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OXYGEN CHEMISORPTION ON WELL CLEANED CARBON SURFACES

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Abstract—Graphon, a highly graphitized carbon black, was first oxidized to 14.4% weight loss in O_2 at 625°C to introduce significant active surface area. Following the cleaning of the activated Graphon surface by heating at 975°C in a vacuum of 10^{-8} torr, chemisorption of oxygen between 25–400°C was studied. The saturation amounts of oxygen adsorbed sharply increase at temperatures above 250°C, suggesting the presence of at least two types of active sites. The maximum amount of oxygen adsorbed is estimated to occupy 2.8 m^2/g or 2.6% of the total surface. The rate of oxygen adsorption on the more active sites is given by $k_0 C n_\infty (1-\theta)^2$, where $k_0 = 7.14 \times 10^9$ exp $(-7{,}400/RT)$ cc/sec mole O_2. Following a large number of adsorption-desorption cycles, the Graphon surface is additionally activated to yield (in part) a fraction of very active sites that are not produced at comparable burn-offs by higher temperature activation between 500–625°C.

1. INTRODUCTION

ALTHOUGH oxygen adsorption on carbon has been extensively studied, much of the work has been performed on poorly defined carbons and/or on carbon surfaces contaminated with significant amounts of previously chemisorbed gases (such as hydrogen and oxygen). Reviews[1–3] summarizing pertinent studies up to 1960 are available. Little of the previous work has been concerned with the kinetics and mechanism of oxygen chemisorption.

BONNETAIN,[4] using various forms of carbon, and DIETZ and MCFARLAND,[5] using high surface area carbon films, have found the rate of oxygen adsorption to be given by the Elovich equation.[6] These studies were conducted at temperatures below 300°C and at O_2 pressures of about 100 millitorr. A similar rate dependence was found by ALLARDICE[7] for oxygen adsorption on a brown coal char at temperatures of 25–250°C and O_2 pressures of 100–760 torr.

Recently, WALKER and co-workers[8] studied the kinetics of oxygen chemisorption on spectroscopic grade, highly crystalline natural graphite at an O_2 pressure of 760 torr and temperatures between 335 and 448°C. The rate of adsorption was followed by measuring the change in thermoelectric power of the graphite as chemisorption proceeded. Unlike the situation which holds when the Elovich equation is applicable, they found the rate constant to be independent of surface coverage.

This paper is concerned with the kinetics and mechanism of oxygen chemisorption on well cleaned carbon surfaces at temperatures between 25 and 400°C and low oxygen pressures (1–15 millitorr).

2. EXPERIMENTAL

2.1 Materials

The carbon used in this study was Graphon (a granular, graphitized carbon black Spheron 6) obtained from the Cabot Corporation. The BET (N_2) surface of the original material was 76 m^2/g. Total impurity content is estimated, by emission spectroscopy, to be below 15 ppm, with the major impurities being Ti, Ca, and Si. Graphon samples were preoxidized to 14.4% weight loss at 625°C at an O_2 pressure of 500 millitorr. This pretreatment increased the BET surface area to 98 m^2/g—a fractional increase of about 1.3. However, the area of the carbon sample which adsorbed oxygen at 300°C increased from 0.23 to 2.3 m^2/g as a result of oxidation to 14.4% weight loss[9]—a sizeable increase of 10-fold. The rate of carbon oxidation above 500°C has been shown to be pro-

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portional to this latter area rather than the BET area.[9] Samples of about 0.1 g of the preoxidized Graphon were used in these studies.

The O_2^{16-16} was Research Grade, obtained from Air Products and Chemicals Company. The major impurities were N_2 (46 ppm), Ar (407 ppm), and water vapor (1.3 ppm). The O_2^{16-16} used for sample preoxidation was Extra Dry Grade, obtained from the Matheson Corp. Its minimum purity was 99.6%; further drying was accomplished using liquid N_2 traps.

The O_2^{18-18} was obtained from YEDA Research and Development Company Ltd. of the Weizmann Institute of Science, Rehovoth, Israel. Mass spectrometric analysis gave 96.8 mole % O_2^{18-18} and 98.6 atom % O^{18}. This O_2 was used without further purification.

2.2 Apparatus and procedure

The apparatus is the same as that described previously.[10-12] A vacuum of about 10^{-8} torr could be achieved in the reaction system while maintaining the carbon sample at 975°C (the temperature used for cleaning the carbon of adsorbed gases) using an 8 l./sec Vac-Ion pump. The reaction system was connected to a modified General Electric mass spectrometer by means of a molecular flow leak. Gas pressures could be monitored continuously during adsorption. The total volume of the reaction system was 1.3×10^4 cc.

The procedure for each adsorption run was similar to that described previously.[11,12] Briefly it was as follows:

1. While pumping, the Graphon sample was heated to 975°C, held there until a vacuum of at least 10^{-8} torr was achieved, and then cooled to adsorption temperature.

2. O_2 was admitted to the closed reaction system and its pressure measured continuously during adsorption. At temperatures below about 300°C, negligible concurrent gasification of the carbon, resulting in the production of CO or CO_2, occurred.

3. At the end of a run, the system was first evacuated at reaction temperature. The carbon was then heated to 950°C, with no pumping, to decompose the chemisorbed oxygen complex. A mass balance showed that 95–100% of the previously adsorbed oxygen could be recovered as CO and CO_2 within 6 hr at 950°C. No O_2 was found in the degassing products, even at lower temperatures. Since the total carbon consumed per run as CO and CO_2 was very small (about 3×10^{-5} g or only 0.03%), the same Graphon sample could be used for a large number of runs.

3. RESULTS AND DISCUSSION

3.1 Amount of oxygen adsorbed as a function of temperature

The maximum amount of oxygen that could be adsorbed on the surface (hereafter called the saturation coverage) of a 14.4% weight loss Graphon sample was measured between 25 and 400°C. This was done by exposing the "cleaned" Graphon to a pressure of 500 millitorr of O_2 until negligible further adsorption took place. For most temperatures, 24 hr was sufficient, with essentially no further adsorption detected for periods of up to 72 hr. Results, which are summarized in Fig. 1, were determined on one sample, with the points being obtained in a random temperature order. Some of the points were redetermined after the series was completed to insure that the shape of the curve was not dependent on the previous few runs. No effect was found and the points were reproducible. Assuming dissociative chemisorption on the prismatic $(10\bar{1}0)$ and $(11\bar{2}0)$ planes,[8,9] with each carbon atom occupying an area of 8.3Å^2, the amount of oxygen adsorbed at 300°C would cover 2.8 m^2/g of surface or 2.6% of the total surface area. This is in close agreement with our previous findings.[9] Results for the 15.2% burn-off sample will be discussed shortly.

The shape of curve A in Fig. 1 suggests the presence of two types of adsorption sites on the carbon surface. Chemisorption from 25 to 250°C primarily involves only one type of site; chemisorption above 300°C involves two types of sites.

3.2 Rates of oxygen adsorption

The rate of adsorption on the sites giving the first plateau of curve A in Fig. 1 (type 1 sites) was studied over the temperature range 100–300°C at O_2 pressures of 1.0–15.0 millitorr. Adsorption times at temperatures above 200°C were kept small to insure that adsorption was essentially only on the first type of site.

The rate of adsorption can be expressed as

$$\frac{dn}{dt} = k_a C n_\infty (1-\theta)^2 \qquad (1)$$

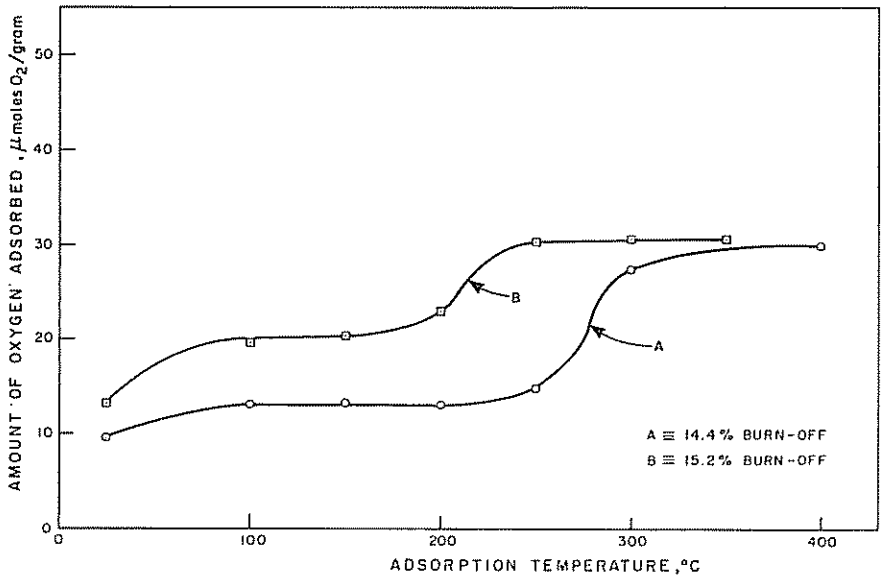

FIG. 1. Saturation amounts of chemisorbed oxygen on Graphon at different temperatures.

where n is the number of moles of oxygen adsorbed at time t, k_0 is the rate constant in cc/sec mole O_2, C is the O_2 concentration in the gas phase in moles O_2/cc, n_∞ is the saturation coverage between 100 and 200°C (which is proportional to the number of type 1 sites), and $\theta = n/n_\infty$ or the fraction of the type 1 sites that are covered at time t.

Equation (1) can be put into terms of oxygen pressure:

$$-\frac{dp_{O_2}}{dt} = \left(\frac{k_0}{V}\right)\left(\frac{T_{Rm}}{T_{Rx}}\right) p_{O_2} n_\infty (1-\theta)^2 + k' p_{O_2} \qquad (2)$$

where p_{O_2} is the O_2 pressure (measured at room temperature, T_{Rm}); V is the volume of the reaction system $= 1.3 \times 10^4$ cc; and T_{Rx} is the reaction temperature. The term $k' p_{O_2}$ is a correction for the amount of O_2 that leaked into the mass spectrometer during adsorption. A value of $k' = 4.5 \times 10^{-6}$ sec^{-1} was determined experimentally with no carbon in the system.

Integration of equation (2) over the limits $t=0$ and $p_{O_2} = (p_{O_2})_0$, $t=t$ and $p_{O_2} = (p_{O_2})_t$ gives:

$$\log (p_{O_2})_t + k't/2.303 = -\left[\left(\frac{k_0}{V}\right)\left(\frac{T_{Rm}}{T_{Rx}}\right)\left(\frac{n_\infty}{2.303}\right)\right] \sum_i \left[\Delta t \overline{(1-\theta)^2}\right]_i + \log (p_{O_2})_0 \qquad (3)$$

where the average values $[\Delta t \overline{(1-\theta)^2}]_i$ were calculated for increments, i, of θ that were small enough to allow the substitution of the summation for the integral. An exact integration is not possible since there are three variables in equation (2), p_{O_2}, t, and θ. A plot of $[\log (p_{O_2})_t + k't/2.303]$ vs. $\sum_i [\Delta t \overline{(1-\theta)^2}]_i$ gave straight lines with slope $-[(k_0/V)(T_{Rm}/T_{Rx})(n_\infty/2.303)]$ and intercept $\log (p_{O_2})_0$ for fresh 14.4% weight loss samples. Figure (2) is a typical plot. The intercept and the measured value $\log (p_{O_2})_0$ agree closely on the fresh samples.

Due to the small amount of carbon weight loss occurring for each adsorption–desorption run, a large number of runs were performed on the same sample. However, after several runs at temperatures below 400°C, it was found that the intercept and the measured value of $\log (p_{O_2})_0$ were no longer equal. Figure (3) is a typical plot obtained on a sample which was originally of 14.4% weight loss but which was converted to a sample of 15.2% weight loss by repeated low temperature adsorp-

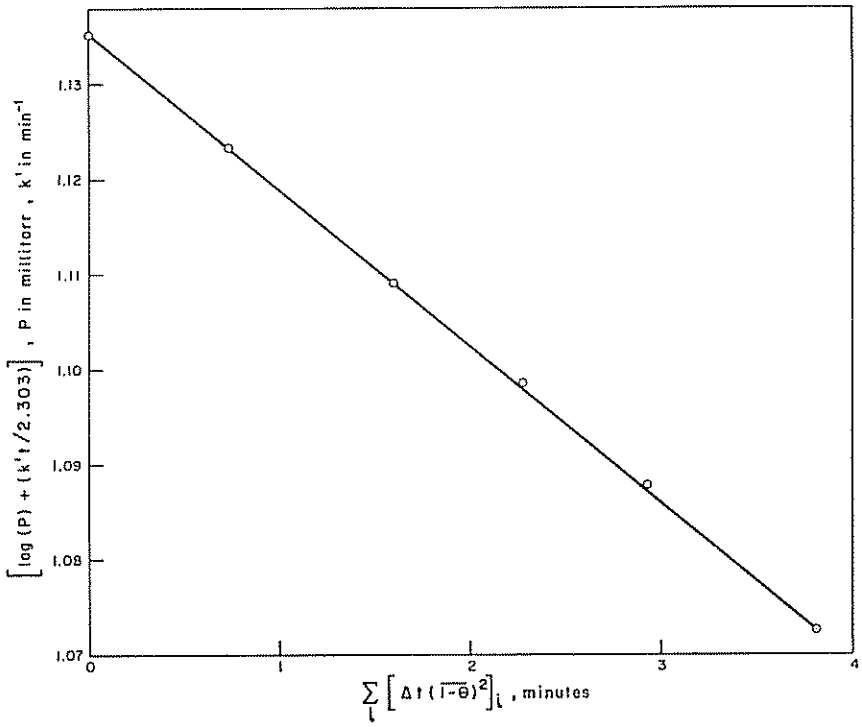

FIG. 2. Plot of equation (3) for oxygen chemisorption on fresh 14.4% burn-off Graphon at 280°C.

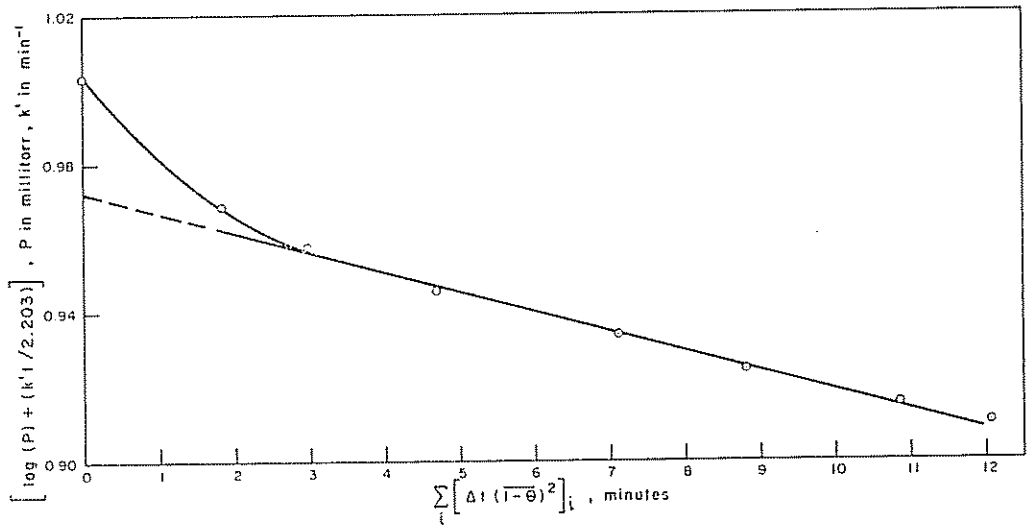

FIG. 3. Plot of equation (3) for oxygen chemisorption on 15.2% burn-off Graphon at 200°C.

tion runs. The extrapolated intercept is significantly lower than the measured value. It appears that another type of adsorption is taking place initially, which is much faster than that measured on type 1 sites on the fresh 14.4% weight loss samples. Since this new type of fast adsorption appears only after a series of low temperature adsorption runs, the process of active site development at these low temperatures must be different than that at 625°C where the 14.4% weight loss samples were prepared initially by direct oxidation.

If the assumption is made that the fast adsorption and the adsorption on the type 1 sites are parallel and independent processes, the amount of adsorption occurring in the fast process can be estimated. The difference in the intercept of a plot, such as in Fig. 3, and the measured $\log(p_{O_2})_0$ value should represent the amount of this fast adsorption. Table 1 gives values of this quantity for various temperatures and pressures. No correlation is apparent between the reaction conditions and the amount adsorbed. It is estimated that the average amount adsorbed occupies 0.38 m^2/g of surface or 0.35% of the total surface area.

Curve B of Fig. 1 gives the saturation coverage values for the 15.2% weight loss sample. From the shape and position of the curve, it appears that the sites responsible for the fast adsorption have been produced at the expense of the sites responsible for the increased oxygen adsorption above 250°C (the type 2 sites) on the 14.4% weight loss sample. The saturation level above about 250°C on curve B is approximately the same as that of curve A above about 300°C. Therefore, the total number of sites available at 300°C has not increased but the energy distribution has been altered.

If the 15.2% burn-off sample, which shows the fast initial oxygen adsorption, was reacted for a short period of time between 500 and 625°C, the adsorption behavior of the sample changed. That is, there was no longer an initial fast adsorption; and the saturation curve was the same as in Fig. 1, curve A, with slightly higher values due to the burn-off. This means that low-temperature adsorption followed by desorption activates the carbon surface in a way quite different from direct combustion between 500 and 625°C.

The importance of the temperature at which oxygen interaction with carbon occurs on the nature of site development was also apparent from visual observation. The Graphon, originally oxidized to 14.4% burn-off at 625°C, was dull black in appearance. Following a large number of cycles of oxygen adsorption below 400°C, desorption at 950°C, and final surface cleaning at 975°C, the surface was shiny gray. Subsequent exposure of the Graphon to O_2 between 500–625°C converted it back to a dull black appearance.

When θ is corrected by subtracting the amount of oxygen put on in the fast adsorption process from the measured n_∞ values, plots such as that in Fig. 2 should be obtained, if parallel and independent adsorption processes occur. Figure 4 is such a plot after correcting the data which were used in Fig. 3. The rate constants obtained from the slopes of such plots agree closely with those obtained from freshly prepared 14.4% weight loss samples.

The Arrhenius plot (Fig. 5) includes rate constants obtained from both kinds of samples. The activation energy for adsorption on type 1 sites is 7.4 kcal/mole O_2, which is considerably less than that obtained by Lussow[13] on Graphon (29 ± 2 kcal/mole O_2) and Walker and coworkers[8] on natural graphite (30 ± 2 kcal/mole O_2). However, since the lowest pressures obtained by these workers was about two orders of magnitude higher than that obtained in this work it is expected that a significant fraction of the type 1 sites were covered when adsorption runs were commenced. Thus we have reason to believe that they were observing adsorption primarily on type

TABLE 1. SATURATION AMOUNTS OF OXYGEN ADSORBED AT VARIOUS TEMPERATURES AND PRESSURES DURING THE FAST ADSORPTION STEP ON 15.2% BURN-OFF GRAPHON

Temperature (°C)	Initial O_2 Pressure (millitorr)	Saturation amounts of O_2 adsorbed during fast adsorption (μ moles O_2/g)
100	2.76	3.26
150	1.83	3.44
180	5.38	4.28
180	3.50	3.89
200	10.04	4.68
250	7.76	4.52
300	2.04	3.24
		Av. value = 3.81

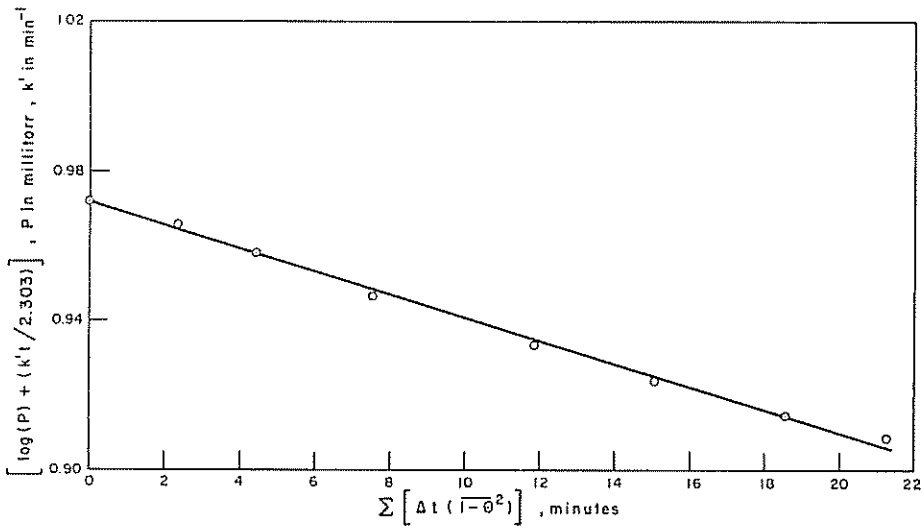

FIG. 4. Plot of equation (3) for oxygen chemisorption on 15.2% burn-off Graphon using θ corrected for the amount of fast adsorption (same data as in Fig. 3) at 200°C.

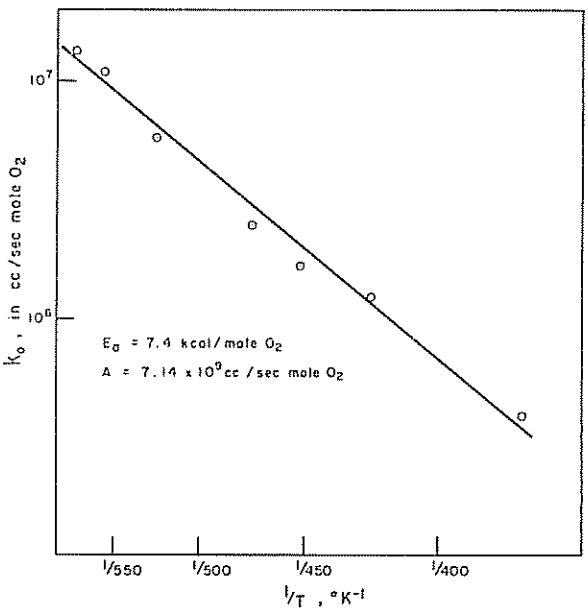

FIG. 5. Arrhenius plot for the adsorption of oxygen on type 1 sites on clean Graphon surfaces between 100–300°C.

2 sites, which are expected to exhibit a higher activation energy for chemisorption. In fact, these workers did study adsorption at temperatures higher than where type 1 chemisorption can be conveniently measured, that is LUSSOW (300–675°C) and WALKER *et al.* (335–448°C).

3.3 O^{18} tracer studies

The $(1-\theta)^2$ term in equation 1 implies, from its theoretical derivation, that the O_2 is dissociating upon adsorption.[7] If the breaking of the oxygen-oxygen bond is involved in the rate limiting step, then $O_2{}^{16-16}$ would be expected to adsorb more rapidly than $O_2{}^{18-18}$. A kinetic isotope effect has been defined as $[(k_{32}/k_{36})-1]100$,[14,15] where k_{32} and k_{36} are the rate constants for $O_2{}^{16-16}$ and $O_2{}^{18-18}$ respectively. The kinetic isotope effect has been predicted theoretically for gas phase reactions but not for gas-solid interactions. However, the high temperature limit of the equation for the gaseous reaction should apply to a process where adsorption is rate limiting. This high temperature limit (where vibrations are fully excited) is given by:[14,15]

$$100\left(\frac{k_{32}}{k_{36}}-1\right)=\left(\sqrt{\frac{\mu_{36}}{\mu_{32}}}-1\right)100 \qquad (4)$$

where μ_{36} and μ_{32} are the reduced masses of the $O_2{}^{18-18}$ and $O_2{}^{16-16}$ species respectively. This equation predicts an isotope effect of 6.3%. The rate constants for the adsorption of a mixture of $O_2{}^{18-18}$ and $O_2{}^{16-16}$ on a 15.2% burn-off Graphon sample were measured at 200°C. The experimental isotope effect was found to be $5.3\pm1\%$ on type 1 sites. This is, therefore, supporting evidence that the adsorption of oxygen is dissociative and that dissociation is involved in the rate limiting step. No conclusion could be drawn concerning a possible isotope effect for the very rapid adsorption, as a result of the uncertainty in the intercept (pressure) values.

3.4 Consideration of the mechanism of oxygen chemisorption on carbon surfaces

Although the activation energy for oxygen chemisorption on type 1 sites on Graphon (7.4 kcal/mole) is considerably lower than that reported by WALKER and co-workers[8] on natural graphite (30 kcal/mole), the pre-exponential values of the rate constants for the two studies agree within a factor of 4. WALKER and co-workers report a value of 2.2×10^9 cc/sec mole O_2; a value of 7.1×10^9 was calculated from Fig. 5 of this study. As discussed at length by WALKER and co-workers, a pre-exponential value of this magnitude is equivalent to an experimental entropy of activation of about 39 e.u. An entropy of activation calculated from absolute rate theory[8,16] agrees well with the experimental value only for an immobile activated complex which has at most one limited degree of rotational freedom.

At least two reasons can be suggested to explain differences in activation energy for oxygen chemisorption on carbons: (i) presence of impurities located close to some active sites and (ii) difference in geometric arrangement of surface carbon atoms. Consider the first reason. Impurities tend to diffuse to and concentrate in the neighborhood of defects in the carbon when it is heated to graphitization temperatures because of essentially geometric considerations, giving rise to the so-called Cottrell cloud.[17] Even though the impurity content of the Graphon used in this study is low, the impurity concentration at surface defects (or active sites), exposed and produced upon oxidation of Graphon to 14.4% burn-off, could be significant. Most impurities are known to enhance the gasification of carbon,[18] presumably by increasing the rate of dissociation of the oxidizing gas molecule to yield very reactive oxygen atoms. WALKER and co-workers,[8] however, have found that the addition of 0.3% Fe to spectroscopic natural graphite only increased the rate of oxygen chemisorption five-fold and produced an insignificant lowering of the 30 kcal/mole activation energy for adsorption. We are not, at this time, able to make a meaningful judgment on the extent to which differences in activation energy might be attributable to impurities. Oxygen chemisorption studies on ultrahigh purity Graphon (<1 ppm) are planned, which should clarify this question.

Consider the second possibility to explain differences in activation energies of oxygen chemisorption. SHERMAN and EYRING[19] have showed theoretically that the activation energy for dissociative chemisorption of hydrogen on carbon is markedly dependent upon the carbon–carbon spacing. They predict a minimum in activation energy for a carbon–carbon spacing of about 3.5Å. At very high spacings of the carbon atoms, the

molecule must effectively be dissociated prior to adsorption. The activation energy is, therefore, high and approaches the heat of dissociation of the molecule (119 kcal/mole for O_2). At very low separations, the activation energy is again high because adsorption is hindered by repulsion forces.

The basal plane of carbon is ideally terminated by two configurations of carbon atoms, the so-called arm chair (or $<10\bar{1}l>$ direction) and zig-zag (or $<11\bar{2}l>$ direction).[20] There are two spacings for the carbon atoms in the arm chair direction, 1.42 and 2.84Å, and one spacing in the zig-zag direction, 2.46Å. In addition, edge surface carbon atoms in two adjacent basal planes are separated by spacings of either 3.35 or 3.62Å. Of course, it is known that the basal plane of carbon is not completely terminated by only arm chair and zig-zag configurations. SAVAGE,[21] for example, in studying the chemisorption of O_2, H_2 and N_2 on graphite wear dust, concluded that the basal planes are, in part, terminated by carbon fragments protruding from the main condensed-benzene ring structure. Recently, SMITH and co-workers,[22] from i.r. spectra, showed that both carbonyl and lactone structures are formed upon exposure of carbon films to O_2 between 25 and 450°C. They concluded that peripheral carbon fragments consisting of either one or two atoms could take part in the formation of lactone rings. Figure 6 shows a schematic arrangement of carbon atoms in a basal plane. Distances between C-36 and C-37 and between C-11 and C-14 are characteristic of spacings in the arm chair direction. Distances between C-5 and C-7 and between C-7 and C-9 are characteristic of spacings in the zig-zag direction. Carbonyl structures could exist on these adjacent carbon atoms, for example. A 6-membered lactone ring could be formed by C-1 closing with an oxygen atom on C-5; a 5-membered lactone ring could be formed by C-16 closing with an oxygen atom on C-18, for example.

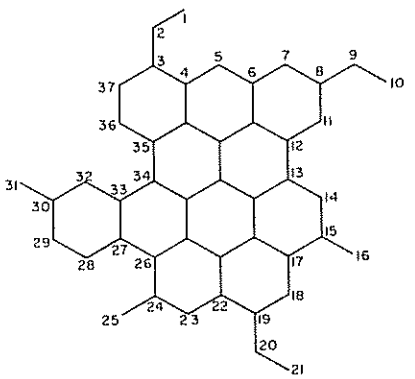

FIG. 6. A schematic arrangement of carbon atoms in a layer plane showing a variety of peripheral carbon fragments and ring positions available for the chemisorption of oxygen (after ref. 22).

SMITH and co-workers suggest, from isotopic studies of WANG and FLEISCHER[23] (who concluded that the two oxygen atoms in CO_2 came almost exclusively from different oxygen molecules during carbon combustion)* that the lactone-ring oxygen comes from dissociation of an O_2 between carbon atoms in adjacent basal planes. It is known, from desorption studies on carbon-oxygen complexes,[9,22] that when their formation temperature is low, they decompose to give primarily CO_2 (presumably from lactone); and when their formation temperature is high, they decompose to give primarily CO (presumably from carbonyl). Thus, the oxygen adsorbed on type 1 sites and the very active sites in this study could primarily involve the formation of lactone groups with carbon fragments; and the oxygen adsorbed on type 2 sites could primarily involve the formation of carbonyl groups at conventional arm chair and/or zig-zag carbon configurations.

Recently, LUSSOW[13] has studied the chemisorption of oxygen on Graphon at temperatures between 300–675°C. In agreement with the

*We are not convinced that WANG and FLEISCHER's experiments justify their conclusion. They reacted O^{18} enriched O_2 with carbon in a closed Pyrex tube by heating with a "micro-burner". They noted that this caused the carbon to spark, with combustion being completed within a few seconds. It was concluded that since O^{18} was randomly distributed in the CO_2 produced, the oxygen atoms in the CO_2 came from different O_2 molecules. However, the sparking carbon indicates a relatively high temperature and suggests that the gas phase oxidation of the primary product CO to yield CO_2 as a secondary product would take place. If, as appears likely, most of the CO_2 recovered was formed by this secondary reaction, no conclusion could be made regarding the mechanism of formation of primary CO_2. We have recently reacted O_2^{16-16} and O_2^{18-18} mixtures with Graphon.[11] In fact, we have shown that CO_2 is a primary product of the reaction and that its formation involves atomic oxygen on the carbon surface.

present studies, he finds the saturation amount of oxygen chemisorbed between 300–400°C to be almost constant. However, he finds a sharp uptake in the amount adsorbed between 400 and 500°C, with the amount adsorbed at 500°C being about 2.5 times that adsorbed at 400°C. This suggests another type of active site, which could be related to one of the carbon–carbon spacings given previously.

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