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C-O Completes

THE ROLE OF THE SURFACE COMPLEX IN THE CARBON-OXYGEN REACTION*†

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Oxygen reacts with carbon to form CO, CO₂, and a carbon-oxygen surface complex. The use of mass spectrometric techniques permits a study of this reaction at low pressures by continuously monitoring the O₂, CO, and CO₂ concentrations. Complex coverages as low as 0.02% of the BET surface area of a carbon can be measured. For this investigation Graphon, previously oxidized to 14.4% burnoff, was reacted in a static system between 300° and 675°C with O₂ at initial pressures ranging from 30 to 500 μ Hg. The Graphon was outgassed at 950°C, *in vacuo*, prior to each run. The surface complex increases during the course of a reaction until a "saturation" coverage is reached; the saturation coverage decreases with increasing temperature. The complex constituting the saturation coverage is stable at the reaction temperature even under high vacuum. To decompose the complex, the carbon must be heated above the reaction temperature. The complex decomposes into CO and CO₂, with *ca.* 95% being recovered following outgassing at 950°C. The amount of complex formed in a low temperature oxidation was used as a measure of the active site area of the Graphon.

I. INTRODUCTION

It is well known that a stable surface complex, in addition to gas-phase CO and CO₂, is formed during the carbon-oxygen reaction¹⁻³. This stable complex can be removed as the oxides of carbon by heating the carbon to temperatures higher than the temperature of complex formation. It was found that this complex is formed upon only a small fraction of the total surface, that is upon the active site area at which the reaction occurs. Because the complex is formed upon this active site area and removes it from the reaction, the complex influences the production of gas-phase CO and CO₂. Until recently, techniques were not available to measure the active site area and to determine the amount of coverage by complex during a

reaction. Therefore, no quantitative measurements of the effect of the surface complex upon the carbon-oxygen reaction have been made.

In this investigation of the carbon-oxygen reaction, particular attention was paid to the role of the surface complex. The surface complex was used to determine the total active surface area and the active surface area unoccupied by complex at any time during a reaction. The effect of the complex build-up upon the reaction order, rates of O₂ depletion and product formation, and the CO-CO₂ product ratio was determined.

II. EXPERIMENTAL

The carbon material used in this investigation was Graphon, which was produced by the heat treatment of the channel black, Spheron-6, to 2800°C. Graphon was chosen because it has a high degree of surface homogeneity, as indicated by numerous adsorption studies⁴⁻⁷. Work done by Gra-

* Based on portions of a Ph.D thesis submitted by N. R. Laine to the Graduate School of the Pennsylvania State University, June, 1962.

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¹ T. Rhead and R. Wheeler, *J. Chem. Soc.* **103**, 461 (1913).

² I. Langmuir, *J. Amer. Chem. Soc.* **37**, 1139 (1915).

M. Shah, *J. Chem. Soc.* **1929**, 2661 (1929).

⁴ D. Graham, *J. Phys. Chem.* **57**, 665 (1953).

⁵ R. A. Beebe and D. M. Young, *J. Phys. Chem.* **58**, 93 (1954).

⁶ D. Graham, *J. Phys. Chem.* **60**, 1022 (1956).

⁷ E. L. Pace, *J. Chem. Phys.* **27**, 1341 (1957).

ham⁸ indicates that the Graphon surface has 1.25% high energy sites (active surface area). However, in the present investigation it was found that the active surface area of Graphon varied depending upon the amount of oxidation which the sample had undergone. The active surface area of the original Graphon was found to increase appreciably for small amounts of burnoffs (ca. 0.1%). By contrast, the active surface area of a sample which had previously been oxidized to 14.4% burnoff remained relatively constant for small amounts of additional burnoff. Thus, a sample previously oxidized to 14.4% burnoff was used in this investigation. This sample had a BET surface area of 98 m²/g. Sample weights of 0.0500 g and 0.1000 g were used. The samples were heated at 950°C, *in vacuo*, for 3 hr before each run in order to remove essentially all of surface complex which may have been present.

The reaction was carried out in the temperature range 575–675°C and at initial O₂ pressures of 30–40 μ Hg. Some adsorption studies were made at 300°C and at an O₂ pressure of 500 μ Hg. A CEC Type 21-611 mass spectrometer was used to determine the concentrations of reactant and product gases. The reactor system (15.5*l*) was connected directly to the inlet leak of the mass spectrometer analyzer tube. The experimental setup was the same as that previously described⁹. The O₂ used in this investigation and purchased from the Matheson Corp., was an extra dry grade. Mass spectrometer analysis showed that the O₂ had a purity of 99.9% with the major impurity being N₂.

III. RESULTS

A. Typical Reaction

Figure 1 illustrates the course of a typical reaction at 625°C. These curves depict the

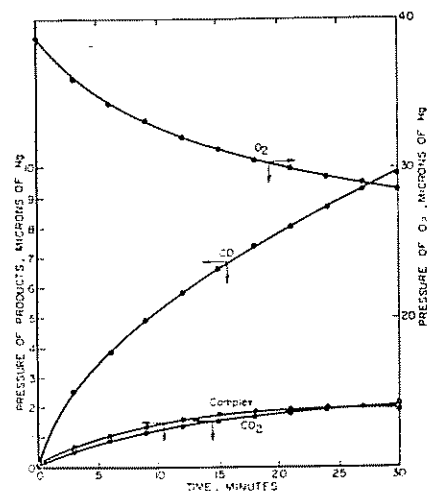
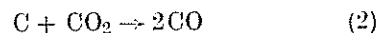


FIG. 1. Typical reaction between Graphon and oxygen at 625°C.

depletion of O₂ and the formation of CO, CO₂, and a stable complex. The partial pressures of the gases were measured directly by the mass spectrometer, while the amount of stable surface complex formed was calculated by an oxygen material balance. The total amount of complex formed was also determined by heating, *in vacuo*, at 950°C at the end of each reaction run and measuring the amount of gases evolved¹⁰.

B. Primary Products

Both CO and CO₂ were found to be primary products of the reaction. This was determined in the following manner. Carbon monoxide can be produced by (1) the direct oxidation of carbon, or (2) the reduction of CO₂ by carbon.



¹⁰ From outgassing results at temperatures above 950°C, it was found that ca. 95% of the total complex formed at reaction temperature up to 675°C was removed at 950°C. Higher outgassing temperatures were not used in this study because of the concern that surface annealing would change the active surface area¹¹.

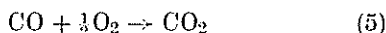
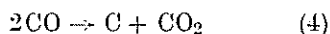
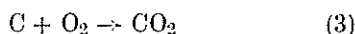
¹¹ F. Boulanger, X. Duval, and M. Letort, *Proc. Third Carbon Conf.*, Pergamon Press (1959), p. 2

⁸ D. Graham, *J. Phys. Chem.* 61, 1310 (1957).

⁹ F. J. Vastola and P. L. Walker, Jr., *J. Chim. Phys.* 58, 20 (1961).

The CO produced by (1) is defined as a primary product, while that produced by (2) is defined as a secondary product. Accordingly, to determine whether CO was a primary or secondary product, the reactivity of CO₂ with Graphon was studied at 775°C. At this temperature, in a period of time in which an equal amount of O₂ would have been essentially reacted, less than 2% of the CO₂ reacted to form CO. This indicates that CO is a primary product.

Carbon dioxide can be produced by (3) the direct oxidation of carbon, (4) the disproportionation of CO, or (5) the oxidation of CO. The CO₂ produced by



reaction (3) is defined as a primary product, while that produced by reactions (4) and (5) is defined as a secondary product. Reaction (4) was disregarded, because it is considerably slower than reaction (2), at the temperatures and pressures used in this investigation¹². That reaction (5) did not occur at a significant rate was shown by exposing Graphon to equal pressures of CO and O₂ at 625° and 775°C. At 625°C there was no increase in the amount of CO₂ produced, while at 775°C there was only a 10% increase. This indicates that CO₂ is also a primary product of the carbon-oxygen reaction.

C. Reaction Kinetics

Figure 2 presents semi-log plots of O₂ pressure vs. time for reaction temperatures of 575, 625 and 675°C. A 0.1000 g sample was used. Where linear, a first order reaction in O₂ depletion is operative. At all reaction temperatures investigated, it is seen that the plots are not linear over the entire reaction period.

First order rate constants, k_{O_2}' , were

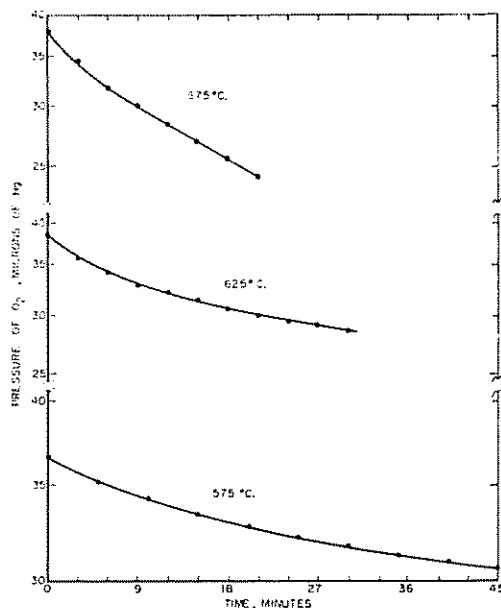


FIG. 2. First-order plot of $\log P_{\text{O}_2}$ vs. time for 3 reaction temperatures.

calculated from Eq. (1), where $-dP_{\text{O}_2}/dt$ is the rate of O₂ pressure decrease and A is the total BET surface area

$$\frac{-dP_{\text{O}_2}}{dt} = k_{\text{O}_2}'(P_{\text{O}_2}')(A) \quad (1)$$

of the Graphon in square meters. Table I

TABLE I

Variation of the Rate Constant for Oxygen Depletion over the Course of the Graphon-Oxygen Reaction at Three Temperatures

Time, min	575°C		625°C		675°C	
	$k_{\text{O}_2}' \times 10^6$, m ² /sec	Time	k_{O_2}'	Time	k_{O_2}'	Time
5	13.5		43.5	3	53.0	
10	10.1		25.7	6	40.8	
15	8.1		20.2	9	36.0	
20	6.4		16.2	12	32.4	
25	5.8		13.8	15	30.2	
30	5.1		12.8	18	31.2	
35	3.8		11.6	21	31.2	
40	3.6		10.3			
45	3.3		9.1			
			9.4			

¹² F. J. Vastola, Ph.D. Thesis, The Pennsylvania State University, January, 1959.

lists the values of k_{O_2}' for different reaction times and temperatures. At 575°C, k_{O_2}' appears to be just reaching a constant value at the end of the run; at 625 and 675°C, a constant k_{O_2}' is essentially attained before the completion of the reaction. The same behavior was found for the first order rate constants for the formation of gas-phase CO and CO₂. Similar results were found when the 0.0500 g sample of Graphon was reacted.

D. Product Ratios

The product ratios are given in Table II

TABLE II

Ratio of Carbon Monoxide to Carbon Dioxide in Product Gases Upon Oxidation of Graphon at Different Temperatures

Sample wt, g	Temp, °C	CO/CO ₂
0.0500	575	3.2
0.0500	625	4.8
0.0500	675	6.3
0.1000	575	3.4
0.1000	625	5.4
0.1000	675	6.3

for different reaction conditions. At each selected reaction condition, the product ratio was found to remain constant during the course of a reaction.

E. Active Surface Area

The amount of surface complex formed at saturation coverage increased with decreasing temperature of its formation. Also the lower the reaction temperature, the less the carbon burnoff which occurred during complex formation. However, as the temperature was decreased the time required to reach saturation coverage increased. Therefore, in order to estimate the maximum amount of complex which could be formed, Graphon was exposed to O₂ at the lowest temperature where the rate of complex formation was sufficiently rapid to be satisfactorily measured. In this investigation, the amount of complex formed at 300°C in a 24 hr period with an initial O₂ pressure of 500 μ Hg was taken as the maximum amount of complex which could be formed on the Graphon surface. Only a negligible amount of complex was formed after 24 hr and this was mostly due to activation of the Graphon surface. The amount of complex present on the surface was determined by outgassing the Graphon sample at 950°C. Figure 3 shows the cumulative evolution of gaseous products. Upon heating to 950°C both CO and CO₂ are evolved. Upon outgassing the complexes formed at various reaction temperatures, it was found that the percentage of CO₂ in the gaseous products decreases with increas-

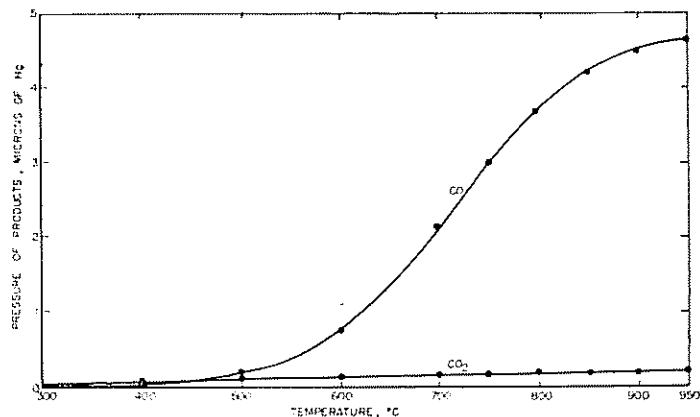


FIG. 3. Gaseous products recovered from Graphon upon heating to 950°C. Graphon previously saturated with oxygen complex at 300°C.

ing formation temperature. However, even for a complex formed at 300°C, the total amount of CO₂ in the outgassing products is relatively small. The evolution of CO₂ virtually ceases above 700°C, whereas CO is evolved up to the final outgassing temperature.

The total active surface area was obtained in the following manner. The outgassing products were converted to equivalent oxygen atom concentration. The assumption was made that the complex consists of one oxygen atom per edge carbon atom. Further, it was assumed that the edge carbon atoms lie in the (100) plane; that is, each carbon atom occupies an area of 8.3 Å².

At reaction temperatures of 575, 625, and 675°C, the amount of active surface area covered at any instant was calculated from the amount of complex on the surface at that instant. At the end of a reaction run, the amount of active surface area covered was further confirmed by decomposing the complex at 950°C.

For the particular Graphon sample used, the total active surface area was found to be 2.3% of the BET surface area. From 73 to 78% of the active surface area was covered by complex at the reaction temperatures used, the higher reaction temperature giving the lower coverage.

IV. DISCUSSION

A. Reaction Kinetics

The reaction rate constants given in Table I were calculated on the basis of the total BET surface area of the Graphon sample. However, the rate constants should be calculated on the basis of unoccupied active surface area. Equation (1), used to calculate k_{O_2}' , may be written as

$$\frac{-dP_{O_2}}{dt} = k_{O_2}(1 - \theta)P_{O_2} \quad (2)$$

where I is the total active surface area and θ

is the fraction of active surface area occupied by complex at any time in a reaction. Therefore, $(1 - \theta)$ is the fraction of the total active surface area which is unoccupied by complex and available for reaction. It should be noted that θ will equal 1 only at saturation at 300°C, which was the temperature at which the total active surface area was estimated. At the reaction temperatures used in this investigation, θ leveled off at some fraction less than 1 at saturation. Because the unoccupied active site area can be measured at any time during a reaction, k_{O_2} can be determined.

It is clear now why the first-order plots in Fig. 2 only became linear at longer reaction times. While the surface complex was building up, $(1 - \theta)$ was decreasing; therefore changing the slope of the plots. Following saturation and the attainment of a constant $(1 - \theta)$, the plots would become linear for a first-order reaction.

Equation (2) was used to recalculate the values of k_{O_2}' given in Table I. The corrected values are given in Table III, for the 0.1000 g

TABLE III

Rate Constants for Oxygen Depletion Calculated on the Basis of Unoccupied Active Surface Area

Time, min	575°C	625°C		675°C	
	$k_{O_2} \times 10^3$, m ² /sec	Time	k_{O_2}	Time	k_{O_2}
5	0.57	3	2.2	3	3.0
10	0.50	6	1.6	6	3.3
15	0.44	9	1.6	9	3.9
20	0.41	12	1.5	12	4.5
25	0.43	15	1.5	15	4.8
30	0.45	18	1.6	18	5.2
35	0.52	21	1.6	21	5.1
40	0.49	24	1.6		
45	0.51	27	1.5		
		30	1.6		

sample. The corrected values calculated for the 575 and 625°C reactions are relatively constant. The variations in these values are

TABLE IV

Rate Constants and Activation Energies for the Reaction of Oxygen with Graphon

Sample wt, g	Temp, °C	$\times 10^3, \text{m}^{-2} \text{sec}^{-1}$				kcal/mole	
		k_{O_2}	k_{CO_2}	k_{CO}	k_{C}	E_{O_2}	E_{C}
0.0500	575	0.46	0.09	0.36	0.45		
0.0500	625	1.5	0.30	1.7	2.0	36	45
0.0500	675	4.9	0.70	6.7	7.4	40	44
0.1000	575	0.51	0.09	0.39	0.48		
0.1000	625	1.6	0.27	1.7	2.0	35	43
0.1000	675	5.1	0.70	7.0	7.7	39	46

thought to be caused by the difficulty of determining the amount of complex formed during a reaction. However, the uniformity of the values of k_{O_2} for reaction temperatures of 575 and 625°C suggests that the approach used is valid. At 675°C, however, the corrected value increased initially until it reached a relatively constant value. Thus, it appears that at 675°C, the unoccupied active surface area is no longer the only factor affecting the reaction rates. The probable reason for this is that the complex is no longer truly stable, but acts as an intermediate in the production of CO and CO₂ as well as being a reaction product itself. It can be seen in Fig. 3 that at 675°C the complex is decomposing rapidly. At the saturation point, an equilibrium is reached between the chemisorption of O₂ and the desorption of complex so that the corrected value for the rate constant of oxygen depletion will attain a steady value. Vastola, Hart, and Walker¹³ have studied the complex with the use of the O¹⁸ isotope and found that even at 575°C some "stable complex" is evolved and fresh oxygen chemisorbs to take its place. From the results given in Table III, it appears that the rate, at which this takes place, becomes appreciable at 675°C.

¹³ F. J. Vastola, P. Hart, and P. L. Walker, Jr., The Study of Carbon-Oxygen Surface Complexes Using O¹⁸ as a Tracer, Preprints of the Fuel Chemistry Division of the American Chemical Society, March 1962.

Rate constants for CO and CO₂ formation and carbon burnoff have also been calculated on the basis of unoccupied active surface areas. Table IV lists values of the four rate constants for the different sample sizes and temperatures. These values were all taken at the end of the runs where the unoccupied site area is known most accurately from out-gassing data. The activation energies of O₂ depletion and carbon burnoff found in the temperature ranges 575–625°C and 625–675°C are also given. The fact that the specific reaction rates were independent of sample size indicates that the reaction was in the chemical control zone¹⁴.

B. Product Ratios

The product ratios (Table II) were constant throughout the course of the reactions. The decrease in unoccupied active surface area affected both CO and CO₂ production equally. However, it was found that the product ratio increased on going from samples with low, total active surface area (original Graphon) to samples with high total active surface area¹⁵. This change in product ratio with change in significant amounts of surface activation possibly is responsible for the

¹⁴ P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin, *Advances in Catalysis*, Academic Press New York, pp. 133–221 (1959).

¹⁵ N. R. Laine, P. L. Walker, Jr., and F. J. Vastola, unpublished work.

divergence in product ratios reported in the literature¹⁶⁻¹⁹.

V. SUMMARY

These results serve to show the importance of the surface complex in the carbon-oxygen reaction. The surface complex, can be used to calculate the unoccupied active surface area throughout the course of a reaction. The unoccupied active surface area must be known in order to calculate appropriate rate constants and other kinetic data which describe the carbon-oxygen reaction.

¹⁶ J. R. Arthur, *Trans. Faraday Soc.* **47**, 164 (1951).

¹⁷ M. Rossberg, *Z. Elektrochem.* **60**, 952 (1956).

¹⁸ R. J. Day, P. L. Walker, Jr., and C. C. Wright, *Industrial Carbon and Graphite Soc. of Chem. Industry* London, p. 348 (1958).

¹⁹ E. Wicke, *Fifth Symposium on Combustion*, Reinhold, New York, p. 255 (1955).

