

# STUDIES ON ULTRA-CLEAN CARBON SURFACES—IV. DECOMPOSITION OF CARBON-OXYGEN SURFACE COMPLEXES

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**Abstract**—Graphon was first activated by preoxidation to 16.6 per cent weight loss at 625°C to introduce a desired amount of active surface area. Varying amounts of oxygen were then chemisorbed on this sample at 100°C by exposure to 0.10 Torr O<sub>2</sub>. Following each chemisorption, the sample temperature was increased at a constant rate of 2°C/min to 950°C. Oxygen was released as CO and CO<sub>2</sub>; these gases were allowed to remain in contact with the sample. The cumulative recovery of CO increases with increasing temperature. Recovery of CO<sub>2</sub>, meanwhile, goes through a maximum because of its reaction at elevated temperatures with nascent carbon sites, produced primarily by the decomposition of the CO-producing complex. The plot of cumulative recovery of CO + CO<sub>2</sub> against temperature shows distinct linear regions, the amount recovered in each linear region showing close agreement with the amount of oxygen previously chemisorbed at different site configurations on the Graphon surface.

## 1. INTRODUCTION

It is well known that oxygen complexes exist on almost all types of carbons. Workers [1-10] have studied the number, nature, composition and stability of these complexes on charcoals and carbon blacks. These complexes are formed either during the preparation of these materials or during their exposure to the atmosphere while in storage. These complexes can also be formed on treatment of these carbons with oxidizing agents in solution [11-14], as well as on treatment with oxidizing gases [15-20]. In every case, they decompose to give CO<sub>2</sub> and CO on heat treatment in vacuum or in an inert atmosphere.

The formation of carbon-oxygen surface complexes, using graphites and graphitized carbon blacks, has also been studied by a number of workers [18-23]. But comparatively few experiments are available where the decomposition of the complex at higher temperatures has been systematically examined. The nature of the decomposition products and the proportions in which they are given off on heat treatment at different

temperatures is of considerable theoretical and practical importance. In this study, the oxygen complex was added on to an ultra-clean carbon surface, and then its decomposition under a constant heating rate was examined.

It has been shown in Parts I and II [22, 23] of this series of papers that the chemisorption of oxygen on a well cleaned Graphon surface involves the existence of different configurations of active sites. Studies on subsequent desorption of this chemisorbed oxygen may lead to further understanding of the mechanism of this chemisorption process. In order to obtain information on this aspect of the problem, it was thought to be of interest to cover the carbon surface with oxygen to different extents in separate experiments and then to study the rates of decomposition at different temperatures.

## 2. EXPERIMENTAL

2.1 *Material.* The carbon sample used in this investigation 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 per cent weight loss at 625°C in 0.5 Torr of O<sub>2</sub> to introduce a significant active surface area, as previously discussed [20]. This preoxidized sample was the same as used previously [22, 23].

**2.2 Formation of the carbon-oxygen complex.** The apparatus and the procedure used have been described in detail [22]. Briefly, the carbon sample (*ca.* 0.1 g) was held in a quartz boat and outgassed at 1000°C for 10–12 hr, a time sufficient to reduce the residual gas pressure to 10<sup>-8</sup> Torr. The sample was cooled under vacuum to 1000°C and a known volume of O<sub>2</sub> allowed to expand into the reactor until the pressure of O<sub>2</sub> was about 0.10 Torr. The decrease in the pressure of O<sub>2</sub> due to adsorption was measured using a Baratron differential manometer. When the desired amount of oxygen had been chemisorbed, most of the remaining O<sub>2</sub> was quickly removed from the system using a diffusion pump. The reactor was then connected to a Vaclon pump to remove additional O<sub>2</sub>, until a vacuum of better than 10<sup>-8</sup> Torr was obtained.

**2.3 Decomposition of the carbon-oxygen complex.** The oxygen complex formed on the Graphon surface was decomposed by heating the sample at a constant heating rate of 2°C/min. The gases evolved were collected in a 5.5 l. system. It was found that the evolved gases were CO<sub>2</sub> and CO, the amount of each measured by using a mass spectrometer. It should be emphasized that the gases collected remained in contact with the sample so that at higher desorption temperatures there was always the possibility of the reaction of CO<sub>2</sub> with the Graphon to produce CO.

### 3. RESULTS AND DISCUSSION

**3.1 Formation of oxygen surface complex.** Four desorption experiments will be discussed. In each experiment, the amount of oxygen adsorbed on the sample is different, although

the temperature of adsorption and the pressure of O<sub>2</sub> over the sample during adsorption have been kept constant. This has allowed us to examine the possibility that different types of sites are involved in the evolution of CO<sub>2</sub> and CO. The amounts of oxygen complex formed by chemisorption at 100°C in the four experiments, prior to desorption studies, is summarized in Table 1.

**3.2 Recovery of carbon dioxide upon desorption.** The oxygen recovered as CO<sub>2</sub> upon heating the oxidized samples of Graphon at a constant heating rate of 2°C/min are shown in Fig. 1. It is seen that, in general, the evolution of CO<sub>2</sub> starts in the 200–300°C temperature range and continues up to at least 650°C. The rate of evolution of CO<sub>2</sub> is a maximum in the temperature range 500–600°C. This is also the temperature range which was found to be optimum for the decomposition of the carbon-oxygen complex by previous workers [1–6].

It is also seen from Fig. 1 that the maximum in the cumulative amount of CO<sub>2</sub> recovered occurs in the temperature range 600–700°C in the case of experiment No. 1. Further, the maximum is sharp. However, in the case of the other experiments, the curves show flat maxima, which occur at a somewhat higher temperature. In fact, the maximum is broader the smaller the amount of oxygen which is previously chemisorbed on the sample at 100°C. The decrease in CO<sub>2</sub> pressure following the maximum is due to its reaction with the carbon surface. It is interesting to note that the extent of reduction in CO<sub>2</sub> pressure

Table 1. Oxygen complex formation at 100°C and 0.10 Torr O<sub>2</sub> pressure

Expt. No.	Adsorption time (min)	Oxygen adsorbed atoms/g × 10 <sup>-18</sup>
1	1400	19.0
2	200	8.6
3	150	7.7
4	30	4.6

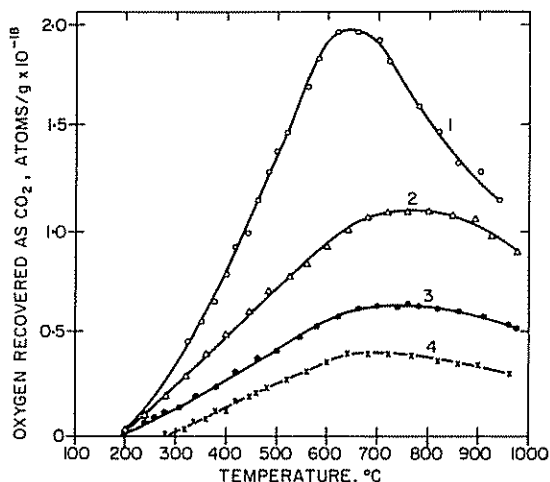


Fig. 1. Cumulative amount of oxygen recovered as  $\text{CO}_2$  as a function of temperature, using a heating-up rate of  $2^\circ\text{C}/\text{min}$ . Oxygen previously chemisorbed at  $100^\circ\text{C}$  and  $0.10$  Torr  $\text{O}_2$  pressure. Expt. No. see Table 1.

from its maximum when the peak outgassing temperature was reached was approximately 40 per cent in experiment No. 1 but only 15 per cent in experiment No. 4. If the rate of reduction was only dependent upon the

partial pressure of  $\text{CO}_2$ , all of the degassing curves in Fig. 1 would be similar in shape. Recent work of Phillips *et al.*[24] has shown that the extent of the back reaction (reduction of  $\text{CO}_2$  to  $\text{CO}$ ) also depends on the availability of nascent sites, which are produced as a result of the decomposition of the carbon-oxygen surface complex. They studied the reaction by introducing  $\text{CO}_2$  over clean and oxidized carbon surfaces. They found the reaction to be much faster over the oxidized surface because of the production of nascent sites as complex decomposed.

3.3 *Recovery of CO upon desorption.* Results are presented in Fig. 2. The evolution of  $\text{CO}$  starts at as low a temperature as  $300^\circ\text{C}$ , but the amounts released are appreciable only above  $400^\circ\text{C}$ . Recovery of  $\text{CO}$  continues up to  $950^\circ\text{C}$ , the cumulative amount recovered being considerably in excess of the amount of  $\text{CO}_2$  recovered in every run. The rate of recovery is most rapid in the temperature range  $600$ – $850^\circ\text{C}$ . This maximum in the recovery rate of  $\text{CO}$  could be attributed to two causes. First, the decomposition rate of the carbon-oxygen surface complex capable

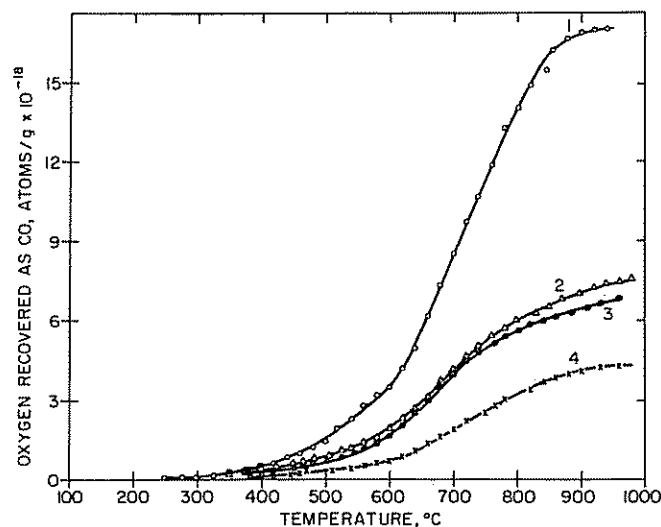


Fig. 2. Cumulative amount of oxygen recovered as  $\text{CO}$  as a function of temperature, using a heating-up rate of  $2^\circ\text{C}/\text{min}$ . Oxygen previously chemisorbed at  $100^\circ\text{C}$  and  $0.10$  Torr  $\text{O}_2$  pressure. Expt. No. see Table 1.

of producing CO is a maximum at these temperatures. Second, the rate of production of nascent sites (resulting from the decomposition of the carbon-oxygen complex) and, hence, the rate of reduction of  $\text{CO}_2$  at these nascent sites (as shown by the maxima in the curves in Fig. 1) is also a maximum at these temperatures.

There is, however, a difference between the findings in the present work and those of Phillips *et al.*[24]. They found linear regions in plots between the cumulative amounts of oxygen recovered as CO and temperature whereas we did not (Fig. 2). This may be due to differences in the experimental conditions under which the oxygen complex was formed. They chemisorbed oxygen at considerably higher temperatures ( $575^\circ\text{C}$  and above). Under these conditions, almost all of the oxygen was subsequently recovered as CO. That is, a still smaller percentage of the oxygen was recovered as  $\text{CO}_2$  than in this study.

3.4 Recovery of total oxygen as  $\text{CO}_2$  and CO. Figure 3 shows plots of the amount of oxygen evolved as  $\text{CO}_2$  and CO as a function of out-

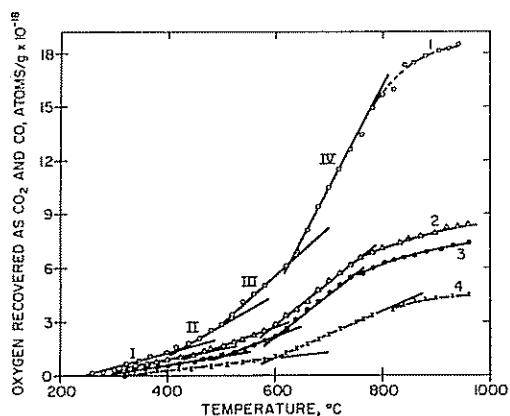


Fig. 3. Cumulative amount of oxygen recovered as CO and  $\text{CO}_2$  as a function of temperature, using a heating-up rate of  $2^\circ\text{C}/\text{min}$ . Oxygen previously chemisorbed at  $100^\circ\text{C}$  and  $0.10$  Torr  $\text{O}_2$  pressure. Expt. No. see Table 1.

gassing temperature. It is seen that the plots are not continuous curves, as shown in Figs. 1 and 2. Instead the plots show linear regions, the number of linear regions depending upon the amount of oxygen on the sample. For example, there are only two linear

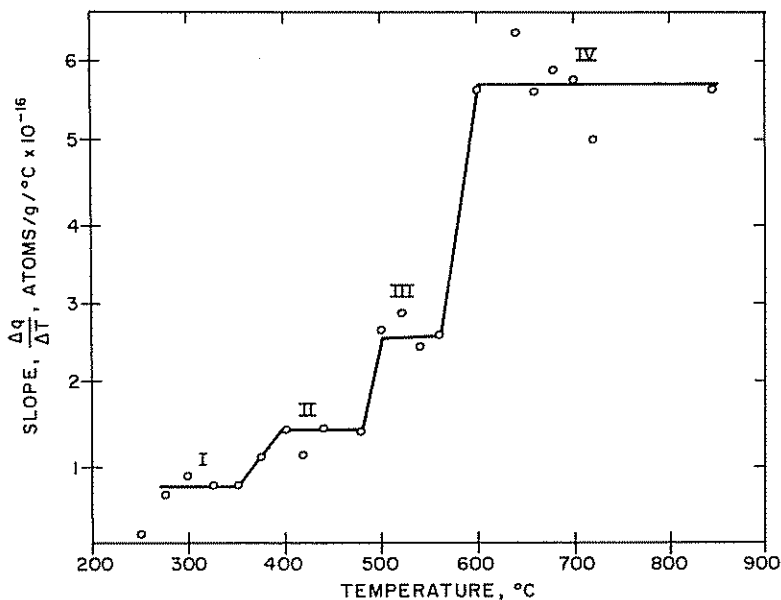


Fig. 4. Slopes of the plot for experiment No. 1 (Fig. 3) as a function of temperature.

Table 2. Comparison of amounts of oxygen recovered in different linear desorption regions with amounts previously chemisorbed in different stages

Linear desorption regions or chemisorption stages	Oxygen recovered (atoms/g $\times 10^{-18}$ )	Oxygen chemisorbed (atoms/g $\times 10^{-18}$ ) [22, 23]
I	1.1	1.2
II	2.3	2.4
III	6.2	5.8

regions in the case of experiment No. 4; whereas, there are four linear regions in experiment No. 1. Furthermore, the location of breaks between linear regions occurs at essentially the same values of total oxygen recovered, independent of how much oxygen complex was originally put on the sample. That is, the break between linear regions I and II occurs after about  $1.1 \times 10^{18}$  atoms of oxygen (as CO and CO<sub>2</sub>) have been recovered; between linear regions II and III, after about  $2.3 \times 10^{18}$  atoms of oxygen have been recovered.

In order to confirm the reality of these linear regions, slopes of the lines ( $\Delta q/\Delta T$ ) for experiment No. 1 were calculated at each data point and are plotted against temperature in Fig. 4. It is seen that the slopes change discontinuously, showing that the breaks are a reality.

If now we refer to our oxygen chemisorption experiments, as discussed in Parts I and II of this series, we find that these results once again support the concept that chemisorption of oxygen takes place on different discrete configurations of sites on the carbon surface. Furthermore, a comparison of the amounts of oxygen recovered in different linear regions (Fig. 3) with the amounts of oxygen required to saturate different groups of sites, given in Table 2, shows close agreement. This strongly suggests that the oxygen is being desorbed from different sites. As the amount of oxygen adsorbed in experiment No. 4 was just sufficient to cover sites I and II [22, 23], we would expect only two linear

regions. Similarly, in the case of experiment No. 1, the amount of oxygen adsorbed can cover sites I, II, III and IV [22, 23]; and, thus, four linear desorption regions could be observed in Fig. 3.

The decrease in the slope of the plots, in Fig. 3, in the temperature range 800–950°C is as expected and represents the completion of the desorption process.

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