for values of Z greater than 3 in Case 2.

For all cases considered, the calculated values of TAS were not constant over the entire range of surface coverage. The values of TAS at low surface coverage appeared to vacillate about some constant value in each case, but at higher coverages the value increased with increasing coverage. For any increment, the calculated TAS values increased in the order: Case 1; Case 2, $Z=2$; Case 2, $Z=3$; and Case 3. The values obtained from the low surface coverage region of Case 3 were in fair agreement with the chemisorption coverages attained in 24 hr at 300°C from an initial O_2 pressure of 0.5 torr (see Table 2). This point is significant since LAINE⁽⁴⁾ and LAINE *et al.*^(5,6) have found this chemisorption coverage to be an index of the reactivity of Graphon surfaces. Because of the agreement between the 300°C chemisorption value and the values calculated from the reactivity data, it is concluded that the surface term, $f(AAS)$, in equation (1) is that derived from dissociative, mobile adsorption (or Case 3) for this portion of the data.

It has been shown, however, that low pressure chemisorption of oxygen at 300°C in 24 hr does not cover the entire surface area capable of forming surface oxides. To account for the additional

chemisorption capacity, one would have to consider that there are at least two types of surface sites on the sample and that the two types of surface sites exhibit different reactivities toward O_2 . The rate of chemisorption on the second and less active group sites did not become appreciable

TABLE 2. SUMMARY OF TAS(I) EVALUATION FOR REACTION OF O₂ WITH GRAPHON SAMPLES

Burn-off (%)	Sample wt. (g)	Reaction temp. (°C)	Initial p_{O_2} (millitorr)	Chemisorption coverage (μ moles O/g)	TAS(I) (μ moles O/g)
0	0.150	625	6.2	5.0	5.0
* 0	0.150	625	39.5	4.4	53.9
* 3.3	0.10	625	39.6	17.8	40.4
* 6.4	0.10	625	37.6	27.6	27.6
7.7	0.10	625	45.8	30.9	28.8
*14.4	0.05	575	36.6	44.4	45.2
*14.4	0.10	575	38.8	44.4	45.2
*14.4	0.10	625	38.7	44.4	44.8
*14.4	0.05	675	37.9	44.4	50.3
18.5	0.10	450	19.8	52.0	49.5
18.5	0.10	450	28.7	52.0	47.8
18.5	0.10	450	47.1	52.0	48.2
18.5	0.10	450	72.8	52.0	50.4
18.5	0.10	550	23.5	52.0	46.0
18.5	0.10	550	23.6	52.0	50.2
18.5	0.10	550	35.7	52.0	47.0
18.5	0.10	550	46.0	52.0	50.7
18.5	0.10	550	64.5	52.0	52.7
18.5	0.10	550	65.5	52.0	53.4
19.9	0.10	575	44.6	54.4	50.0
*25.8	0.10	575	44.4	65.0	64.6
*25.8	0.10	625	43.4	65.0	65.0
*34.9	0.05	675	37.9	82.0	76.0

*After LAINE.⁽⁴⁾

at low O₂ pressures and 24 hr exposure time until the chemisorption temperature exceeded 400°C. For purposes of discussion, the most active group of surface sites will be designated as TAS(I); these are the sites covered by chemisorption in 24 hr at 300°C from an initial O₂ pressure of 0.5 torr. The less active sites will be designated as TAS(II); these are the sites that require more stringent chemisorption conditions before coverage occurs. The rate of oxygen consumption by TAS(I) sites would be described by

$$-R_{O_2}(I) = k_{O_2}(I)p_{O_2}TAS(I)[1 - \theta(I)]^2. \quad (5)$$

Simultaneously, the reaction of oxygen with the second group of sites, TAS(II), will occur at a rate $R_{O_2}(II)$. The total observed rate of O₂ consumption will be the sum of the rates on types I and II sites. The form of the rate expression for oxygen chemisorption on TAS(II) is unknown at present.

For the following analysis to be valid, the reaction rate on TAS(I) would have to be much faster than the reaction rate on TAS(II), when the fraction of the total surface covered by the oxides is small. When this condition is satisfied, the reactivity data can be used to evaluate the magnitude of TAS(I).

Because of the scatter in the data, it was necessary to use an averaging method to determine the calculated value of TAS(I) representative of low coverage reactivity data. The method used was to rearrange the expression for dissociative, mobile adsorption into the following form:

$$(CAS)_n = TAS(1 - \sqrt{k_{An}/k_{A1}}). \quad (6)$$

Since TAS is a constant, one can plot the experimental values of surface coverage against the relative reactivity term and use the slope of the best line through the initial points to evaluate TAS(I).

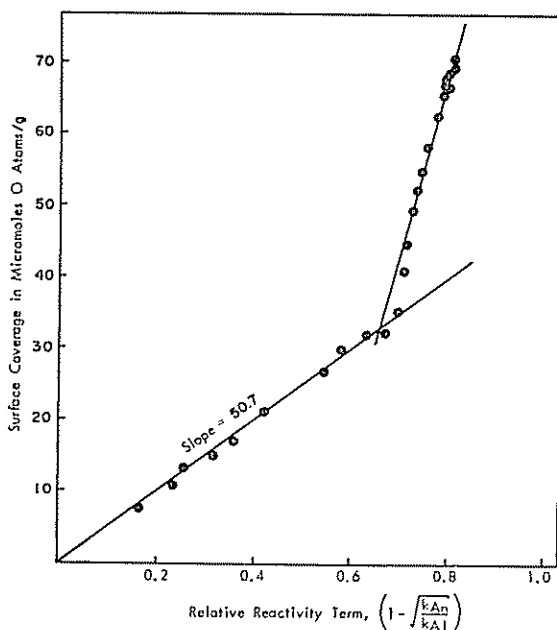


FIG. 4. Graphical evaluation of total active sites (I) for a reactivity run with 0.1 g of 18.5% burn-off Graphon at 550°C from an initial O_2 pressure of 46 millitorr.

Figure 4 shows an example of the graphical method used to evaluate TAS. The example is taken from the data for a 0.1 g sample of 18.5% burn-off Graphon reacting at 550°C from an initial O_2 pressure of 46 millitorr. This plot shows the appearance of two essentially linear regions. In the first region, the data points fall randomly about a straight line whose slope is equal to TAS(I). The second portion, although it appears to be linear in the figure, is not a true straight line. The graphical representations appear to be linear in the second region because of lack of sensitivity of the plot after the point of inflection. This second region will be discussed in greater detail later.

The graphical method of evaluating TAS(I) was applied to reactivity data obtained using a variety of reaction conditions for samples covering the entire burn-off range from 0 to 34.9%. The applicability of this method is illustrated for some selected reactions in Fig. 5. A complete summary of the results of this analysis is presented in Table 2. The first four columns describe the sample and the conditions under which the reactivity determinations were made. The fifth column lists the

surface coverage determined by chemisorption for 24 hr at 300°C from an initial O_2 pressure of 0.5 torr, for comparison with the calculated values of TAS(I) presented in column 6. The results show good agreement between these chemisorption coverages and the calculated TAS(I) values for burn-off levels exceeding 6%. The chemisorption values of the lower burn-off samples are much less than predicted by TAS(I) calculated from LAINE's reactivity data for these samples. The rate of oxide build-up on the surface of the two low burn-off samples with LAINE's reaction conditions was rapid enough to completely cover TAS(I) in 1–2 min of reaction time. The rapid attainment of this coverage value suggests that the observed reactivity was significantly influenced by the reaction on the second group of active sites, TAS(II). To verify this explanation, a slower reaction was performed on a zero per cent burn-off sample. The same sample weight (0.15 g) and temperature (625°C) were used as before, but the

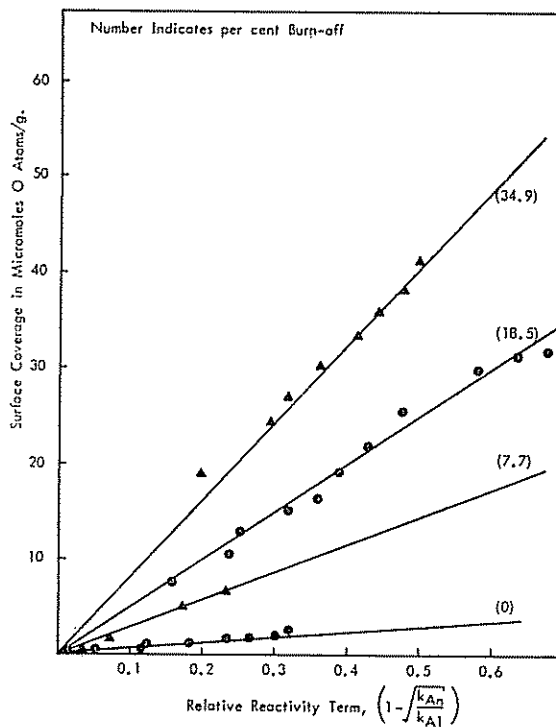


FIG. 5. Graphical evaluation of total active sites (I) for reactivity runs between O_2 and Graphon samples previously activated to different burn-off levels.

rate was decreased by taking advantage of the pressure dependency of the reaction. The initial pressure was about seven times less than that used by LAINE. Referring to Table 2, one can see that the value calculated for TAS(I) from these data agree well with the 300°C chemisorption value. These results point out the necessity of obtaining the reactivity data under the proper conditions to insure that the observed reactivity is not being unduly influenced by the reaction on TAS(II).

It is concluded that the number of active sites that comprise TAS(I) on samples of Graphon that have been subjected to prior burn-off in the range of 0–34.9% can be calculated from reactivity data taken at low surface coverage on the respective samples. This means that the contribution of TAS(II) to the rate of O₂ consumption is small when $\theta(I)$ is small. At some point, however, as $\theta(I)$ increases the contribution of the less active sites becomes significant; and breaks in the plots such as Fig. 4, are observed. It is noted in Fig. 4 that the break occurs at a surface coverage of about 36 micromoles oxygen atoms/g, which is equal to a $\theta(I)$ of about 0.7 for this sample. Thus, following the break in the plot the results represent contributions from coverage on Types I and II sites.

The rate constant for the interaction of oxygen with TAS(I) can be evaluated from the integrated form of equation (5). The integration was performed by the same approximation method as before. The equation was integrated over sufficiently small reaction increments so that the surface coverage could be considered a constant over each increment. The surface coverage used for each increment was the average coverage during that increment. For the particular reactor design used in the present study, only a small portion (about 100 cc in a total volume of 12.4 l.) of the reactor volume was heated to the reaction temperature. The data were corrected for the difference in temperature between the measured gas and the gas in the heated zone.⁽¹⁶⁾ The final form of the expression used to evaluate the corrected rate constant for O₂ consumption by TAS(I) was

$$k_{O_2}(I) = \frac{\ln(p_{O_2})_1 - \ln(p_{O_2})_2}{(t_2 - t_1) \text{TAS(I)} [1 - \theta(I)]^2} (V_R)(T_{RX}/T_{RM}) \quad (7)$$

where $(p_{O_2})_1$ and $(p_{O_2})_2$ are the O₂ pressures at times t_1 and t_2 respectively; $\text{TAS(I)}[1 - \theta(I)]^2$ is the average number of site pairs available for reaction during the reaction interval extending from times t_1 to t_2 ; V_R is the static reactor volume; and T_{RX} and T_{RM} are, respectively, the reaction temperature and room temperature (25°C). The units are: pressure in millitorr, time in seconds, V_R in cm³, temperature in °K, and available site pairs as effective surface area in cm². The area per site was chosen to be the area per carbon atom in the (10 $\bar{1}0$) plane, 8.3A², as discussed by LAINE⁽⁴⁾ and WALKER *et al.*⁽⁷⁾

The detailed variation of $k_{O_2}(I)$ with time, and thus surface coverage, for some selected reactions is given elsewhere.⁽¹⁵⁾ The values of $k_{O_2}(I)$ calculated from equation (7) showed little variation as the number of adjacent site pairs available for reaction decreases. The rate of oxygen depletion was determined for a number of reaction conditions. The average rate constants calculated from equation (7) for each run are presented in Table 3. The first four columns list the reaction conditions for each determination; the fifth column tabulates the average rate constant for each run. The values reported for each temperature show no significant trend with reaction conditions. The activation energy for $k_{O_2}(I)$ was calculated from the Arrhenius expression by the method of least squares using the data of Table 3. Within 95% confidence limits, the rate constant for O₂ consumption, in units of cm sec⁻¹ is

$$k_{O_2}(I) = 1.6 \times 10^{-5} \exp(-29 \pm 2 \times 10^3/RT)$$

in the temperature range 450–675°C for pressures between 6.2 and 72.3 millitorr, when the reaction is occurring on the active site area designated as TAS(I). The activation energy has units of kcal/mole.

To determine the nature of the transition state complex leading to chemisorption of oxygen by the Graphon surface, one can compare the experimental value of the entropy change for the reaction with the entropy change from theoretical models. The thermodynamic rate constant, K , is related to the experimental rate constant by

$$K = k_{O_2}(I) N_o C_o \quad (8)$$

where N_o is the gram moles of active sites in TAS(I) at unit activity and C_o is the standard state

TABLE 3. SUMMARY OF $k_{O_2}(I)$ FOR TAS(I) FOR REACTION OF O_2 WITH GRAPHON

Temperature (%)	Burn-off (%)	Sample wt. (g)	Initial O_2 pressure millitorr	$k_{O_2}(I)$ (cm sec ⁻¹ × 10 ⁴)
450	18.5	0.10	19.8	2.03
450	18.5	0.10	28.7	2.50
450	18.5	0.10	47.1	1.96
450	18.5	0.10	72.8	2.10
550	18.5	0.10	23.5	18.7
550	18.5	0.10	23.6	23.7
550	18.5	0.10	35.7	17.6
550	18.5	0.10	46.0	11.8
550	18.5	0.10	64.5	26.0
550	18.5	0.10	65.5	26.2
*575	14.4	0.05	36.6	37.4
*575	14.4	0.10	38.8	36.1
575	19.9	0.10	44.6	29.7
*575	25.8	0.10	44.4	26.6
625	0.0	0.15	6.2	113.0
*625	6.4	0.10	38.1	96.0
625	7.7	0.10	45.8	238.0
*625	14.4	0.10	38.7	131.0
*625	25.8	0.10	43.4	120.0
*625	34.9	0.10	38.9	147.0
*675	14.4	0.05	37.9	178.0

*After LAINE.⁽⁴⁾

gas phase concentration of O_2 in moles/nl. The standard state for unit surface activity is taken to be $\theta=0.5$ and the standard state for the gas phase O_2 is the concentration at one atmosphere pressure.

The experimental pre-exponential factor is related to the thermodynamic rate constant through the Arrhenius equation

$$k = AN_o C_o \exp(-E/RT) \quad (9)$$

where A is the pre-exponential factor calculated from the Arrhenius plot of the experimental rate constant. The Arrhenius pre-exponential term may be expressed through the absolute reaction rate theory⁽⁷⁾ as

$$AN_o = \frac{k_B T}{h} \exp(\Delta\Phi/R) \quad (10)$$

where $\Delta\Phi$ is defined by

$$\Delta\Phi = \Delta S_T^\circ - (\Delta H_T^\circ - \Delta H_o^\circ)/T \quad (11)$$

Using expressions (10) and (11), one can calculate

the experimental entropy change for the reaction from the experimental Arrhenius pre-exponential factor. The experimental entropy calculated from the data of Table 3 for the reaction at 825°K is -21 e.u.

The entropy of a gaseous molecule of oxygen contains contributions from three degrees of translational freedom and two degrees of rotational freedom; the contributions from the vibrational freedom are small and have been neglected. Translational entropy changes were calculated as described by TRAPNELL,⁽¹⁴⁾ using the relationships

$${}_3S_T^\circ = R \ln(M^{3/2} T^{5/2}) - 2.30 \quad (12)$$

$${}_2S_T^\circ = R \ln(MT) + 65.80 \quad (13)$$

${}_3S_T^\circ$ is the entropy of three degrees of translational freedom for a free gas molecule weight M at the standard state of one atmosphere pressure. ${}_2S_T^\circ$ is the entropy of two degrees of translational freedom for a gas molecule constrained to move in two

dimensions within an area A on a surface. The area A in this case is the area occupied by two adjacent adsorption sites in the (10 $\bar{1}$ 0) plane of the carbon surface. The rotational entropy of the free gaseous oxygen molecule is given by GLASSTONE⁽¹⁷⁾ as

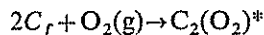
$$S_r^\circ = \ln I + \ln T + 88.59 \quad (14)$$

where I is the moment of inertia of the molecule. The entropy change, if all three degrees of translational freedom were lost in forming the activated complex, would be -41 e.u.; but if only one degree of translational freedom were lost the entropy change would be -23 e.u. If all of the rotational freedom were lost, the change in entropy would be -16 e.u.

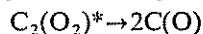
If chemisorption occurred through an immobile transition state complex, the oxygen would lose three degrees of translational freedom and probably some, if not all, of its rotational freedom. The minimum entropy change that could be expected for the formation of an immobile transition state complex, assuming that no rotational freedom was lost, would be -41 e.u. This value is significantly greater than calculated from the experimental data and indicates that the formation of an immobile transition state complex leading to chemisorption is not likely.

In the formation of a mobile transition state complex, the molecules lose one degree of translational freedom and probably some of their rotational freedom. On the other hand, the activated complex will gain some vibrational freedom terms. The gain in vibrational freedom could cancel out the loss in rotational freedom. The minimum entropy change in this case would be -23 e.u. Considering that the uncertainty of ± 2 kcal/mole in the activation energy leads to an uncertainty in the entropy change of ± 3 e.u., the calculated entropy change for the formation of a mobile transition state complex and the experimental entropy change calculated from the reactivity data are in reasonable agreement.

These results suggest the following mechanism for the interaction of O_2 with Graphon surfaces between 450 and 675°C. Oxygen molecules react with the Graphon surface to form a mobile transition state complex with two adjacent surface sites.



The surface oxygen molecule dissociates to form two surface oxygen atom complexes:



each of which are mobile on the surface. The results discussed here and the proposed mechanism are valid only on the most active group of surface sites, TAS(I).

Recently, HART *et al.*⁽¹⁸⁾ reported that the activated complex formed preceding dissociative chemisorption of O_2 on Graphon between 100–300°C was immobile. Further, the activation energy for chemisorption was only 7.4 kcal/mole. It was suggested⁽¹⁸⁾ that chemisorption of oxygen in the lower temperature regions was taking place on different carbon sites than was chemisorption between 450–675°C as reported in the present study. It is obvious now that both the entropy and enthalpy of activation of oxygen chemisorption are dependent upon where such chemisorption is occurring on the carbon surface.

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