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Studies on Ultraclean Carbon Surfaces

II. Kinetics of Chemisorption of Oxygen on Graphon

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The chemisorption of oxygen on activated Graphon was studied over the temperature range −78° to 160°C at an oxygen pressure of 100 millitorr. The Graphon was activated by preoxidation to 16.6% weight loss at 625°C. The oxidized sample had a BET surface area of 100 m²/gm. Prior to adsorption measurements, the sample was outgassed at 1000°C at residual pressures $<10^{-8}$ torr. Adsorption was followed for times up to 24 hr. Plots of amount of oxygen adsorbed versus log of time showed linear regions. In all, five linear regions were identified. The activation energy for chemisorption changed little within a linear region. However, it changed abruptly in going from one linear region to the next, increasing overall from 3.1 kcal/mole for the first linear region to 12.4 kcal/mole for the last. It is concluded that each linear region represents adsorption on different discrete types of sites on the carbon surface.

I. INTRODUCTION

Chemisorption of oxygen on an ultraclean Graphon surface at room temperature (25°C) and at different starting pressures of oxygen (varying from 7×10^{-4} to 7.6×10^{2} torr) was discussed in Part I of this series.[1] Plots of the chemisorption data were discontinuous straight lines, indicating the existence of different kinetic stages. Each of the kinetic stages appeared after the adsorption of a definite amount of oxygen (which was independent of pressure) and corresponded to adsorption on a different group of active sites. In all, five different groups of active sites were observed in experiments at room temperature.

Chemisorption of oxygen on the same sample of Graphon at different temperatures can give additional useful information. The data can be used to calculate the activation energies of chemisorption on different groups of active sites. Data at lower and higher temperatures can also give useful information about the possible existence of other more active or less active groups of sites.

Chemisorption of oxygen at different temperatures (varying from 25° to 400°C) on different types of carbons has been studied by a number of workers (2–12). Activation energies calculated from the adsorption results show wide variations. Several workers (2–5) interpreted their results on the basis of the Elovich equation and found that the activation energy increased linearly with coverage. However, there were instances where this relation was not found (5, 13).

Recently, Walker and co-workers (9) studied the adsorption of oxygen on well-cleaned carbon surfaces and observed the existence of more than one group of active sites. The activation energy of adsorption on the more active sites was found to be 7.4 kcal/mole. However, a detailed study was not made. The present paper describes the kinetics of oxygen chemisorption at temperatures varying from −78° to 160°C at a constant starting pressure of oxygen.

II. EXPERIMENTAL

A. Materials. The carbon sample used in these investigations was the well-known graphitized carbon black, Graphon, which had a total metallic impurity content of <15 ppm. The major impurities were Ti, Ca and

Si. The particular sample studied was preoxidized to 16.6% weight loss at 625°C in 0.5 torr of oxygen to introduce a significant active surface area, as previously discussed (14). The oxidized sample was the same as used previously (1).

B. Apparatus and Procedure. The apparatus and the procedure used have been described in detail (1). A brief description is given here. The apparatus is a combination of an ultrahigh vacuum system and an ultrasensitive measuring unit. It has been assembled using stainless steel valves and flanges. Incorporated as part of the vacuum system is a vacion pump. A vacuum better than 10^{-9} torr could be attained. The reactor is a double-walled quartz tube with the sample suspended from a metal flange at the top. The jacket of the reactor is evacuated continuously to 10^{-6} torr to reduce to a minimum the inward diffusion of gas when the reactor is at elevated temperatures. A Pt-Pt 10% Rh thermocouple is used to measure the temperature of the sample inside the reactor.

The adsorption measuring unit has a residual gas analyzer, a Baratron differential manometer, and a UHV microsorption balance. The residual gas analyzer is a mass spectrometer (CEC 21-614), which has been placed directly on the reactor so that it can monitor gas pressures down to 10^{-10} torr. The microsorption balance (Cahn RG) has been enclosed in a stainless steel container connected to the high vacuum portion of the measuring unit through a stainless steel valve so that it conforms to the high purity requirements of the system. The balance can measure accurately weight changes of the order of 2×10^{-6} gm.

The carbon sample (ca. 0.1 gm) was held in a quartz boat and suspended by means of a quartz fiber. Outgassing at 1000°C for 10–12 hr was sufficient to reduce the residual gas pressure to 10^{-8} torr. After cooling to the desired temperature under vacuum, a known volume of O_2 was expanded into the reactor and adsorption was continuously followed for times up to 1400 min using a residual gas analyzer (mass spectrometer), a differential manometer, or a microsorption balance where applicable. Analysis of the gas with the mass spectrometer at different stages of adsorption showed that insignificant amounts of CO and CO_2 were formed, indicating negligible gasification of the carbon. Therefore, the measured decrease in pressure in the system was due to adsorption of oxygen. Following an adsorption run, the system was first outgassed to a residual gas pressure of $< 10^{-8}$ torr at the adsorption temperature, and then the sample was heated to 1000°C, with the amount of oxygen desorbed as CO and CO_2 measured. In all cases, the amount of oxygen recovered agreed very closely with the amount of oxygen adsorbed. Adsorption was definitely chemical and probably, from our previous studies, dissociative (9–11).

III. RESULTS

A. Rates of Chemisorption. Oxygen chemisorption on the Graphon surface at ca. 100 millitorr starting pressure of oxygen at temperatures varying from −78° to 160°C is shown in Fig. 1. The curves show the usual characteristics of adsorption, namely, a rapid initial rate which quickly decelerates. Adsorption was measured for a period of 24 hr, but in the figure adsorption is shown only up to 700 min for the sake of clarity. Also for the sake of clarity, the number of data points shown in the plots is smaller, compared to the actual number observed during any one experiment. About 50 data points were taken for each experiment. The volume of the reactor system was sufficiently large that the decrease in pressure of the gas due to adsorption, during a run, does not result in a significant decrease in the adsorption rate. In all experiments, the maximum decrease in gas pressure was <5%.

Plots of oxygen adsorbed (q) versus log of time are presented in Fig. 2. These plots are discontinuous straight lines, indicating the existence of different kinetic stages. It is suggested that each of these kinetic stages corresponds to adsorption on a different group of active sites. It is noteworthy that these different stages appear after the adsorption of a definite amount of oxygen independent of the temperature at which the run is made (cf. Table I). These amounts are almost exactly equivalent to those obtained in experiments at 25°C at different starting

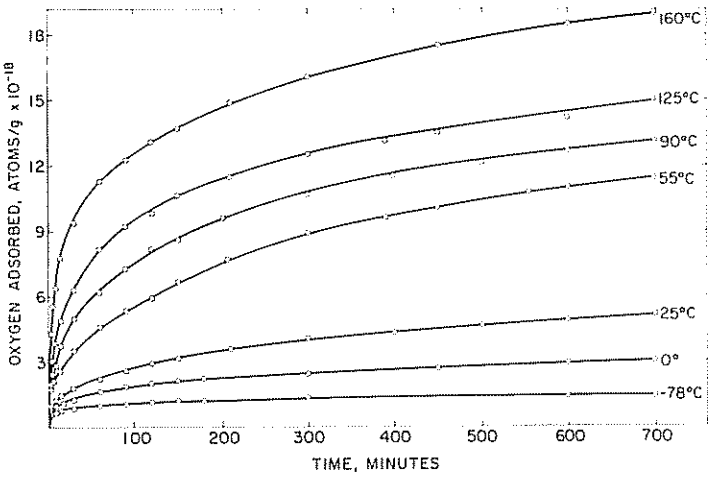

FIG. 1. Oxygen chemisorption on Graphon at 100 millitorr pressure and temperatures from −78° to 160°C. Graphon was previously activated in oxygen to 16.6% weight loss.

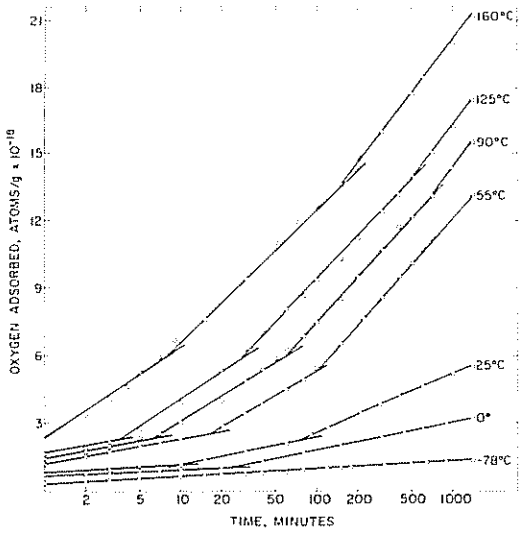

FIG. 2. Elovich plots of oxygen chemisorption on Graphon at 100 millitorr pressure and temperatures from −78° to 160°C. Graphon was previously activated in oxygen to 16.6% weight loss.

TABLE I

AMOUNTS OF OXYGEN CHEMISORBED BY GRAPHON IN DIFFERENT STAGES AT 100 MILLITORR PRESSURE AND AT DIFFERENT TEMPERATURES

Temperature (°C)	Oxygen chemisorbed in different stages (atoms/gm × 10^{-18})				
	I	II	III	IV	V[a]
−78	1.32	—	—	—	—
0	1.10	—	—	—	—
25	1.25	1.20	—	—	—
55	—	1.32	3.35	—	—
90	—	1.30	3.45	7.92	12.4
125	—	1.25	3.40	8.10	12.3
160	—	—	3.45	7.95	12.4
25[b]	1.25	1.40	3.45	8.00	11.3

[a] The amount of oxygen adsorbed on the fifth stage has been calculated by subtracting the total adsorbed in the first four stages from the saturation amount at 160°C, that is 26.3 × 10^{18} atoms/gm.

[b] These values are the average of the values obtained at 25°C at different pressures of oxygen (1).

pressures of oxygen (1). It is evident, therefore, that adsorption of oxygen proceeds at different rates on different groups of sites. Increased temperature has the same effect as increased pressure and simply results in an earlier appearance of any one kinetic stage. At low temperature, the rate of adsorption is slow and chemisorption on only the most active group of sites can be followed for times up to 1400 min. As the temperature is increased, adsorption on less active groups of sites can be followed. At 160°C, the rate of chemisorption is so rapid on the most active sites (groups 1 and 2) that complete coverage occurs in less than 1 min and cannot be conveniently followed.

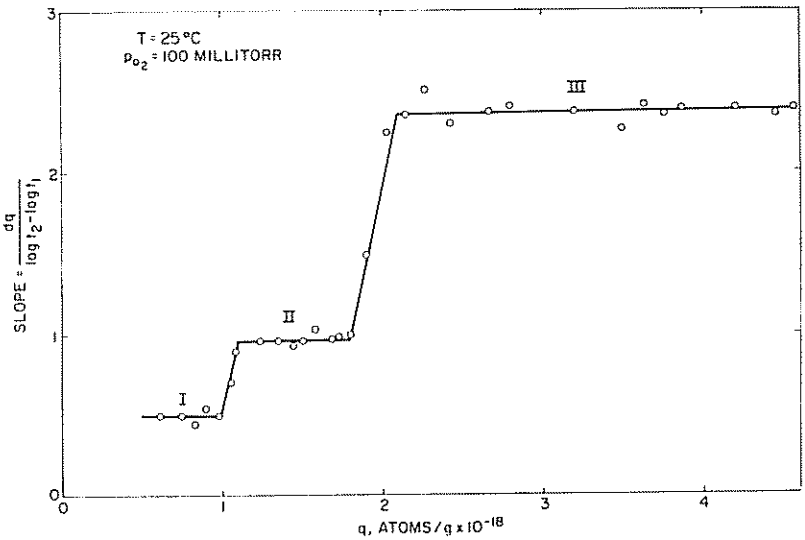

FIG. 3. Slopes of Elovich plots as a function of amount of oxygen adsorbed at 25°C

One of the reasons for studying adsorption down to −78°C was to see if there were more active sites on the Graphon surface than were previously observed at 25°C (1). For an oxygen pressure of 100 millitorr, the q-log t plot shows no break up to 1400 min, suggesting that adsorption of oxygen was going only on one type of site. When the oxygen pressure was decreased to 11 millitorr, adsorption was too slow to be followed accurately. As will be discussed shortly, we think that the adsorption we observed at 100 millitorr at −78°C was on the same sites which we called "most active" from our previous studies at 25°C (1).

In order further to verify that these q-log t plots are not continuous curves but do show linear regions, slopes were measured at each data point for the plots at 25°C and 125°C. The plots of the slope versus q are shown in Figs. 3 and 4. The slope changes only in a discontinuous manner, thus strongly supporting the existence of linear regions in the q-log t plots of the chemisorption data.

These results then further support the concept that there are different, discrete types of sites on the carbon surface on which chemisorption of oxygen can take place. In all, adsorption on five groups of active sites was observed.

B. Effect of Temperature on Parameters in Elovich Equation. In recent years many workers have found the Elovich equation to be applicable to their adsorption data on a wide variety of systems (15). The equation is

$$\frac{dq}{dt} = a_1 \exp(-\alpha q), \qquad [1]$$

where q is the amount adsorbed and a and α are constants. The integrated form of Eq. [1] is

$$q = \frac{1}{\alpha} \ln(1 + a\alpha t). \qquad [2]$$

If $a\alpha t$ is $\gg 1$, a plot of q versus ln t should be a straight line, as is observed in the present study, with a slope of $1/\alpha$. For each region at each temperature, values of α and a have been calculated from the data in Fig. 2. At the start of each new stage, q was taken as equal to zero and t was taken as $\rightarrow 0$. Values of α and a are presented in Table II.

It is seen that both a and α have different values for adsorption in different adsorption regions. However, in the same adsorption region a is strongly temperature dependent, whereas α is more or less independent of the adsorption temperature. The fact that α is independent of the adsorption temperature will be discussed later in the paper.

C. Activation Energy. In order to calculate activation energies from the present data,

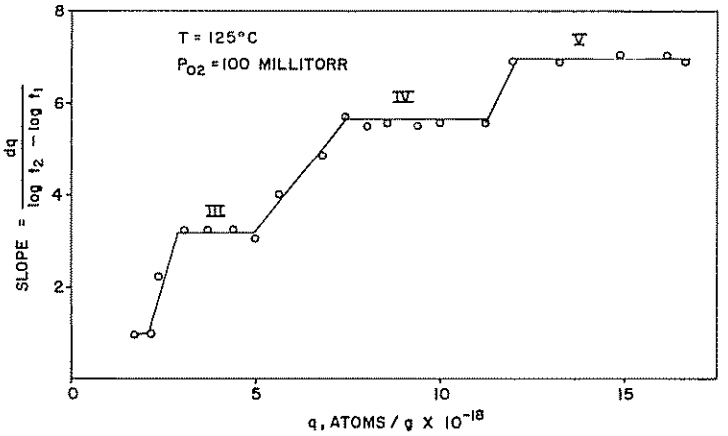

FIG. 4. Slopes of Elovich plots as a function of amount of oxygen adsorbed at 125°Cu

TABLE II

PARAMETERS IN THE ELOVICH EQUATION FOR ADSORPTION OF OXYGEN ON GRAPHON AT DIFFERENT STAGES AND TEMPERATURES

Temp (°C)	Stage I		Stage II		Stage III		Stage IV		Stage V	
	α*	a†	α	a	α	a	α	a	α	a
−78	5.47	0.26	—	—	—	—	—	—	—	—
0	5.11	2.40	2.35	0.020	—	—	—	—	—	—
25	4.90	4.44	2.30	0.060	0.75	0.014	—	—	—	—
55	—	—	2.19	0.17	0.74	0.051	0.43	0.007	—	—
90	—	—	2.05	0.52	0.68	0.19	0.42	0.034	0.35	0.003
125	—	—	2.00	1.20	0.64	0.52	0.41	0.13	0.35	0.013
160	—	—	—	—	0.64	1.30	0.42	0.37	0.34	0.048

* Atoms^{-1} gm × 10^{18}.

† Atoms gm^{-1} min^{-1} × 10^{-18}.

the instantaneous rates were calculated for adsorption on the various groups of sites at different amounts of surface coverages. The Arrhenius plots of the instantaneous rates for three surface coverages in each adsorption region are shown in Fig. 5. The plots show equal slope for adsorption in any one stage, indicating that the activation energy is independent of surface coverage in any one stage. On the other hand, the activation energy is clearly different for adsorption in different stages. This is shown in Fig. 6, where activation energy has been plotted against the amount of oxygen adsorbed. Overall the activation energy changes from 3.1 to 12.4 kcal/mole as chemisorption proceeded from Stage I through Stage V.

A constant activation energy in any one region is a direct result of the experimental observation that α is independent of adsorption temperature, as can be shown. The rate of adsorption (r) at any fixed value of q is given by the Elovich equation (written in log form) as

$$\ln r = \ln a - \alpha q. \qquad [3]$$

Differentiating Eq. [3] with respect to $1/T$ gives

$$\frac{d(\ln r)}{d(1/T)} = \frac{d \ln (a)}{d(1/T)} - q \frac{d(\alpha)}{d(1/T)} \qquad [4]$$

or

$$\frac{d(\ln r)}{d(1/T)} = -\frac{E_a}{R} - q \frac{d(\alpha)}{d(1/T)}, \qquad [5]$$

where E_0 is the initial activation energy. The activation energy is given by the Arrhenius equation (written in the log form) as

$$\ln r = \ln A - E/RT. \qquad [6]$$

Differentiating Eq. [6] with respect to $1/T$ gives

$$\frac{d(\ln r)}{d(1/T)} = -\frac{E}{R}. \qquad [7]$$

Equating Eqs. [5] and [7], we get

$$-\frac{E}{R} = -\frac{E_0}{R} - q\frac{d(\alpha)}{d(1/T)}. \qquad [8]$$

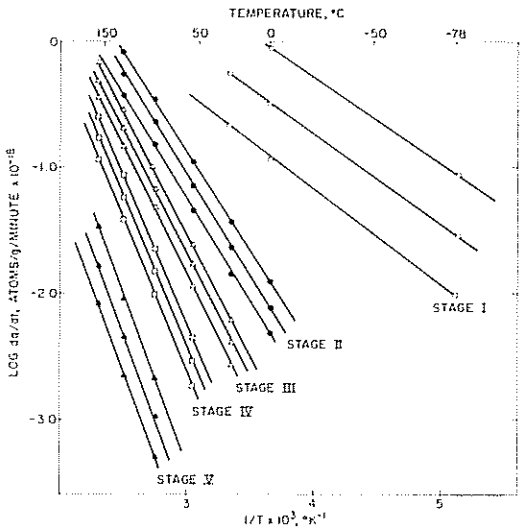

FIG. 5. Arrhenius plots of oxygen chemisorption rates in the various stages of adsorption on Graphon.

If α is independent of the adsorption temperature, then $qd(\alpha)/d(1/T) = 0$. Therefore, $E/R = E_0/R$ and $E = E_0$. The activation energy has a single value independent of surface coverage.

Normally when chemisorption results conform to the Elovich equation values of α decrease with adsorption temperature (15, 16), although there have been instances when α was independent of temperature (5, 16).

Taylor and Liang (17) and Low (15) have suggested caution in calculating activation energies from Elovich-type plots, especially when the plots show multiple adsorption stages. This is true for most of the chemisorption data when different temperature effects are detected for each kinetic stage. In such cases the ratio of α_1/α_2 for any two stages undergoes undulatory changes; and, therefore, the criteria used to determine activation energy do not correspond to comparable stages in the adsorption process. In the present case, however, the ratio α_1/α_2 remains almost the same at all temperatures. Thus the activation energy can be properly determined, since a given volume of gas is adsorbed on the same area at the various temperatures.

IV. DISCUSSION

It is to be emphasized we conclude that the chemisorption of oxygen on all five stages is dissociative. Previous studies in this laboratory, using O_2^{16-16} and O_2^{18-18}, have

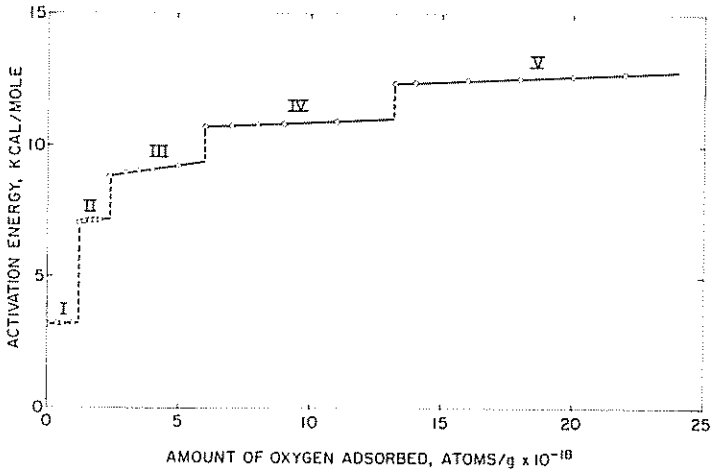

FIG. 6. Change of activation energy for oxygen chemisorption on Graphon with amount adsorbed

shown that when oxygen interacts with carbon both carbon monoxide and carbon dioxide are produced through an atomic oxygen intermediate (10). In the present study, molecular oxygen was never removed upon heating the Graphon containing adsorbed oxygen to an elevated temperature. The products recovered were always carbon monoxide and carbon dioxide—the former consisting of 90% of the total oxides of carbon removed.

The chemisorption of oxygen on carbon has been studied extensively in our laboratory in recent years. Hart and co-workers (9) studied the kinetics of chemisorption of oxygen on a cleaned Graphon surface at temperatures between 100° and 300°C and observed that chemisorption involved at least two types of sites. The activation energy for chemisorption on the more active sites was found to be 7.4 kcal/mole. This value is in close agreement with the activation energy found in this study for adsorption on the second most active group of sites (7.1 ± 0.2 kcal/mole). It appears, therefore, that the sites which they called most active correspond with our Stage II sites. There can be two reasons for this. Firstly, since the lowest pressure obtained by these workers during outgassing and surface cleaning was at least one order of magnitude higher than that obtained in this work, it is reasonable to believe that a significant fraction of the group I sites was covered when adsorption runs were commenced. Secondly, for the oxygen pressures used (1–15 millitorr) these workers studied chemisorption at temperatures higher than where adsorption on group I sites can be conveniently followed (see our Fig. 2).

Lussow and co-workers also studied the chemisorption of oxygen on Graphon between 300° and 625°C (11). In agreement with Hart and co-workers (9), they found a plateau in the amount of oxygen adsorbed in the temperature range 300°–400°C. However, they then found a progressive increase in chemisorption up to 550°C, which amounted to roughly three times that found between 300° and 400°C and also three times the maximum chemisorption reported by us in the first paper of this series for adsorption at 25°C and 760 torr pressure. Lussow and co-workers reported an activation energy of 29 kcal/mole for adsorption between 450° and 675°C. Above 400°C, significant gasification of carbon by oxygen occurs, concurrent with chemisorption. This work of Lussow and co-workers suggests that nascent sites, which are highly active for chemisorbing oxygen, are produced during gasification. At some rate, some of these carbon sites become less active because of surface diffusion (18) and/or hybridization to a divalent state (19).

Differences in activation energy of adsorption on the various groups of active sites can be attributed to differences in the geometric arrangement of the surface carbon atoms. The basal plane of carbon is, ideally, terminated with the carbon atoms in either a $(10\bar{1}0)$ or $11\bar{2}0)$ configuration (20). The carbon-carbon distances of importance, for forming a carbon-oxygen activated complex, are 1.42, 2.46, and 2.84Å. However, an oxygen molecule could also approach the surface with its bond essentially parallel to the c-axis of the graphite crystallites and form an activated complex with carbon atoms in adjacent layer planes. In this case, carbon-carbon distances of importance are 3.35 and 3.62Å. Also the basal plane need not be terminated in an ideal manner but can have carbon fragments protruding from it. This will present other carbon-carbon spacings to the incoming oxygen molecule.

The activated complex formed between O_2 and two surface carbon atoms would be expected to have different potential energy configurations, dependent upon the spacings between the carbon atoms. Thus, the activation energy for the dissociative chemisorption of oxygen would be expected to vary. In fact, Sherman and Eyring (21) have shown, theoretically, that the activation energy for dissociative chemisorption of H_2 on carbon will vary with the carbon-carbon spacings. However, no attempt appears to have been made to estimate theoretically the activation energy of oxygen chemisorption on graphite.

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 with that calculated from theoretical models. The experimental value of the entropy change to form the activated complex can be calculated from the experimental pre-exponential factor (A_{exp}) of the Arrhenius plot by using the usual equation

$$A_{exp} = \frac{kT}{h} \exp\left(\Delta S_T^{0\ddagger}/R\right) \qquad [9]$$

as discussed at length by Walker and coworkers (6). The entropy changes ($\Delta S_T^{0\ddagger}$) calculated for adsorption on the various groups of active sites are −46.6, −49.6, −50.1, −50.8, and −54.6 eu, respectively.

The entropy change, if all three degrees of translational freedom are lost in forming the activated complex, is given by the equation (22)

$${}_3S_T^0 = R \ln (M^{3/2}T^{5/2}) - 2.30 \qquad [10]$$

The entropy change at 160°C would be −38.2 eu. The change in entropy if both degrees of rotational freedom are lost is given by the equation (23)

$$S_r^0 = \ln I + \ln T + 88.59, \qquad [11]$$

where I is the moment of inertia of the molecule. This entropy change is −11.2 eu. Comparison of the experimental and theoretical entropy changes suggests that the transition state complex is immobile and has lost between one and two degrees of rotational freedom depending upon the particular adsorption stage.

In conclusion, we find that a carbon surface very active to oxygen can be obtained under the conditions used in this research. Chemisorption on ultraclean carbon surfaces is of considerable fundamental importance in understanding the behavior of these surfaces towards different gaseous species. These studies are also of importance in understanding the origin of the gas contents in carbon and graphite artifacts when they are heated to elevated temperatures. Further work on the adsorption of other gaseous species such as H_2, CO and N_2 is in progress. The influence of various treatments, such as the degree and type of carbon burn-off, irradiation and boron doping, on the chemisorption of oxygen and other gaseous species is also being studied.

ACKNOWLEDGMENTS

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REFERENCES

1. Walker, P. L., Jr., Bansal, R. C., and Vastola, F. J., "The Structure and Chemistry of Solid Surfaces," p. 81. John Wiley, New York, 1969.
2. Bonnetain, L., Duval, X., and Letort, M., *Proc. 4th Carbon Conf.*, p. 107 (1960).
3. Bonnetain, L., *J. Chim. Phys.* **56**, 266 (1959).
4. Dietz, V. R., and McFarlane, E. F., *Proc. 5th Carbon Conf.* **2**, 219 (1963).
5. Allardice, D. J., *Carbon* **4**, 255 (1966).
6. Walker, P. L., Jr., Austin, L. G., and Tietjen, J. J., "Chemistry and Physics of Carbon," Vol. 1, pp. 327–365. Marcel Dekker, New York, 1966.
7. Carpenter, D. L., and Giddings, D. G., *Fuel* **43**, 375 (1964).
8. Carpenter, D. L., and Sergeant, G. D., *Fuel* **45**, 311 (1966).
9. Hart, P. J., Vastola, F. J., and Walker, P. L., Jr., *Carbon* **5**, 363 (1967).
10. Walker, P. L., Jr., Vastola, F. J., and Hart, P. J., "Fundamentals of Gas-Surface Interactions," p. 307. Academic Press, New York, 1967.
11. Lussow, R. O., Vastola, F. J., and Walker, P. L., Jr., *Carbon* **5**, 591 (1967).
12. Sevenster, P. G., *Fuel* **40**, 7 (1961).
13. Emmett, P. H., and Brunauer, S., *J. Am. Chem. Soc.* **56**, 35 (1934).
14. Laine, N. R., Vastola, F. J., and Walker, P. L., Jr., *J. Phys. Chem.* **67**, 2030 (1963).
15. Low, M. J. D., *Chem. Rev.* **60**, 267 (1960).
16. Taylor, H. A., and Thon, N., *J. Am. Chem. Soc.* **74**, 4169 (1952).
17. Taylor, H. S., and Liang, S. C., *J. Am. Chem. Soc.* **69**, 1306 (1947).
18. Boulangier, F., Duval, X., and Letort, M., *Proc. 3rd Carbon Conf.*, p. 257 (1959).
19. Coulson, C. A., *Proc. 4th Carbon Conf.*, p. 215 (1960).
20. Thomas, J. M., "Chemistry and Physics of Carbon," Vol. 1, p. 129. Marcel Dekker, New York, 1966.
21. Sherman, A., and Eyring, H., *J. Am. Chem. Soc.* **54**, 2661 (1932).
22. Hayward, D. O., and Trapnell, B. M. W., "Chemisorption," p. 298. Butterworths, London, 1964.
23. Glasstone, S., "Thermodynamics for Chemists," p. 195. Van Nostrand, New York, 1957.