

A STUDY OF CARBON-OXYGEN SURFACE COMPLEXES USING O¹⁸ AS A TRACER*

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Abstract—Upon the reaction of carbon with O₂, three products form: CO, CO₂, and a carbon-oxygen surface complex. The CO and CO₂ are produced through two paths: (1) via a fleeting oxygen surface intermediate and (2) via the breakdown of an oxygen surface complex. O₂¹⁶⁻¹⁶ and O₂¹⁸⁻¹⁸ were used in this study to ascertain the extent to which the breakdown of the surface complex contributes to the formation of CO and CO₂ during the combustion of Graphon at temperatures between 505 and 555°C. The rate of complex breakdown to CO and CO₂ is a function of the total rate of carbon gasification, the fraction of active surface area covered with complex, and the reaction temperature through a participation factor. The fraction of the total CO and CO₂ produced which is contributed by complex breakdown decreases with increasing combustion temperature. In a complementary study, again using O₂¹⁶⁻¹⁶ and O₂¹⁸⁻¹⁸, it was shown that the ease of oxygen complex desorption from the surface of Graphon is independent of its time of information.

1. INTRODUCTION

MANY workers have been concerned with the nature of carbon-oxygen surface complexes and the kinetics of their formation from O₂.⁽¹⁻⁴⁾ The presence of these surface complexes drastically affect the chemical behavior of carbon surfaces to gases and liquids.⁽⁵⁻⁷⁾

Recently it has been shown that carbon-oxygen surface complexes play a significant role in the combustion of carbon, when this combustion occurs at relatively low temperatures.^(8, 9) That is, upon combustion three products are formed: gaseous CO, gaseous CO₂ and a carbon-oxygen complex. The complex builds up on the active sites of the carbon undergoing combustion, resulting in a decrease in reaction rate.^(8, 9) Most recent studies⁽⁹⁾ have shown that meaningful rate constants (*k*) for the combustion of Graphon in the temperature range 575-675°C can be obtained if the rate is given by $k(P_{O_2})(ASA)(1-\theta)$, where ASA is the active site area and θ is the fraction of

the ASA covered with complex. In this kinetic expression, two significant conditions are taken as operative: (1) The rate is proportional to the ASA unoccupied by oxygen surface complex. (2) The contribution of the oxygen surface complex to the production of gaseous CO and CO₂ (by desorption) is insignificant. That is, the majority of the gaseous products comes from a fleeting carbon-oxygen surface intermediate. The amount of this intermediate on the carbon surface at any time is immeasurably small.

This paper is concerned with the further examination of the above conditions by the direct measurement of the contribution which the stable carbon-oxygen surface complex makes to the total amount of gaseous CO and CO₂ produced by the combustion of carbon. This study is made possible by the use of both O₂¹⁶⁻¹⁶ and O₂¹⁸⁻¹⁸.

2. EXPERIMENTAL

2.1 Materials used

The carbon used in this investigation was Graphon, which was produced by the heat treatment of the channel black, Spheron 6, to 2800°C in the absence of oxidizing gases. The original Graphon has a very low ASA.⁽⁹⁾ Since a relatively

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large area was desirable in this study, the original material was preoxidized at 650°C at an oxygen pressure of 0.50 torr to 14.4 per cent burn-off. Oxidation of the original Graphon to this burn-off increased the BET surface area (calculated from N₂ adsorption at 77°K) from 76 to 98 m²/g and the ASA (calculated from O₂ chemisorption at 300°C) from 0.22 to 2.2 m²/g.⁽⁹⁾ Following this substantial burn-off, there was a negligible increase in the ASA with the small, additional amounts of oxidation resulting from the present study. Prior to each combustion run, the preoxidized Graphon samples were outgassed at 930°C *in vacuo* (*ca.* 10⁻⁵ torr) for 3 hr to effectively remove all of the stable carbon-oxygen complex formed during prior oxidation at 650°C.

The O₂ enriched in O¹⁸ was obtained from the Weizman Institute of Science, Rehovoth, Israel. This oxygen contained 98.4 atomic per cent O¹⁸ (96.8 mole per cent O₂¹⁸⁻¹⁸), 0.6 atomic per cent O¹⁷ and 1.0 atomic per cent O¹⁶. The normal O₂ used contained 99.76 atomic per cent O¹⁶.

2.2 Apparatus

The reactivity apparatus was simple in design. The Graphon sample was held in a 10 mm dia. by 60 mm long Vycor test tube which rested on the bottom of a 2 cm dia. by 35 cm long Vycor reactor tube. The volume of the reactor system was 0.93 l. The reactor was in turn connected to a reservoir having a volume of 5.0 l. During a run, the reactor was heated by a resistance furnace, with a temperature held to ±1°C by an automatic temperature controller. The entire apparatus was directly connected through a molecular-flow leak to the analyser tube of a modified General Electric mass spectrometer. Since the gaseous products to be analysed were CO, O₂ and CO₂ with both O¹⁶ and O¹⁸ present, the masses of concern were: 28-CO¹⁶, 30-CO¹⁸, 32-O₂¹⁶⁻¹⁶, 34-O₂¹⁶⁻¹⁸, 36-O₂¹⁸⁻¹⁸, 44-CO₂¹⁶⁻¹⁶, 46-CO₂¹⁶⁻¹⁸ and 48-CO₂¹⁸⁻¹⁸.

3. RESULTS AND DISCUSSION

3.1 Desorption of the stable carbon-oxygen surface complex

Prior to investigating the role which the carbon-oxygen surface complex plays in the combustion of Graphon, it was necessary to study the desorption of the complex in the absence of combustion. As has been reported previously,⁽⁸⁻¹⁰⁾ the kinetics of complex release obeys the Elovich equation. This

indicates an increasing activation energy for complex removal, as the amount of coverage of the surface with complex decreases. This change of desorption activation energy with surface coverage can be caused by surface heterogeneity^(11, 12) and/or by induced heterogeneity.^(13, 14) Indeed, surface heterogeneity does not necessarily produce a changing desorption activation energy. It depends upon whether the prior adsorption is mobile or immobile.⁽¹⁵⁾ Be that as it may, we were concerned as to whether the changing desorption activation energy also meant that the oxygen complex which went on the Graphon surface first was the most strongly held and consequently the last to be desorbed as CO or CO₂. If, in fact, this was the case it would not be possible to use O¹⁸ in conjunction with O¹⁶ to measure the role of the carbon-oxygen surface complex in combustion, as will be obvious shortly.

To label the complex with respect to its time of formation, a 0.10 g Graphon sample was heated to 280°C and exposed to O₂¹⁶⁻¹⁶ at a pressure of 0.49 torr for a period of 2.5 hr. At the end of this exposure, the system was evacuated for 45 min at 280°C. Prior studies have shown that subsequent evacuation at the temperature of complex formation results in the removal of a negligible amount of complex.⁽⁹⁾ The Graphon was now exposed to O₂¹⁸⁻¹⁸ at a pressure of 0.44 torr for a period of 6 hr. Following each exposure period, the residual gas contained <1 mole per cent CO and CO₂, indicating a very low combustion rate of O₂ with Graphon at 280°C, as expected from previous studies.⁽⁹⁾ The total exposure time at 280°C (8.5 hr) was sufficient, however, to essentially saturate the active surface of the Graphon with an oxygen complex.

The complex formed in this two-step exposure was removed in increments by heating the Graphon at a series of temperatures between 280 and 880°C. About 90 per cent of the complex was recovered as CO; and, therefore, Table 1 gives only the cumulative amount of each isotopic species of CO removed, following outgassing up to and including selected temperatures. The isotopic distribution in the CO₂ was the same as that found for the CO. It is seen that the concentration of CO¹⁸ in the carbon monoxide of the decomposition products is *ca.* 23 mole per cent throughout the entire outgassing range, indicating that the time of formation

TABLE 1. ISOTOPIC DISTRIBUTION OF CO IN OUTGASSING PRODUCT FOLLOWING INITIAL TWO-STEP REACTION OF GRAPHON WITH O₂¹⁶⁻¹⁸ AND O₂¹⁸⁻¹⁸

Temperature (°C)	Pressure (torr × 10 ³)		Mole %, CO ¹⁸
	CO ¹⁶	CO ¹⁸	
400	0.72	0.23	24.2
500	2.60	0.77	22.9
600	6.02	1.66	21.6
700	13.7	4.35	24.1
800	21.1	6.25	22.8
900	24.0	6.95	22.5

of the surface complex at 280°C had little effect upon the temperature (its activation energy) of removal.

3.2 Combustion of Graphon

To find the contribution of the surface complex to the production of gaseous CO and CO₂ during the combustion of Graphon, reactions were conducted between 505 and 555°C. First, samples were exposed to initial O₂¹⁸⁻¹⁸ pressures of *ca.* 0.05 torr in order to cover a fraction of the ASA with oxygen complex. From the decrease in O₂¹⁸⁻¹⁸ pressure and the increase in CO¹⁸ and CO₂¹⁸⁻¹⁸ pressures, the amount of O¹⁸ complex formed could be calculated by difference. Following evacuation at reaction temperatures to remove O₂¹⁸⁻¹⁸ and the gaseous products, the samples were exposed to O₂¹⁶⁻¹⁶ at an initial pressure of *ca.* 0.05 torr. The decrease in O₂¹⁶⁻¹⁶ pressure and the build-up in CO and CO₂ pressures were followed continuously during reaction. Following reaction with O₂¹⁶⁻¹⁶, the reaction system was evacuated and the samples

were outgassed up to 880°C, in temperature increments, to remove the oxygen complex.

Table 2 summarizes the results of the runs. It should be noted that run #5 was conducted with a Graphon sample previously oxidized to 20.8 per cent burn-off (ASA of 2.6 m²/g).⁽⁹⁾ It was desirable to explore the effect of the extent of surface heterogeneity on the contribution of the oxygen complex to the gaseous products formed during combustion.

As discussed previously,⁽⁹⁾ the oxygen complex builds up on the carbon surface during reaction, approaching a saturation amount. The saturation amount progressively decreases (and covers a smaller percentage of the ASA) with increasing reaction temperature. For the runs in Table 2, saturation coverage with O¹⁸ complex had not been reached in any case, prior to reaction with O₂¹⁶⁻¹⁶. In fact, in run #4 surface coverage with O¹⁸ was less than 50 per cent of saturation coverage, as will be seen shortly.

Results in Table 2 show that portions of O¹⁸ complex were removed in each run during reaction of the Graphon with O₂¹⁶⁻¹⁶. The results are

TABLE 2. RESULTS ON REACTION BETWEEN O₂¹⁶⁻¹⁶ AND GRAPHON SURFACES WHICH ORIGINALLY CONTAINED SOME O¹⁸ COMPLEX

Run #	Temp. (°C)	Duration of exposure to O ¹⁸ (hr)	Duration of exposure to O ¹⁶ (hr)	II	% of initial O ¹⁸ complex removed during exposure to O ₂ ¹⁶⁻¹⁶	Mole % O ¹⁸ in final complex
1	505	2	1	0.483	5.9	76.0
2	530	2	1	0.421	10.5	76.8
3	530	3½	1	0.433	6.9	82.8
4	555	¼	1½	0.371	51.2	20.6
5*	555	2	1½	0.368	16.0	63.4

*Graphon sample used had 20.8% burn-off.

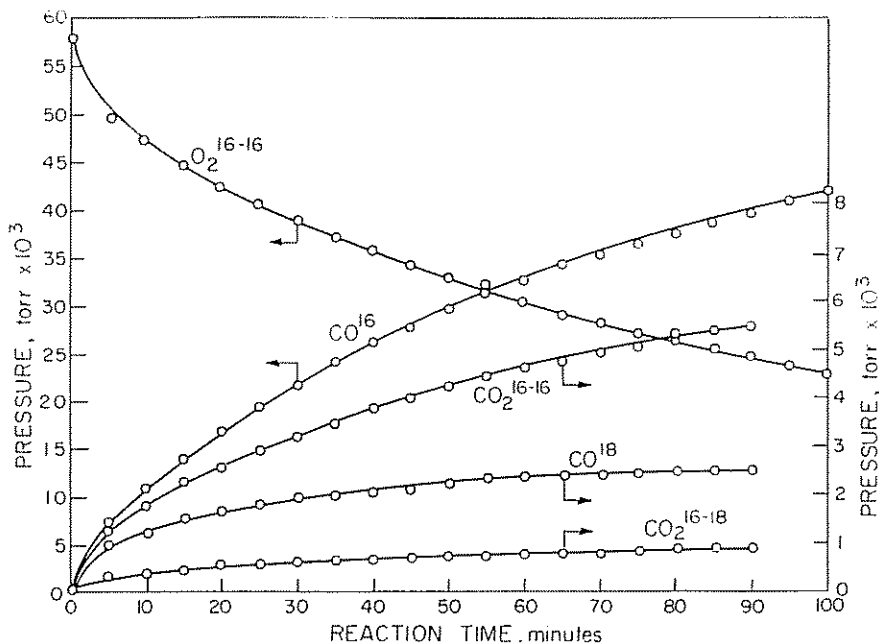


Fig. 1. Typical reaction between O_2^{16-16} and Graphon, which had a fraction of its ASA covered with O^{18} complex (run #4 at $555^\circ C$).

expanded upon in Figs. 1 and 2, for run #4. From Fig. 1, it is seen that the O^{18} complex which left the Graphon surface ended up as both CO^{18} and CO_2^{16-18} . CO_2^{18-18} was observed only when the complex was essentially all O^{18} , and then it was only a very minor part of the product gas. The results for CO_2 production are thought to be of particular significance. That is, there has been considerable controversy as to whether CO_2 is a primary product of the combustion of carbon. Workers in this laboratory have recently concluded that CO_2 is a primary product.^(8, 9) One of the main possibilities given for the secondary production of CO_2 is the reaction of CO with oxygen complex.* Results in Fig. 1 show that, even though some CO_2 may be coming from this reaction, it is not the primary source of CO_2 . That is, in the early stages of the

*At $555^\circ C$ the equilibrium constant $[CO][C(O)]/[CO_2][C_f]$, has a value of 4×10^{-3} , where $C(O)$ is the occupied ASA and C_f is the free ASA¹⁶. Since $C(O)/C_f$ is *ca.* 1, or greater, during the O_2^{16-16} reaction, CO/CO_2 is not greater than 4×10^{-3} . Therefore, equilibrium favors the reaction $CO + C(O) \rightarrow CO_2 + C_f$ under the present conditions.

reaction of Graphon with O_2^{16-16} most of the complex on the surface is O^{18} . Despite this fact, the rate of production of CO_2^{16-16} considerably exceeds the rate of production of CO_2^{16-18} in the early stages of reaction.

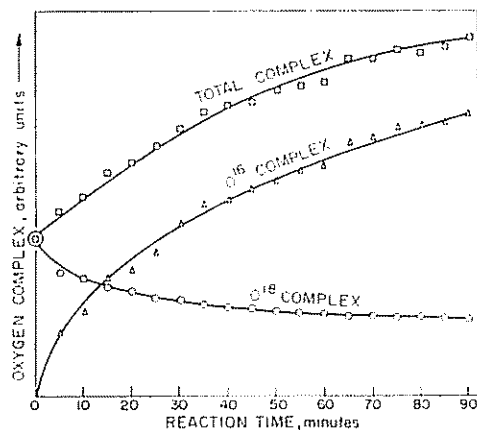


Fig. 2. Change in amount and composition of surface-oxygen complex during reaction between O_2^{16-16} and Graphon which originally had a fraction of its ASA covered with O^{18} (run #4 at $555^\circ C$).

The possibility of the exchange reaction, $\text{CO}^{16} + \text{C(O)}^{18} \rightleftharpoons \text{CO}^{18} + \text{C(O)}^{16}$, affecting the product gas composition was examined. An O¹⁸ complex was formed at 555°C from O₂¹⁸⁻¹⁸, and the reaction volume was then evacuated. CO¹⁶, at a pressure of 0.05 torr, was introduced; and the CO¹⁶ and CO¹⁸ concentrations were monitored for 2 hr. No exchange could be detected. Exchange in the reaction, $\text{CO}_2^{16-16} + \text{C(O)}^{18} \rightleftharpoons \text{CO}_2^{16-18} + \text{C(O)}^{16}$, is also a possibility. However, since the amount of CO₂ obtained was only ca. 15 per cent of the total gas produced, this reaction was not examined at this time. In any case, in the early stages of reaction between Graphon and O₂¹⁶⁻¹⁶ exchange would proceed to the right, increasing the amount of CO₂¹⁶⁻¹⁸. Therefore, our previous argument on the relative unimportance of the reaction, $\text{CO} + \text{C(O)} \rightarrow \text{CO}_2 + \text{C}_f$, in producing CO₂ is still valid.

Figure 2 shows the build-up in oxygen complex on the Graphon surface in run #4 and the change in its composition during reaction with O₂¹⁶⁻¹⁶. The amount of O¹⁸ complex falls continuously with reaction; however, the total amount of complex builds up toward saturation coverage since the net rate of O¹⁶ complex build-up exceeds the rate of O¹⁸ complex removal.

Qualitatively, it can be seen from Fig. 2 that the rate of removal of O¹⁸ complex is not solely proportional to the amount of O¹⁸ complex on the surface. Further, if the activation energy for the removal of complex were to decrease with increasing coverage because of induced heterogeneity, the rate of O¹⁸ complex removal would go through a maximum with increasing reaction time in O₂¹⁶⁻¹⁶. This is seen to not be the case. Rather the rate of O¹⁸ complex removal is given by

$$\frac{d(\text{O}_{\text{rem}}^{18})}{dt} = \Pi(\theta^{18}) \frac{d(\text{C}_g)}{dt}, \quad (1)$$

where θ^{18} is the fraction of ASA covered with O¹⁸, $d(\text{C}_g)/dt$ is the rate of total carbon gasified (including that from complex decomposition) and Π is a participation factor (that is, a factor reflecting the participation of the complex in producing gaseous CO and CO₂). If we choose small increments of carbon gasified, $(\Delta\text{C}_g)_i$, we can calculate the corresponding increment of O¹⁸ complex removed, $(\Delta\text{O}_{\text{rem}}^{18})_i$, and the average θ^{18} , $(\bar{\theta}^{18})_i$, for the incre-

ment. Equation (1) can now be written in the form (time independent)

$$(\Delta\text{O}_{\text{rem}}^{18})_i = \Pi(\bar{\theta}^{18})_i(\Delta\text{C}_g)_i. \quad (2)$$

From equation (2) it is seen that a plot of $\Sigma_i(\Delta\text{O}_{\text{rem}}^{18})_i/(\bar{\theta}^{18})_i$ versus $\Sigma_i(\Delta\text{C}_g)_i$ should be a straight line of slope Π . Figure 3 shows a typical plot obtained from the experimental data for run #4. A straight line is obtained of slope 0.371. The other runs listed in Table 2 also gave straight line plots for the reaction of Graphon with O₂¹⁶⁻¹⁶. The values of the slopes are reported in Table 2.

Before examining further the implications and significance of the participation factor Π , it is desirable to consider the results of outgassing the complex following reaction in O₂¹⁶⁻¹⁶. Figures for the mole per cent O¹⁸ in the final complex are given in Table 2. As found previously upon outgassing the complex formed at 280°C, the ratio of O¹⁸ to O¹⁶ in the CO and CO₂ recovered was independent of degassing temperature up to 880°C. This result takes on added importance in this case, however, since there was some gasification of carbon between the time the O¹⁸ complex was placed on the surface and the residual complex containing O¹⁸ and O¹⁶ was removed by outgassing. It might have been thought that progressive alteration of the surface through gasification would have produced a dependency between the time of complex formation and its ease of removal.

On the basis of the above result, it appears reasonable to extend the interpretation of Π to include removal of both the O¹⁸ and O¹⁶ complex from the surface during combustion. That is, from Fig. 3 Π has the units of O¹⁸ removed from the complex per carbon atom gasified per fraction of ASA covered with O¹⁸ complex. If the ease of removal of complex is taken to be independent of the time of its formation, the units of Π can then be taken as O¹⁸ + O¹⁶ removed from the complex per carbon atom gasified per fraction of ASA covered with O¹⁸ + O¹⁶ (or total) complex.

The amount of complex removed per carbon atom gasified is seen to be a function of temperature as well as coverage. At this time, it is not understood why the participation factor for complex removal is a function of combustion temperature. The relationship is plotted in Fig. 4 for the three reaction temperatures studied for coverages between zero and one (of course, maxi-

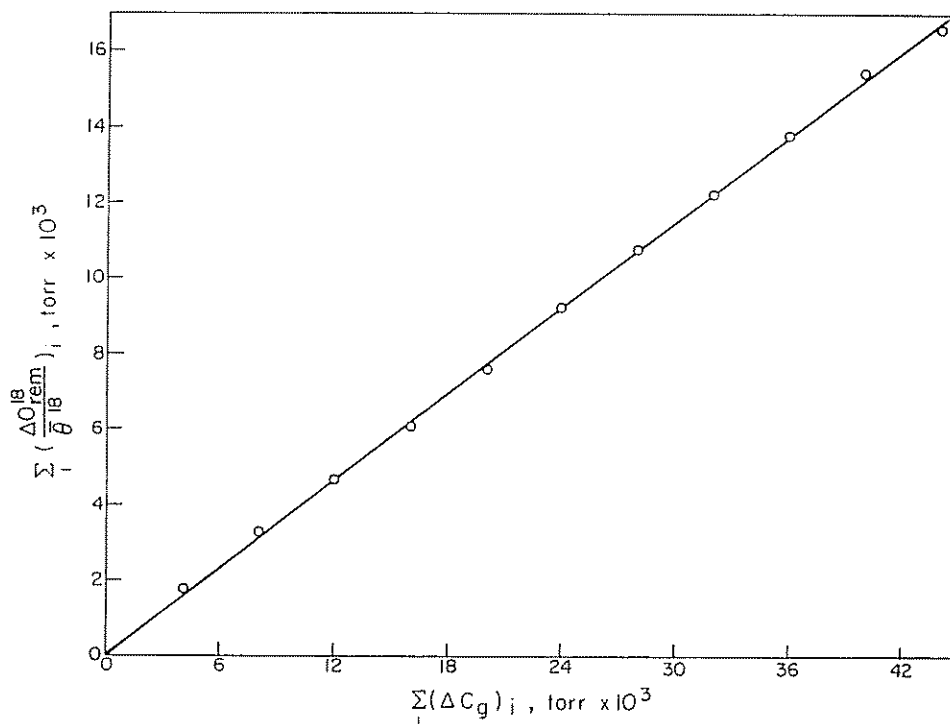


FIG. 3. Plot of equation (2) for run #4.

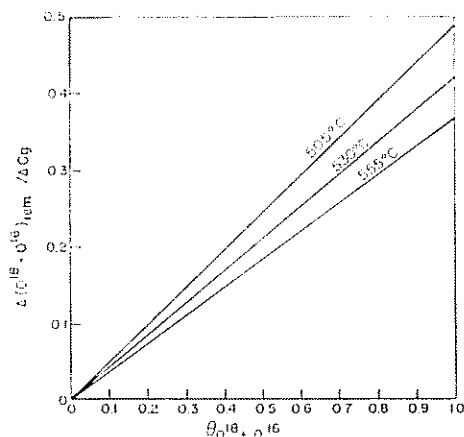


FIG. 4. Atoms of oxygen complex removed per atom of carbon gasified as a function of reaction temperature and ASA covered with complex.

num coverage at these temperatures is less than one). With increasing reaction temperature and at saturation coverage, the amount of complex removed per carbon atom gasified decreases both

because of a decrease in Π and because of a decrease in saturation complex coverage.

It is now obvious that the rate of carbon gasification is given by the sum of two terms. That is

$$\frac{-d(C_g)}{dt} = k_c(P_{O_2})(ASA)(1-\theta) - \Pi(\theta) \frac{d(C_g)}{dt} \quad (3)$$

where the first term is the carbon gasified through a fleeting carbon-oxygen surface intermediate, as previously discussed,⁽⁹⁾ and the second term is the carbon gasified by breakdown of the carbon-oxygen complex. In the second term the atoms of carbon gasified are equated to the atoms of oxygen complex removed since most of the product gas is CO. Equation (3) can be rearranged to give

$$\frac{-d(C_g)}{dt} = \frac{k_c(P_{O_2})(ASA)(1-\theta)}{[1-\Pi(\theta)]} \quad (4)$$

Let us consider the reaction between O_2 and Graphon at 625°C, since it was previously shown⁽⁹⁾ that the kinetics of this reaction are reasonably well approximated by taking into account only the

first term on the right-hand side of equation (3). One typical result shown was the variation in kc with reaction time for the 14.4 per cent burn-off sample. Between a reaction time of 6 and 30 min, kc increased more or less monotonically from 4.9 to 6.9. From a linear extrapolation of the Π versus temperature results in this paper, $\Pi = 0.207$ at 625°C. At 6 and 30 min, the θ values are *ca.* 0.25 and 0.76, respectively. Some of the increase in kc with increasing reaction time then can be attributed to previously ignoring the fact that $[1 - (\Pi\theta)]$ decreases with increasing reaction time (or that the complex is contributing to the reaction products).

Values of kc were also calculated for Graphon samples with burn-offs from 3.3 to 34.9 per cent from rate data in the region where the surfaces had closely reached saturation coverage. They were found to be essentially independent of burn-off. Considering that Π has been found in this paper to be independent of burn-off for the 14.4 and 20.8 per cent reacted samples and that θ at saturation coverage only varies from 0.68 to 0.81 at 625°C over the burn-off range studied,⁽⁹⁾ the essential constancy of kc appears reasonable. The kc values are high, however, by about 20 per cent.

As discussed previously, the kinetics of desorption of oxygen complexes on carbon obey the Elovich equation, indicating an increasing activation energy with decreasing surface coverage. It is of interest that the ease of breakdown of the complex to gaseous products during the combustion of Graphon is not dependent upon the extent of complex coverage of the surface. That is, Π is independent of θ , which is shown very well in Fig. 3 for run #4. At the beginning of the reaction

of the Graphon sample with O₂¹⁶⁻¹⁶ in this run, complex coverage was less than 50 per cent of saturation coverage. Despite the fact that the coverage continued to increase during the reaction with O₂¹⁶⁻¹⁶ (as seen in Fig. 2), the line drawn through the data in Fig. 3 is of constant slope throughout the run. The authors plan to examine this phenomenon more completely.

REFERENCES

1. LOEBENSTEIN W. V. and DEITZ V. R., *J. Phys. Chem.* **59**, 481 (1955).
2. SMITH R. N., DUFFIELD J., PIEROTTI R. A. and MOOI J., *J. Phys. Chem.* **60**, 495 (1956).
3. SMITH R. N., *Quart. Rev. (Lond.)* **13**, 287 (1959).
4. CULVER R. V. and WATTS H., *Rev. Pure Appl. Chem. (Aust.)* **10**, 95 (1960).
5. HARKER H., JACKSON C. and WYNNE-JONES W. F. K., *Proc. Roy. Soc. (London)* **262A**, 328 (1961).
6. HALLUM J. V. and DRUSHEL H. V., *J. Phys. Chem.* **62**, 110 (1958).
7. STUDEBAKER M. L., *Rubber Chem. Technol.* **30**, 1400 (1957).
8. LAINE N. R., VASTOLA F. J. and WALKER P. L., JR., *Proceedings of the Fifth Carbon Conference*, Vol. 2, p. 211. Pergamon Press, Oxford (1963).
9. LAINE N. R., VASTOLA F. J. and WALKER P. L., JR., *J. Phys. Chem.* **67**, 2030 (1963).
10. BONNETAIN L., *J. Chim. Phys.* **58**, 34 (1961).
11. ROGINSKII S. Z. and TODOS O., *Acta Physicochim. SSSR* **21**, 519 (1946).
12. KUMMER J. T. and EMMETT P. H., *J. Am. Chem. Soc.* **73**, 2886 (1951).
13. BOUDART M., *J. Am. Chem. Soc.* **74**, 1531 (1952).
14. BOUDART, M., *J. Am. Chem. Soc.* **74**, 3556 (1952).
15. TRAPNELL B. M. W., *Chemisorption*. Butterworths, London (1955).
16. TONGE B. L., *Proceedings of the Fourth Carbon Conference*, p. 87. Pergamon Press, Oxford (1960).