

THE EFFECT OF OXYGEN PRESSURE AND CARBON BURN-OFF ON THE PRODUCT RATIO OF THE CARBON-OXYGEN REACTION

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Abstract—The reaction of Graphon with O_2 has been studied at $625^\circ C$ in a static system, using initial O_2 pressures between 25 and 750 mTorr. and samples pre-oxidized to varying degrees of burn-off between 0 and 20 per cent. The reaction temperature was low enough for secondary reactions to be neglected. A mass spectrometer was used to monitor the partial pressures of O_2 , CO and CO_2 . During a reaction, after a brief induction period corresponding to the formation of stable complex on the carbon surface, the incremental product ratio CO/CO_2 became constant. This product ratio increased with initial carbon burn-off and decreased with initial O_2 pressure. Stable complex formation increased with initial carbon burn-off and initial oxygen pressure. It is suggested that for a particular burn-off the product ratio is a function of both the amount of stable complex on the surface and the relative extent to which CO and CO_2 -generating sites are deactivated by stable complex formation.

1. INTRODUCTION

There are three products of the carbon-oxygen reaction: CO, CO_2 and a stable surface complex. Until recently there was much controversy as to whether both CO and CO_2 are primary products. The matter is complicated by the fact that the two oxides of carbon can be transformed one to the other by reactions which are not connected with the principal reaction of combustion. Some authors[1-4] have concluded that CO_2 is the only primary product and that CO arises from the reduction of CO_2 by the carbon surface. Others[5] have considered CO to be the primary product, CO_2 arising from subsequent oxidation of CO by O_2 .

There is now general agreement[6-11] that the conclusion first reached by Rhead and Wheeler[12], that both CO and CO_2 are primary products of the carbon-oxygen reaction, is valid. Conclusive proof of this has recently been obtained by Hart *et al.*[13], using oxygen-18.

Several workers have investigated the factors which influence the ratio of CO to CO_2 produced during the reaction. It has become clear that the reaction temperature is a major factor[6, 7, 9, 11]; there appears to be an exponential relationship between the product ratio and the reaction temperature. It has generally been found that the product ratio is influenced by the type of carbon used[7, 9, 11], although Arthur[6] found similar results for a natural graphite and a coal char. Certain impurities appear capable of reducing the CO/CO_2 ratio[14]. There is doubt as to the effect of oxygen pressure. Some workers have found no effect[9], while others have observed that the ratio can be reduced by increasing the oxygen pressure[15, 16].

The purpose of the work described in this paper has been to investigate the possible effects of oxygen pressure and carbon burn-off on the product ratio of the carbon-oxygen reaction. A very pure graphitized

carbon black was reacted in a static system under conditions which obviate secondary reactions and allow for chemical rather than diffusion control.

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 a l'Energie 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, which had been graphitized between 2700° and 2800°C. The BET area of the sample provided by Dr. Lang was 74 m²/g for zero burn-off, as contrasted to 76 m²/g for our 2700°C Graphon sample. X-ray diffraction patterns for the two materials were almost identical, indicating similar spacing between the graphitic planes and similar crystallite dimensions.

The oxygen used was research grade, supplied by Air Products and Chemicals Co., Allentown, Pennsylvania. The major specified impurities were nitrogen (11 ppm), argon (5 ppm), and water (0.76 ppm).

2.2 *Apparatus*

The apparatus used was similar to that described previously[13]. 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 reaction system was 19.8 l. Graphon samples were 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. The reaction system was evacuated initially by a 20 l./sec oil diffusion pump backed by a rotary oil pump, and then by an 8 l./sec Ultek ionization pump to an ultimate vacuum of 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 a reaction. The leak rate was very low; thus it was found unnecessary to correct for the small amount of gas lost through the leak.

2.3 *Experimental procedure*

Experimental conditions were chosen so that mass transport effects would be minimized. Reactions were performed at a relatively low temperature (625°C) at initial oxygen pressures between 25 and 200 mTorr., using a finely divided sample. It has been shown[10] that under these conditions secondary reactions can be neglected.

A Graphon sample of 0.2977 g initial weight was placed in the quartz bucket in the reaction tube; and after evacuating the system, the surface of the sample was cleaned by raising the furnace temperature to 950°C for 12 hr. The temperature was then reduced to 625°C and the pumps were isolated. The system was filled with 100 mTorr. of O₂ and the partial pressures of O₂, CO and CO₂ were measured at intervals during the reaction. Reaction was allowed to proceed until most of the O₂ had reacted. The system was then evacuated at the reaction temperature and heated at 950°C in order to remove the stable complex from the surface. The temperature was reduced to 625°C and another reaction was performed with an initial pressure of 25 mTorr.,

following the procedure already described. A third reaction was performed with a starting pressure of 200 mTorr., a fourth at 100 mTorr., a fifth at 25 mTorr. and so on until a burn-off of about 20 per cent had been achieved. A few runs were performed at 50 and 70 mTorr. The burn-off at any stage could be calculated from the total amount of CO and CO₂ that had been evolved since the beginning of the experiment. When a burn-off of 11 per cent had been reached, it was realized that an accurate knowledge of the amount of stable complex on the surface would be useful; and so in subsequent runs this measurement was made by decomposing the complex in a closed system and measuring the products.

A second Graphon sample, of initial weight 0.2995 g, was used to repeat the experiment from zero to 13 per cent burn-off. This set of experiments included reactions at 525°, 575° and 675°C, but only those at 625°C will be discussed in this paper. At intervals during this second set of experiments, measurements of the 300°C 'active surface area' (ASA) were made, following the method previously developed in this laboratory [10, 11].

3. RESULTS AND DISCUSSION

For each reaction, changes of partial pressures of the gaseous species with time were qualitatively similar to those shown in previous papers from this laboratory [10, 11, 18]. The amount of stable complex on the surface at any time could be found by a material balance, although the accuracy of the values obtained, particularly for the reactions at 100 and 200 mTorr. starting pressures, was poor. Early in the reaction the amount of stable complex on the surface increased until a fairly constant value was reached, after which the depletion of O₂ followed first order kinetics.

Figure 1 shows the relation between CO and CO₂ pressures during a reaction lasting 30 hr. Except near the origin, the graph is

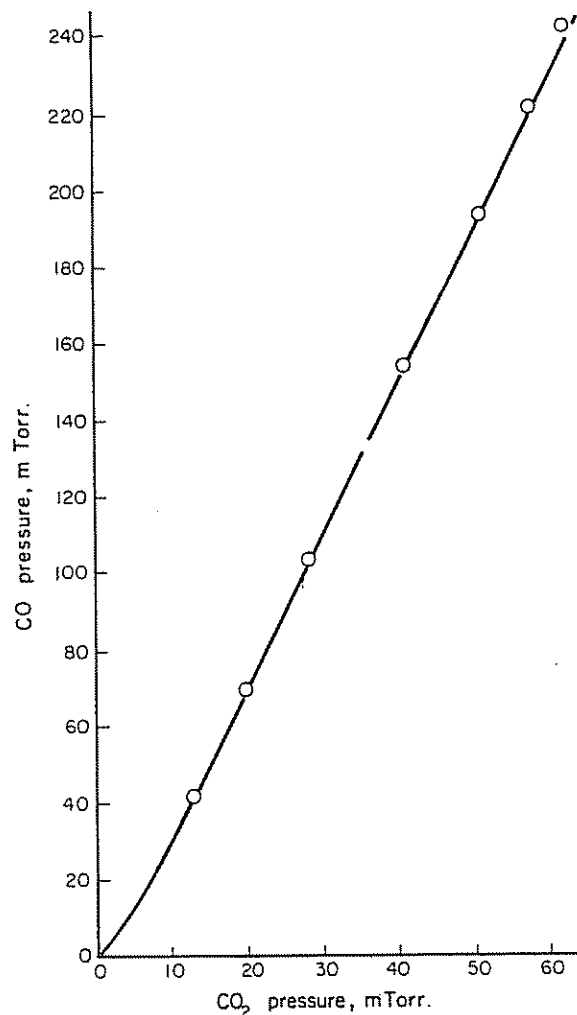


Fig. 1. Relation between amount of CO and CO₂ produced during a 30-hr reaction of Graphon (12 per cent burn-off) with O₂ at 625°C. Initial O₂ pressure, 200 mTorr.

linear. After a short induction period, the ratio of evolution of the two gaseous products becomes constant. The induction period was found to correspond to the period of formation of the stable complex. Since the O₂ pressure decreased during the course of the reaction, it is clear that there is no relationship between the 'steady state' product ratio and the *instantaneous* O₂ pressure. However, results do show that there is a relationship between the 'steady state' product ratio and the *initial* O₂ pressure, as shown in Fig. 2 for Graphon samples of varying burn-off. A set of results obtained with an initial O₂ pressure of 750 mTorr.,

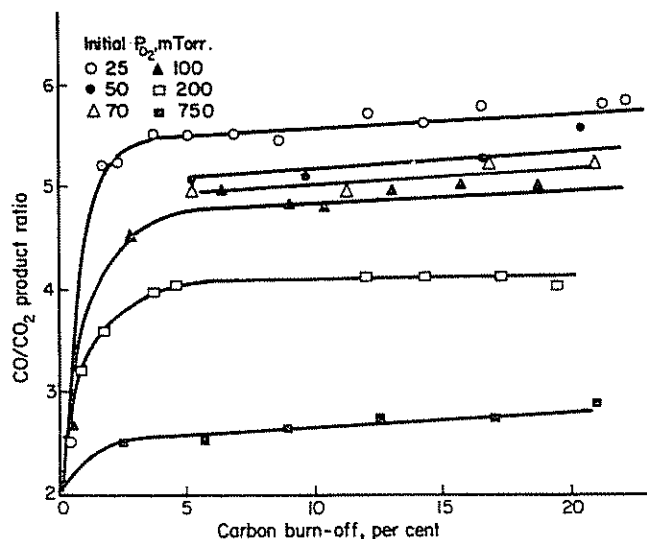


Fig. 2. Effect of carbon burn-off on CO/CO₂ product ratio for varying initial O₂ pressures during oxidation of Graphon at 625°C.

under similar experimental conditions, are included for comparison. The initial (or more properly, the maximum) O₂ pressure is a major factor determining the product ratio. The degree of burn-off is also important, as was previously found [11], although its effect is small at values above 5 per cent.

The amount of stable complex formed during a reaction was strongly dependent upon the initial O₂ pressure, as shown in Fig. 3. Figure 4 presents the relationship between the CO/CO₂ product ratio and the amount of stable complex formed for

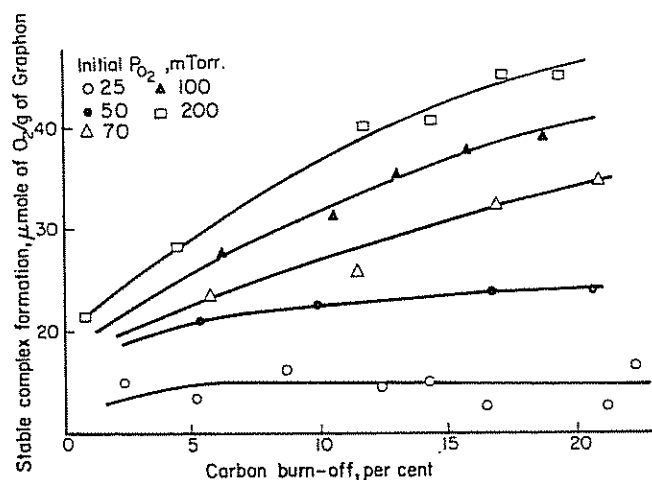


Fig. 3. Effect of carbon burn-off on the amount of stable oxygen complex formed for varying initial O₂ pressures during oxidation of Graphon at 625°C.

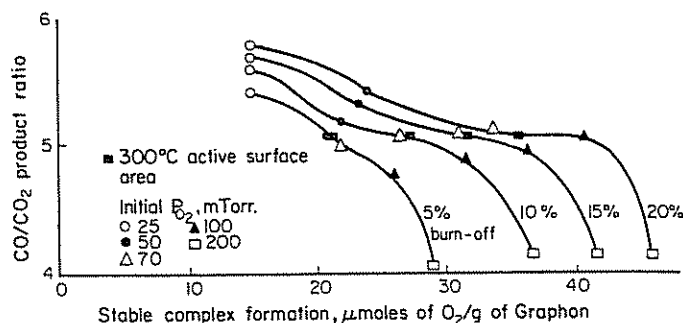


Fig. 4. Relation between CO/CO₂ product ratio and amount of stable oxygen complex formed at different levels of burn-off during oxidation of Graphon at 625°C.

different levels of carbon burn-off. Each curve contains a point of inflection, corresponding to a product ratio of about 5.0. The significance of the points of inflection becomes clear in the light of previous work [10, 11, 18]. Laine and co-workers found that only a small fraction of the total BET area of Graphon is chemically active but that the fraction increases very strongly with burn-off. Laine, using reaction temperatures between 575° and 675°C and initial O₂ pressures of 40 m Torr., found that the total active area corresponded to that which would chemisorb oxygen at 300°C when exposed to 500 mTorr. O₂ pressure for 24 hr. The 300°C ASA was 0.29 per cent of the BET area for an original sample of Graphon and rose to 3.1 per cent of the BET area for a 35 per cent burn-off sample. Lussow *et al.* [18], working at pressures between 6 and 70 mTorr., and temperatures between 450° and 675°C, agreed with the conclusion of Laine *et al.* but noted that more vigorous conditions, either higher temperatures or higher pressures, significantly increased the amount of oxygen chemisorbed. They postulated that less active sites, which they called 'Type II', were present as well as the more active 'Type I' sites measured by the 300°C ASA.

Lang and Magnier [17], using the same highly purified Graphon employed in this work, studied the reaction with O₂ using

dry air at 620°C and atmospheric pressure. They found that the specific rate of carbon loss, measured in g/m^2 of BET area/hr, remained constant for samples between 10 and 58 per cent burn-off. These authors concluded that their results were in opposition to those of Laine *et al.*, but this is in fact not the case. Laine's conclusion is that the total active surface area increases markedly with burn-off and that the index of reactivity under any experimental conditions is that part of this total active surface which remains unoccupied by stable complex. In the present study, the measurements of 300°C ASA showed an increase with burn-off which paralleled that observed by Laine.* Measurements of the experimental first order rate constants for the depletion of O_2 at the highest starting pressures used in this study indicated that above 5 per cent burn-off, values calculated in units of $\text{m}^{-2}(\text{BET}) \text{sec}^{-1}$, were almost independent of burn-off. This observation agrees with that of Lang and Magnier. However, the correct conclusion is not that the BET area is a satisfactory index of reactivity but that the increase in stable complex formation with burn-off is paralleling the increase in total active surface area in such a way that the unoccupied active surface area is not changing at a greater rate than the BET area.

The points of inflection in Fig. 4 correspond, for each burn-off, to a stable complex formation equivalent to the measured 300°C ASA, i.e. the Type I surface. It appears that gasification reactions at 25 and 50 mTorr. initial O_2 pressure take place predominantly on the Type I sites. On the other hand, at 100 and 200 mTorr. gasification takes place

*It should be noted at this stage that the values of 300°C ASA measured in this work and by others using similar vacuum conditions[13] are somewhat higher than those obtained by Laine and Lussow, both of whom worked at an ultimate vacuum of about 10^{-5} Torr. The discrepancy is attributed to the improved vacuum conditions which allow for a more thorough cleaning of the carbon surface prior to oxygen chemisorption.

predominantly on the Type II sites, as in this case most or all of the Type I sites are rendered inactive by stable complex. The point of inflection is thought to represent a transition between reactions on the two types of sites. It appears that the product ratio for a particular reaction temperature is dependent, firstly, on the type of surface which is reacting and, secondly, on the extent to which that surface is not covered by stable complex and is, therefore, available for reaction.

Recent work in our laboratory[19] on the chemisorption of oxygen on ultra-clean Graphon surfaces at room temperature has shown that the Type I surface is not homogeneous but rather consists of at least five different types of sites. Bansal has shown that upon desorption of the oxygen complex, CO_2 comes predominantly from the two most active groups of sites and CO comes predominantly from the three less active groups of sites. The gasification process at 625°C is obviously different from the chemisorption process at room temperature, but it is suggested that each distinct type of sub-site is predestined to give either CO or CO_2 , but not both, when an intermediate complex on it decomposes.

The product ratio for reaction on a clean surface will be determined by the relative number and activity of the various types of sub-sites. If when the surface is progressively covered with stable complex, CO -producing sites are covered more rapidly than CO_2 -producing sites, the product ratio will decrease, as is seen experimentally.

It has been demonstrated[11] that when a stable complex formed at 300°C is decomposed by heating to progressively higher temperatures, most of the CO_2 is obtained below 600°C, while most of the CO is obtained above this temperature. This suggests that at 625°C, CO_2 -generating sites will not form stable complex as readily as CO -generating sites. This is further demonstrated in Fig. 5, which shows how the experimental first order rate constants for depletion of O_2 and

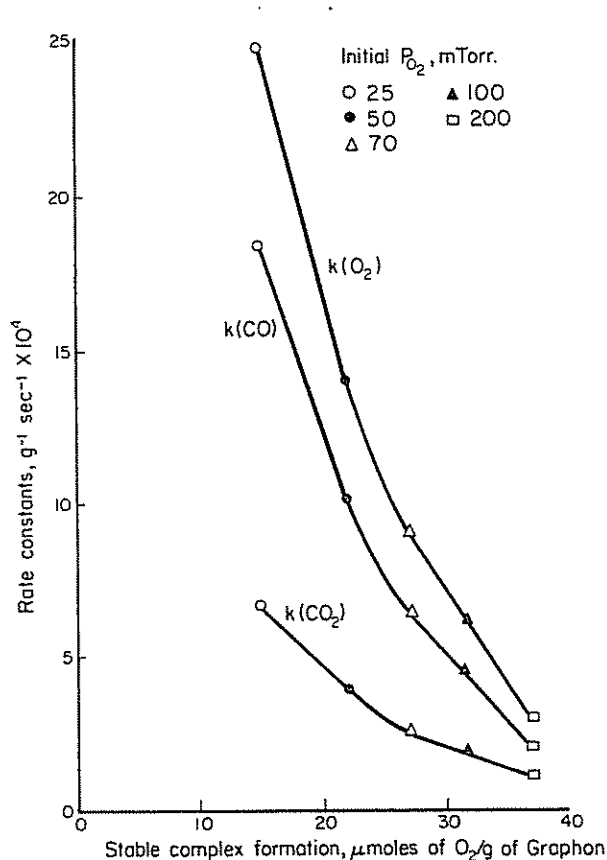


Fig. 5. Relation between first order rate constants and amount of stable oxygen complex formed during oxidation of Graphon (10 per cent burn-off) at 625°C.

evolution of CO and CO₂ vary with stable complex formation for Graphon of 10 per cent burn-off. The experimental rate constants are given by $k(\text{O}_2) = -(dp_{\text{O}_2}/dt) (1/p_{\text{O}_2})$, $k(\text{CO}) = (1/2 dp_{\text{CO}}/dt) (1/p_{\text{O}_2})$, and $k(\text{CO})_2 = (dp_{\text{CO}_2}/dt) (1/p_{\text{O}_2})$. The values of k were derived from the straight line portions of $\log p_{\text{O}_2}$ vs. time plots, i.e. for situations when stable complex formation was complete. The values have been multiplied by the factor 898/298 to allow for the fact that although the reaction took place at 898°K, only an insignificant fraction of the total gas in the reaction system was heated to this temperature, most of the gas being at room temperature. It is seen that with increasing stable complex formation, both CO and CO₂ generating sites are being occupied by stable complex and thereby rendered inactive. However, the decrease in $k(\text{CO})$ is more

pronounced than the decrease in $k(\text{CO}_2)$, indicating that the CO-generating sites are being occupied by stable complex more readily than the CO₂-generating sites. Distinct changes in the slopes of the plots take place at a stable complex formation of about 26 $\mu\text{mole O}_2/\text{g}$ which is close to the coverage on the 300°C ASA. This suggests that a transition from reaction predominantly on Type I sites to reaction predominantly on Type II sites has occurred.

Figure 6, which shows how the distribution of oxygen between CO and CO₂ depends on stable complex formation, similarly shows a transition in the region of the 300°C ASA.

Another observation which requires explanation is the fact that the ultimate stable complex formation is so highly dependent on initial O₂ pressure. One might have expected that the carbon surface would have a certain number of sites capable of forming stable complex at the reaction temperature and that although the rate of formation would be pressure dependent, the ultimate amount would not be. It is observed that the 300°C ASA (which incidentally is almost identical to the 400°C ASA) represents the maximum

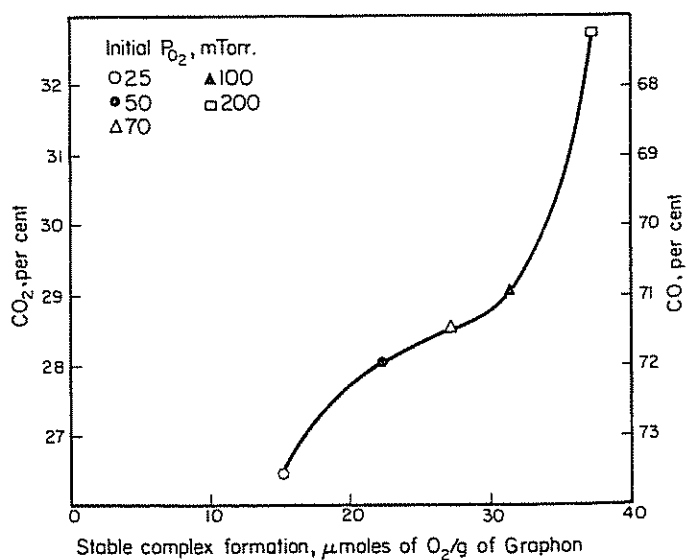


Fig. 6. Relation between formation of gaseous oxides of carbon and amount of stable oxygen complex formed during oxidation of Graphon (10 per cent burn-off) at 625°C.

area which will chemisorb in the absence of substantial gasification. In order to chemisorb on Type II sites, gasification is necessary. A large increase in chemisorption takes place between 400° and 500°C [18], an increase which is paralleled by a large increase in rate of gasification. It is suggested that gasification promotes chemisorption by producing 'nascent' sites which are very active. The initial rate of gasification is much higher at 200 mTorr. than at 25 mTorr., and the difference in nascent site production may explain the difference in stable complex formation.

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