

THE STUDY OF CARBON-OXYGEN SURFACE COMPLEXES USING O^{18} AS A TRACER*

F. J. Vastola, P. J. Hart, and P. L. Walker, Jr.

Department of Fuel Technology, The Pennsylvania State University
University Park, Pennsylvania

When O_2 reacts with carbon, CO and CO_2 are the gaseous reaction products. However, not all of the O_2 consumed appears in the form of these products. Some of the oxygen remains chemically bound to the carbon surface in the form of an oxygen surface-complex. To define the mechanism of the carbon-oxygen reaction, the nature of this complex must be more fully understood. For the investigation of the role of these complexes, techniques have been developed whereby the reaction can be studied using low O_2 gas pressures in conjunction with relatively high carbon surface areas^{1,2}. Under these conditions, the effect of the formation of a given amount of surface complex is greatly magnified.

In studying the reaction between Graphon and O_2 in the pressure region below 0.1 Torr,³ it has been found that only a small fraction of the total BET surface area of the Graphon is capable of chemisorbing oxygen (less than 2%)². The extent of this chemisorbing area is dependent upon the pretreatment of the Graphon sample and reaction temperature. A fraction of the O_2 consumed continuously goes into this chemisorbed surface complex until the complex coverage reaches a "saturation" value. After saturation is reached, most of the reacting O_2 appears in the form of gaseous reaction products. The complex thus formed is stable in that it will remain on the carbon surface, at reaction temperature, in vacuo (ca. 10^{-5} Torr). To remove this surface complex, it is necessary to heat the carbon to temperatures greater than the reaction temperature. Upon heating of the carbon to a selected higher temperature, the complex decomposes into CO and CO_2 ; the rate of this decomposition decaying from an initially large value to an immeasurably low value.

Among the points in question concerning the behavior of the surface complex, some can be answered by the use of isotopic tracer techniques. In particular, this investigation was undertaken to clarify two main points - (1) the importance of the oxygen surface complex as an intermediate in the conversion of O_2 to CO and (2) the possible relation between the time of formation of the complex and its ease of removal upon outgassing at higher temperatures following reaction.

EXPERIMENTAL

Materials Used - The carbon used in this investigation was Graphon, which was produced by the heat treatment of the channel black, Spheron 6³, to 2800°C. Since the surface capable of chemisorbing oxygen increases rapidly with small amounts of oxidation in the low burn-off region, the samples were preoxidized at 650°C. at an O_2 pressure of 0.5 Torr to 14.4% burn-off. Oxidation of the original Graphon to this burn-off increased the BET surface area from 76 to 98 m.²/g. Following this substantial amount of burn-off, there was a negligible change in active surface area

*Results of research supported by the National Science Foundation on Grant 6023.

** 1 Torr = 1 mm of mercury.

with the small, additional amounts of oxidation resulting from the present study. The preoxidized Graphon samples were outgassed at 950°C. in vacuo (ca. 10^{-5} Torr) for 3 hrs. prior to each run.

The O_2 enriched in O^{18} was obtained from the Weizman Institute of Science, Rehovoth, Israel. This oxygen contained 98.4 atomic % O^{18} (96.8 mole % O_2^{18-18}), 0.6 atomic % O^{17} , and 1.0 atomic % O^{16} .

Apparatus - Figure 1 shows the apparatus used in this investigation. The Graphon sample is placed in a 10 by 60 mm. Vycor test tube which rests in the bottom of a 2 by 35 cm. Vycor reactor. The volume of the reactor system is 0.79 l.; the reservoir has a volume of 4.9 l. The reactor is evacuated by a diffusion pump. McLeod and thermocouple gages are used for pressure measurements. The reactor is heated by a resistance furnace, with furnace temperature regulated by an automatic temperature recorder-controller. The entire apparatus is directly connected through a molecular-flow leak to the analyzer tube of a modified General Electric mass spectrometer. Since the gaseous products to be analyzed are CO, O_2 , and CO_2 with both O^{16} and O^{18} present, the masses of concern are: 28- CO^{16} , 30- CO^{18} , 32- O_2^{16-16} , 34- O_2^{16-18} , 36- O_2^{18-18} , 44- CO_2^{16-16} , 46- CO_2^{16-18} , and 48- CO_2^{18-18} .

RESULTS

To label the complex with respect to time of formation, a 0.100 g. Graphon sample was heated to 300°C. and exposed to O_2^{16-16} at a pressure of 0.490 Torr for a period of 2.5 hrs. At the end of this exposure, the O_2^{16-16} was removed and replaced with O_2^{18-18} (96.8 mole % O_2^{18-18}) at a pressure of 0.435 Torr for a period of 6 hrs. Table I gives the analysis of the gas present after the two oxidation periods. The species O_2^{16-18} and O_2^{17-18} are a consequence of the O^{16} and O^{17} in the original O^{18} sample.

TABLE I
ANALYSIS OF OXYGEN AFTER EXPOSURE TO GRAPHON AT 300°C.

Species	2.5 hr. Exposure (O_2^{16-16}) Concentration, mole %	6 hr. Exposure (O_2^{18-18}) Concentration, mole %
O_2^{16-16}	98.1	0.01
O_2^{16-18}	-	1.27
O_2^{17-18}	-	1.10
O_2^{18-18}	-	95.6
CO^{16}	1.58	0.09
CO^{18}	-	1.52
CO_2^{16-16}	0.38	-
CO_2^{18-18}	-	0.32

The complex formed in this two-step reaction was removed in increments by heating the carbon at a series of temperatures between 300 and 900°C. Most of the complex was recovered as CO. Table II gives the cumulative amount of each isotopic species of CO removed, following outgassing up to and including selected temperatures.

TABLE II
ISOTOPIC DISTRIBUTION OF CO IN OUTGASSING PRODUCT FOLLOWING
INITIAL TWO-STEP REACTION OF GRAPHON WITH OXYGEN AT 300°C.

<u>Temp., °C.</u>	<u>Press., Torr x 10³</u>		<u>Mole %, CO¹⁸</u>
	<u>CO¹⁶</u>	<u>CO¹⁸</u>	
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

To determine the role played by the surface complex in the carbon-oxygen reaction, the Graphon sample was then heated to 575°C. and reacted with O₂¹⁸⁻¹⁸ at a pressure of 0.032 Torr. After a period of 45 min., the reactor was evacuated and O₂¹⁶⁻¹⁶ at a pressure of 0.041 Torr was introduced. During the second reaction, the mass spectrometer monitored the partial pressures of O₂, CO¹⁶ and CO¹⁸. Table III gives the amount of CO¹⁶ and CO¹⁸ at various times of reaction. After 45 min., the reactor was evacuated and most of the complex that remained on the surface was removed by heating the Graphon to a temperature of 900°C. The CO resulting from the complex contained 53% CO¹⁸.

TABLE III
ISOTOPIC DISTRIBUTION OF CO PRODUCED DURING REACTION OF
O₂¹⁶⁻¹⁶ WITH GRAPHON AT 575°C.
IMMEDIATELY FOLLOWING REACTION OF O₂¹⁸⁻¹⁸ WITH GRAPHON AT 575°C.

<u>Time, min.</u>	<u>Pressure, Torr x 10³</u>		<u>Mole %, CO¹⁸</u>
	<u>CO¹⁶</u>	<u>CO¹⁸</u>	
5	0.55	0.02	3.5
10	0.98	0.07	6.7
15	1.33	0.12	8.6
20	1.70	0.18	9.6
25	2.06	0.23	10.0
30	2.39	0.28	10.5
35	2.62	0.32	10.9
40	2.86	0.35	10.9
45	3.09	0.38	11.0

DISCUSSION

At any given temperature, a certain amount of surface complex will remain on the carbon surface. This effect (a varying activation energy of desorption) could be due to the nature of the carbon surface or the extent of surface complex coverage. If the changing activation energy of desorption is due to the nature of the carbon surface, that is, if there is a distribution of site activity, one would expect the strong sites to be the first to chemisorb oxygen and to require the highest temperature to release the oxygen in the form of CO. However, if the activation

energy for desorption is a function of the amount of complex remaining on the surface at that particular moment, one would not expect to find a relationship between time of adsorption and temperature of desorption.

The results of the decomposition of the surface complex formed at 300°C., as given in Table II, support the latter reason for a changing activation energy of desorption with coverage. This complex was produced by first exposing the Graphon sample to O₂¹⁶⁻¹⁶ for a period of 2.5 hrs. and then O₂¹⁸⁻¹⁸ for 6 hrs. It is seen that the concentration of CO¹⁸ in the decomposition products is about 23 mole % throughout the entire outgassing period, indicating that the time of formation of the surface complex has little effect upon the temperature (its activation energy) of removal.

Table I gives the composition of the oxidizing gas at the end of a 2.5 hr. reaction period (O₂¹⁶⁻¹⁶) and a 6 hr. reaction period (O₂¹⁸⁻¹⁸). Even though there was a relatively large amount of O¹⁶ surface complex present during the time of the O₂¹⁸⁻¹⁸ exposure, a negligible amount of CO¹⁶ was produced. This indicates: (1) that the oxygen in the gaseous CO produced during the reaction of O₂ with Graphon came almost entirely from the O₂ reacting at that instant and not from oxygen which had previously gone into a surface complex and (2) that there was little carbon monoxide-complex interaction.

In the 575°C. reactions, the first run with O₂ produced an O¹⁸ complex. This complex was not removed prior to the O₂¹⁶⁻¹⁶ run. Since the O¹⁸ complex will behave in the same manner as the O¹⁶ complex, the amount of O¹⁸ appearing in the gas phase as CO¹⁸, during the O₂¹⁶⁻¹⁶ reaction, affords a direct measure of complex decomposition. Therefore, the amount of CO¹⁸ in the gas phase is an indication of the effectiveness of the complex as an intermediate in the reaction, eg.



Table III gives the concentration of CO¹⁸ in the products of the O₂¹⁶⁻¹⁶ reaction. It is seen that the contribution of CO¹⁸ to the product gases increases as the reaction proceeds. This result is contrary to what would be expected if CO was predominately being produced through reaction (2). If this were the case, the CO¹⁸ in the total CO produced would have been a maximum at the beginning of the reaction of Graphon with O₂¹⁶⁻¹⁶, when the O¹⁸ complex on the Graphon surface was at a maximum and the O¹⁶ complex was at a minimum. However, the increasing concentration of CO¹⁸ in the gas phase as the reaction proceeds indicates that the complex plays an increasingly important role in the production of CO. As the coverage of O¹⁶ complex increases (the O¹⁶ complex amounted to 47% of the total complex remaining after the O₂¹⁶⁻¹⁶ reaction), the activation energy of desorption of both the O¹⁶ and O¹⁸ complex becomes less. As a result, CO production by reaction 2 becomes significant.

At the end of the O₂¹⁶⁻¹⁶ reaction, most of the complex which had formed was removed by heating at 900°C. Throughout its removal, the CO¹⁸ concentration remained constant (53 mole %), again indicating no differentiation of the O¹⁸ and O¹⁶ complex as a result of its time of formation.

REFERENCES

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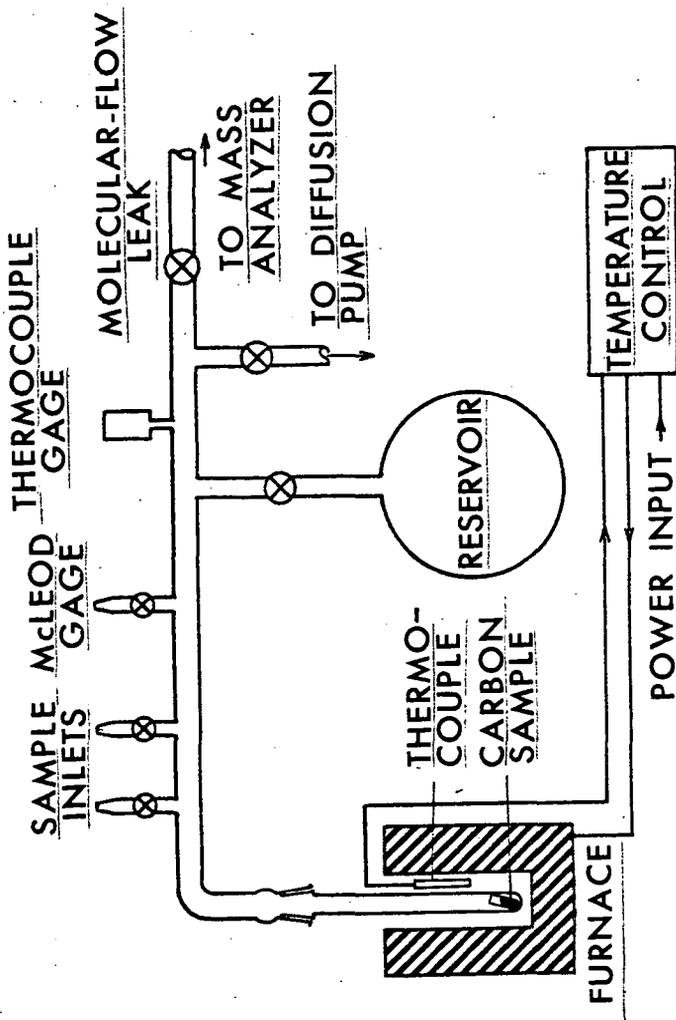


Figure 1. REACTOR