

# THE THERMAL DECOMPOSITION OF SURFACE OXIDES FORMED ON GRAPHON

ROGER PHILLIPS, F. J. VASTOLA and P. L. WALKER, Jr.

Department of Materials Science, Pennsylvania State University, University Park, Penna. 16802, U.S.A.

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**Abstract**—The thermal decomposition of surface oxides formed during the low pressure oxidation of Graphon was studied. Oxidation reactions were performed at 525°, 575° and 625°C in a static reactor, using initial O<sub>2</sub> pressures between 10 and 200 mtorr. The amount of surface oxide formed was found to increase with decreasing reaction temperature and increasing initial O<sub>2</sub> pressure. The surface oxides were decomposed by raising the temperature at 3°C per min up to 950°C in a closed system and measuring the partial pressures of the CO and CO<sub>2</sub> produced at frequent intervals. Each graph of accumulated CO against temperature consisted of a series of intersecting linear portions, suggesting that desorption was taking place from a number of discrete types of sites. The accumulated CO<sub>2</sub> measured was found to pass through a maximum at about 700°C, after which the partial pressure decreased due to the reaction of CO<sub>2</sub> with the Graphon surface. The rate of this secondary reaction was found to be strongly dependent on the rate of decomposition of the surface oxide, and it is suggested that decomposition of surface oxide leaves highly reactive 'nascent' sites on the Graphon surface at which CO<sub>2</sub> can react.

## 1. INTRODUCTION

It is well known that during the reaction of Graphon with oxygen a surface oxide is formed[1]. The amount formed is a function of reaction temperature, O<sub>2</sub> pressure, and degree of burn-off to which the Graphon sample has previously been subjected[2]. The thermal decomposition of the surface oxide yields a mixture of CO and CO<sub>2</sub>. Workers investigating the decomposition have normally carried out the desorption in a series of isothermal stages at successively higher temperatures[3, 4]. These isothermal desorptions have usually been found to obey the Elovich equation. Tucker and Mulcahy have concluded that the activation energy for desorption is a linear function of coverage [4].

The experiments which will be described in this paper were designed to determine the decomposition characteristics of surface

complexes formed on a Graphon sample of about 25 per cent burn-off as a function of the conditions of formation.

## 2. EXPERIMENTAL

### 2.1 Materials

The carbon used in this study was a sample of Spheron 6, a fine particle channel black supplied by the Cabot Corporation, Boston, Massachusetts, which had been graphitized by Dr. Lang of Commissariat à l'Énergie Atomique, Saclay, France, at a temperature of over 3000°C with the intention of obtaining an ultrapure carbon. Total ash content was found to be 25-35 ppm. The material is similar to the Graphon which has been used extensively in this laboratory, having been graphitized between 2700° and 2800°C. BET areas and X-ray diffraction patterns of the two materials were almost identical.

The O<sub>2</sub> used was research grade, supplied

by Air Products and Chemicals Co., Allentown, Pennsylvania. The major specified impurities were  $N_2$  (11 ppm), Ar (5 ppm), and water (0.76 ppm). The  $CO_2$  used was tank grade. Mass spectrometric analysis showed that it was better than 99.9 per cent pure, the only measurable impurities being traces of Ar and water.

## 2.2. Apparatus

The apparatus used was similar to that described previously[5]. The reaction system was constructed of Pyrex glass, except for the reaction tube which was double walled fused quartz. The annular volume enclosed by the double wall was evacuated to prevent diffusion into the reaction tube from the atmosphere at the highest temperatures used in this study. Glass stopcocks were lubricated with Apiezon 'H' grease. The total volume of the system was 19.3 l. The Graphon sample was placed in a fused quartz bucket which was suspended in the vertical reaction tube. The tube was heated by an electric furnace, the temperature of which was controlled by a Leeds and Northrup temperature controller, using a chromel-alumel thermocouple placed in close proximity to the sample. Ultimate evacuation of the system was by means of an 8 l/sec Ultek ionization pump which was capable of producing a measured vacuum approaching  $10^{-8}$  Torr.

The reaction system was connected to a General Electric mass spectrometer through a molecular leak. The mass spectrometer was used to monitor the partial pressures of the gaseous components in the reaction system during the reaction. The leak rate was very low and it was found unnecessary to correct for the small amount of gas lost through the leak.

## 2.3. Experimental procedure

All the experiments were performed on the same Graphon sample of which the original weight had been 0.300 g. The sample

had been oxidized to a weight loss of 24.2 per cent in a large number of small increments at temperatures ranging from 300° to 675°C and initial  $O_2$  pressures between 10 and 500 mTorr., prior to the beginning of these experiments.

Two variables for the formation of the surface oxide were considered, initial  $O_2$  pressure and temperature. Prior to each oxidation reaction, the surface of the sample was cleaned by heating for several hours at 950°C *in vacuo*. Reactions were then performed using the total volume of the reaction system (i.e. 19.3 l.); reaction temperatures of 525°, 575° and 625°C; and initial  $O_2$  pressures between 10 and 200 mTorr. These oxidation reactions were allowed to proceed until first order kinetics were well established, showing that surface oxide formation had reached a steady value. The system was evacuated to the background of the mass spectrometer (a process which took about 5 min) and then the temperature was allowed to fall to 400°C. The temperature was then raised at a rate of 3°C/min to 950°C, the sample being isolated from the pumping system at a temperature 25°C lower than the reaction temperature used to form the surface oxide, in a 6.3 l. volume connected to the mass spectrometer through the molecular leak. Previous work has shown that the surface oxide formed at a particular temperature decomposes only very slowly at temperatures below the formation temperature. It was, therefore, considered that during the rise in temperature no appreciable decomposition of surface oxide would take place until within a few degrees of the formation temperature. The purpose of the drop in temperature to 400°C was to allow an accurate rate of increase in temperature to be established before decomposition began. Measurement of the 28 ( $CO^+$ ) and the 44 ( $CO_2^+$ ) peaks were made every few degrees until 950°C was reached. The temperature was then maintained at 950°C for several hours to complete the decomposition of the oxide.

Analysis of the data from the first few experiments provoked an interest in the reaction of evolved  $\text{CO}_2$  with the Graphon surface. This reaction will hereafter be referred to as the 'secondary' reaction. Two reactions of  $\text{CO}_2$  on a clean Graphon surface in the 6.3 l. system were performed, using an increase in temperature of  $3^\circ\text{C}/\text{min}$  in one case and  $10^\circ\text{C}/\text{min}$  in the second. In both reactions the starting pressure was 2.27 mTorr., and the starting temperature was  $600^\circ\text{C}$ . Two surface oxide decompositions were performed using the faster heating rate, the first following oxide formation at  $525^\circ\text{C}$  and 50 mTorr. starting pressure

and the second following oxide formation at  $525^\circ\text{C}$  and 10 mTorr. starting pressure.

Each of the experiments caused a small increment of burn-off. Table 1 shows the experiments that were performed in chronological order. When all the experiments had been completed, the total burn-off had reached 28 per cent. The small increases which took place in the BET area and the active surface area are not considered to be of particular importance.

### 3. RESULTS AND DISCUSSION

#### 3.1 Evolution of CO

Figures 1, 2 and 3 show the evolution of

Table 1. Order of performing experiments

Experiment	Description	Condition	Initial pressure (mTorr.)
1	a	$625^\circ\text{C}$	10
2	b	$3^\circ\text{C}/\text{min}$	
3	a	$525^\circ\text{C}$	10
4	b	$3^\circ\text{C}/\text{min}$	
5	a	$525^\circ\text{C}$	50
6	b	$3^\circ\text{C}/\text{min}$	
7	a	$625^\circ\text{C}$	200
8	b	$3^\circ\text{C}/\text{min}$	
9	a	$625^\circ\text{C}$	50
10	b	$3^\circ\text{C}/\text{min}$	
11	a	$575^\circ\text{C}$	50
12	b	$3^\circ\text{C}/\text{min}$	
13	a	$525^\circ\text{C}$	100
14	b	$3^\circ\text{C}/\text{min}$	
15	a	$525^\circ\text{C}$	25
16	b	$3^\circ\text{C}/\text{min}$	
17	a	$525^\circ\text{C}$	50
18	b	$10^\circ\text{C}/\text{min}$	
19	a	$525^\circ\text{C}$	15
20	b	$3^\circ\text{C}/\text{min}$	
21	a	$525^\circ\text{C}$	10
22	b	$10^\circ\text{C}/\text{min}$	
23	c	$3^\circ\text{C}/\text{min}$	2.27
24	c	$10^\circ\text{C}/\text{min}$	2.27
25	a	$525^\circ\text{C}$	200
26	b	$3^\circ\text{C}/\text{min}$	
27	a	$525^\circ\text{C}$	50
28	b	$3^\circ\text{C}/\text{min}$	

a, Reaction with  $\text{O}_2$ .

b, Decomposition of surface oxide.

c, Reaction with  $\text{CO}_2$ .

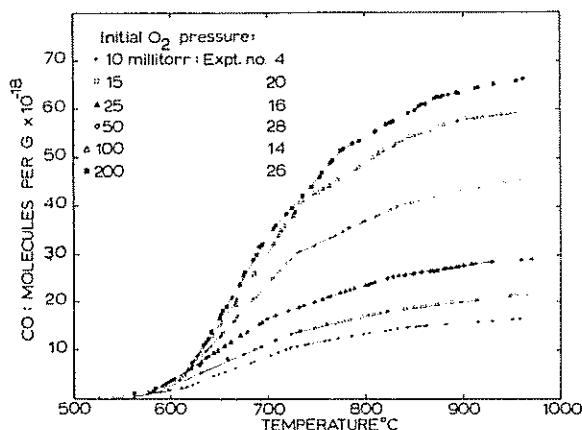


Fig. 1. Production of CO upon heating Graphon to 950°C at a heating rate of 3°C/min. Oxygen complex previously formed at 525°C using different initial O<sub>2</sub> pressures.

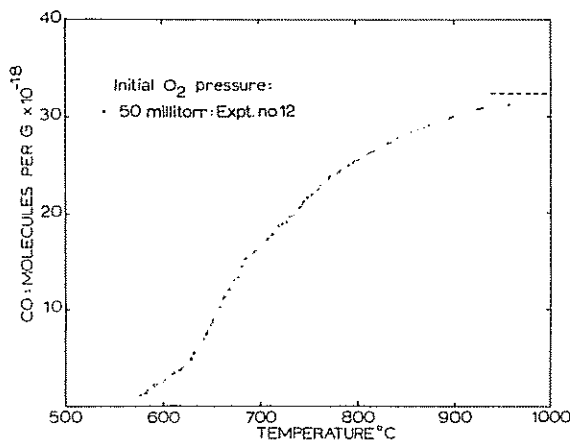


Fig. 2. Production of CO upon heating Graphon to 950°C at a heating rate of 3°C/min. Oxygen complex previously formed at 575°C.

CO from surface oxides formed at 525°, 575° and 625°C, respectively, at a heating rate of 3°C/min. These are the actual values measured. No attempt has been made to correct for CO arising from the secondary reaction of CO<sub>2</sub> with the Graphon surface. This amount, however, was very small compared with that produced by decomposition of the surface oxide. Clearly, for any particular initial O<sub>2</sub> pressure, the total amount of CO evolved decreases with in-

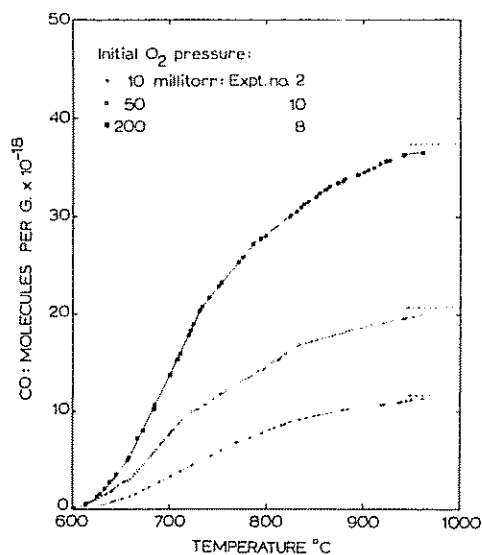


Fig. 3. Production of CO upon heating Graphon to 950°C at a heating rate of 3°C/min. Oxygen complex previously formed at 625°C using different initial O<sub>2</sub> pressures.

creasing reaction temperature; and, similarly, for any particular reaction temperature, the total amount of CO evolved increases with initial O<sub>2</sub> pressure. Our studies have indicated that the optimum temperature for surface oxide formation is about 500°C. It is also clear that the surface oxide formed at 525°C is much more stable at its formation temperature than that formed at 575° or 625°C.

It was found to be quite impossible to draw smooth curves through the experimental points, and there are definite discontinuities in the gradients. In fact, the graphs appear to consist of a series of intersecting straight lines. Recent work by Bansal *et al.*[6] on the chemisorption of oxygen on ultra-clean Graphon surfaces at low temperatures has suggested that the active surface of Graphon may consist of at least five discrete types of sites. We consider that our results support his conclusions.

### 3.2 Evolution of CO<sub>2</sub>

Figure 4 shows the cumulative evolution

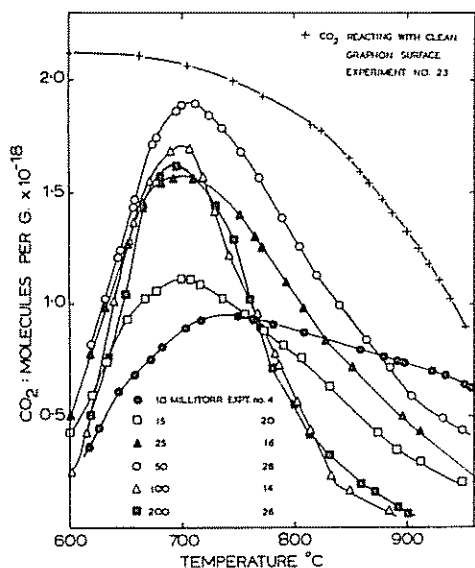


Fig. 4. Production of  $\text{CO}_2$  upon heating Graphon to  $950^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$ . Oxygen complex previously formed at  $525^\circ\text{C}$  using different initial  $\text{O}_2$  pressures. Consumption of  $\text{CO}_2$  by reaction with clean Graphon surface is also shown.

of  $\text{CO}_2$  from surface oxides formed at various pressures at  $525^\circ\text{C}$ , using a heating rate of  $3^\circ\text{C}/\text{min}$ . Figure 5 shows the evolution of  $\text{CO}_2$ , using the same heating rate from surface oxides formed at various pressures at  $625^\circ\text{C}$ . There are two processes which take place. The first is the evolution of  $\text{CO}_2$  generated by the breakdown of the surface oxide and the second is the secondary reaction of the evolved  $\text{CO}_2$  with the Graphon surface to form  $\text{CO}$ . These two effects acting together give rise to the maxima observed.

It can be seen that the maximum amounts of  $\text{CO}_2$  measured after surface oxide formation at  $525^\circ\text{C}$  are considerably higher than those measured after formation at  $625^\circ\text{C}$ , suggesting that  $\text{CO}_2$  generating sites are far less likely to form surface oxide at  $625^\circ$  than at  $525^\circ\text{C}$ .

The shapes of the curves were seen to vary considerably, in a peculiar but systematic way. It had been expected that the peak pressure of  $\text{CO}_2$  would be greatest for the

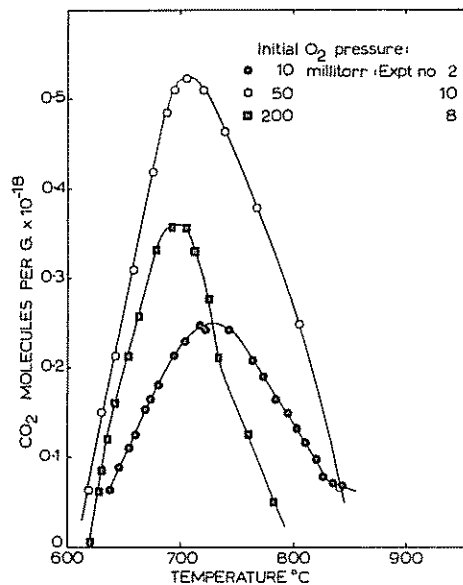


Fig. 5. Production of  $\text{CO}_2$  upon heating Graphon to  $950^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$ . Oxygen complex previously formed at  $625^\circ\text{C}$  using different initial  $\text{O}_2$  pressures.

surface oxides formed at the highest  $\text{O}_2$  pressures, i.e. when surface oxide formation is greatest. However, this was not found to be the case; the surface oxides formed at 50 mTorr, yielded the greatest peak pressure of  $\text{CO}_2$ . It was seen that for each temperature of formation the peak becomes sharper with increase in total surface oxide formation.

At these temperatures and pressures, the reaction of  $\text{CO}_2$  with carbon is effectively first order[7] so that the rate (per unit pressure of  $\text{CO}_2$ ) of the reaction could be conveniently measured as  $(dp_{\text{CO}_2}/p_{\text{CO}_2})/dt$  for any particular temperature. It had been anticipated that at any particular temperature, the rate of the secondary reaction would be lowest for the case when the most surface oxide remained on the surface, since the surface oxide would be expected to block active sites and so inhibit the reaction. However, almost the opposite phenomenon was seen. In all cases except Experiment No. 4, the rate of the secondary reaction

was higher than the rate of reaction of  $\text{CO}_2$  with a clean Graphon surface under the same heating conditions. In the cases where surface oxide formation had been highest, the rate of the secondary reaction was also highest. It became very clear that there was a remarkable correlation between the rate of the secondary reaction and the rate of evolution of CO as shown in Figs. 1 and 3. Discontinuities can be observed in the curves in Figs. 4 and 5, which correspond exactly to those in Figs. 1 and 3.

A quantitative analysis of the data was attempted but the idea was abandoned for two reasons. First, the total amount of  $\text{CO}_2$  evolved from the surface and the temperature at which evolution ceased were unknown. It is highly likely that  $\text{CO}_2$  evolution was complete by  $750^\circ\text{C}$ . Second, in many cases the rate of the secondary reaction could not be measured with sufficient accuracy.

Further evidence for a relationship between the secondary reaction and the rate of evolution of CO was provided by the use of a faster heating rate. The evolution of CO in Experiments No. 18 and 22 is shown in Fig. 6. Unfortunately, because the time taken by these desorptions was far less than in the case of those performed at  $3^\circ\text{C}/\text{min}$ , far fewer experimental points were obtained and the discontinuities, if they exist, were not seen. It is evident that, compared with the equivalent desorptions carried out at  $3^\circ\text{C}/\text{min}$ , the actual rate of evolution of CO with respect to time is about three times faster. Figure 7 shows the  $\text{CO}_2$  measured in Experiments Nos 4, 18, 22, 23, 24 and 28. It can be seen that the rate of the reaction of  $\text{CO}_2$  (with respect to time) with the clean Graphon surface, at any particular temperature, is independent of the heating rate. However, the rate of the secondary reaction is found to be approximately three times faster in Experiment No. 18 than in Experiment No. 28 and approximately three times faster in Experiment No. 22 than in Experiment No. 4. These observations lend

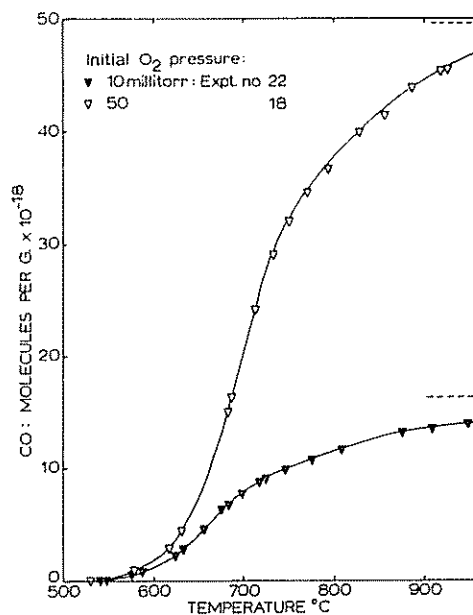


Fig. 6. Production of CO upon heating Graphon to  $950^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . Oxygen complex previously formed at  $525^\circ\text{C}$  using different initial  $\text{O}_2$  pressures.

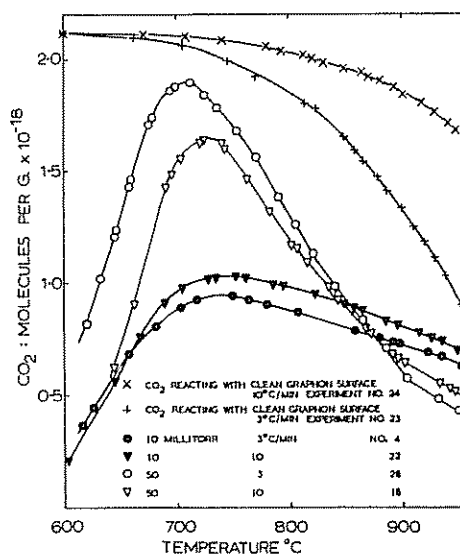


Fig. 7. Production of  $\text{CO}_2$  upon heating Graphon to  $950^\circ\text{C}$  at heating rates of both  $3^\circ\text{C}/\text{min}$  and  $10^\circ\text{C}/\text{min}$ . Oxygen complex previously formed at  $525^\circ\text{C}$  using different initial  $\text{O}_2$  pressures. Consumption of CO by reaction with clean Graphon surface is also shown.

further elegant support to the theory that the rate of the secondary reaction was strongly influenced by the rate of desorption of CO.

The conclusions from this work may be summarized as follows: as has been observed many times before, Graphon, in its reaction with O<sub>2</sub>, readily forms a surface oxide. The amount formed for a sample of particular burn-off is dependent on the reaction temperature and the initial O<sub>2</sub> pressure. This surface oxide is fairly stable at its formation temperature, although the stability decreases as the formation temperature increases. When the temperature is raised above the formation temperature, decomposition to CO and CO<sub>2</sub> takes place. The characteristics of the evolution of CO support the concept of a limited number of discrete types of active sites on the Graphon surface.

When the decomposition takes place in a closed system, the evolved CO<sub>2</sub> back reacts with the Graphon surface to form CO. This reaction is strongly influenced by the rate

of decomposition of the surface oxide, and it is suggested that the decomposition of the surface oxide leaves highly active 'nascent' sites [2] with which CO<sub>2</sub> can react readily.

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