

FACTORS AFFECTING THE PRODUCT RATIO OF THE CARBON-OXYGEN REACTION—II. REACTION TEMPERATURE

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 reaction of Graphon with O₂ has been studied at temperatures between 525° and 675°C, using initial O₂ pressures between 10 and 200 mTorr. and a sample varying in burn-off between zero and 28 per cent. Reaction temperatures were low enough for secondary reactions to be neglected. A mass spectrometer was used to monitor the partial pressures of O₂, CO and CO₂. The amount of stable oxygen complex on the surface was determined by decomposing it at elevated temperatures. Using an interpolation technique, the variation of product ratio with temperature at various constant carbon burn-offs and surface oxide formations could be determined. The variation of product ratio, CO/CO₂, with temperature is given by $A \cdot \exp(-E/RT)$ where $E = 6.4$ kcal/mole and is independent both of carbon burn-off and surface-oxide formation. On the other hand, the pre-exponential factor A increases with increasing carbon burn-off and decreasing surface oxide coverage.

1. INTRODUCTION

The reaction between carbon and oxygen is thought to proceed by means of an intermediate complex, which can either relax to form a surface oxide, which is stable at the reaction temperature, or can decompose to give either CO or CO₂. This mechanism explains fairly satisfactorily the role of the surface oxide in the kinetics of the reaction, although it is known that the surface oxide does decompose slowly at the reaction temperature. This mechanism implies that both CO and CO₂ are primary products of the reaction. Thus, the factors which determine the ratio of CO to CO₂ have received considerable attention. Unfortunately the situation is complicated by the fact that under certain circumstances secondary reactions can occur. CO can be oxidized to CO₂, and CO₂ can be reduced by the carbon surface to CO. Most of the workers who have investigated the product ratio have recognized this problem and have taken steps to minimize or

eliminate the possibility of secondary reactions.

Of the factors which have been investigated, reaction temperature has probably received the most attention, although, despite all the work that has been done, few general conclusions can be drawn with confidence.

Arthur[1] found that for both natural graphite and coal char the product ratio for the temperature range 460°–900°C could be expressed by $CO/CO_2 = 10^{3.1} \exp(-12,400/RT)$, where R is the gas constant expressed in cal/mole deg and T is the absolute temperature. He used a flow system with partial pressures of O₂ between 38 and 190 Torr. POCl₃ was added to the gas stream with the intention of inhibiting the secondary oxidation of CO to CO₂.

Rossberg[2] also used a flow system and studied the oxidation of two electrode carbons over the temperature range 520°–1420°C. He avoided secondary reactions by

the use of high flow rates. He found for the two samples that the product ratio could be expressed as: $\text{CO}/\text{CO}_2 = 10^{3.3} \exp(-14,300/RT)$ and $10^{3.9} \exp(-18,700/RT)$.

Day, Walker and Wright[3] used high flow rates and high temperatures (between 1500 and 2300°K) to study the combustion of a variety of carbonaceous materials. These authors concluded that at flow rates of 10,000 ft/min and above, secondary oxidation of CO did not take place, and the product ratio increased with temperature very rapidly between 1800° and 2300°K. They found that the product ratio under particular experimental conditions was markedly dependent on the type of carbon used.

Bonnetain, Duval and Letort[4] also used a flow system but at much lower O₂ pressures (0.1–70 mTorr.) and temperatures between 400° and 700°C to study a variety of graphite samples. They found exponential relationships between the product ratio and the reaction temperature, but with activation energies rather lower than those of Arthur and Rossberg, 6–8.5 kcal/mole. They also found a dependence on pressure. The product ratio increased gradually as the pressure was decreased below 30 mTorr.

In a recent paper, Otterbein and Bonnetain[5] compared the kinetics of oxidation of two widely differing carbons, a vitreous carbon and a spectroscopic graphite. They found similar values of product ratio for the two types of carbon. This work was done using a flow system at low pressures; a dependence on O₂ pressure was again found. For the vitreous carbon at 600°C, the product ratio was 3.8 at 19 mTorr., 3.3 at 65 mTorr. and 2.7 at 120 mTorr. Product ratios were measured over a temperature range of 500°–650°C. Comparison of product ratios measured at the same O₂ pressure gave an exponential dependence on temperature with an activation energy of 6 kcal/mole.

Laine, Vastola and Walker[6] also used low O₂ pressures (about 50 mTorr.) but in a static system. The material used was Graphon

and the temperature range was 575°–675°C. Their absolute values of the product ratio were higher than those of Bonnetain and his coworkers, but the activation energy for the exponential temperature dependence was similar.

In a previous paper[7] we have discussed the effect of burn-off and O₂ pressure on the product ratio of the reaction of Graphon with O₂ at 625°C. This work was principally concerned with the influence of the state of the carbon surface on the product ratio. The degree of burn-off determines the total active surface of the Graphon sample, while the initial O₂ pressure determines the extent to which this total active surface is deactivated by the formation of stable surface oxide during the reaction. It was considered that any active site is predestined to give either CO or CO₂ when an oxygen complex on it is decomposed, and the product ratio is effectively determined by the relative numbers of CO and CO₂-generating sites and their relative activity. At 625°C, as surface oxide is formed, CO generating sites are blocked much more readily than CO₂ generating sites. Thus, the ratio of available CO generating sites to available CO₂ generating sites decreases, and so does the product ratio.

It is our contention that in order to make a rigorous examination of the influence of reaction temperature on the product ratio of the carbon–oxygen reaction, it is necessary to maintain constant all other factors which could influence the ratio. One of these factors is surface oxide formation, the amount of which is partly determined by reaction temperature, so that it is not strictly valid to compare product ratios measured at the same O₂ pressure at different reaction temperatures, as Bonnetain did.

The work that will be described in this paper consists of an examination of the influence of reaction temperature on the product ratio of the reaction of Graphon with O₂. It is well known that impurities, both in the carbon[8] and in the O₂[9] can have a

considerable effect on the product ratio; and we have been careful to use a very pure form of carbon and Research Grade O₂. Experimental conditions were chosen so as to eliminate the possibility of secondary reactions and to allow for chemical rather than diffusion control. An interpolation technique has enabled us to effectively maintain constant all factors which influence the product ratio except reaction temperature.

2. EXPERIMENTAL

The carbon used was an ultra-pure form of Graphon prepared by Dr. Lang of Commissariat a l'Energie Atomique, Saclay, France[9]. Ash content was 25–35 ppm. The O₂ 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).

The experimental technique was similar to that used previously and described in the first paper[7], with the following changes. The reaction system was rebuilt to allow for more efficient evacuation, it had a total volume of 19.3 l. instead of 19.8 l. All the results were obtained with one Graphon sample of initial weight 0.300 g. Reaction temperatures between 525° and 675°C and initial O₂ pressures between 10 and 200 mTorr. were used. A total of 96 reactions were performed, after which the burn-off reached 28 per cent. Measurements of the Type I surface were made at intervals following the method of Laine[6], although it was eventually found that chemisorption at 350° rather than 300°C gave more reproducible results.

The sequence of reactions was chosen to allow for a fairly uniform scatter of reactions at a particular temperature/pressure combination over the entire burn-off range, but otherwise the sequence was random.

3. RESULTS AND DISCUSSION

The results obtained are in agreement with

those described in our previous paper[7]. During each reaction, after a short induction period, the depletion of O₂ followed first order kinetics; and the ratio of the rate of production of CO to that of CO₂ became constant. It was found, however, that if reactions were performed at 625° or 675°C with an initial O₂ pressure of 100 or 200 mTorr. (i.e. at the higher temperatures and pressures) and allowed to proceed until almost all the O₂ was depleted, the empirical first order rate constant for the depletion of O₂ (as measured by the gradient of the plot of $\log p_{O_2}$ against time) began to increase towards the end of the reaction. It is known that the surface oxide is not completely stable at the reaction temperature and that there is a continual formation and decomposition of surface oxide. A balance between the two processes maintains the total amount of surface oxide substantially constant during a large part of the reaction, a fact which explains the first order kinetics observed. During the induction period, however, formation of surface oxide predominates, while towards the end of the reaction, when the partial pressure of O₂ is very low, the decomposition of the surface oxide predominates. Therefore, there is an increase in the effective active surface area, which leads to the observed increase in the empirical first order rate constant during this part of the reaction. In order to eliminate this problem, care was taken to end reactions while the depletion of O₂ was still following first order kinetics. This ensured that decomposition of the oxide at the end of a reaction gave a measure of the amount of oxide on the surface during the period of first order kinetics.

During the induction period, the ratio of the rate of production of CO to that of CO₂ was lower than it was after the induction period. This may be due to the gasification of highly active 'dangling' carbon atoms to CO₂ at the beginning of the reaction.

Graphs were drawn of surface oxide formation and product ratio for each pressure/

temperature combination vs. burn-off. The values of surface oxide formation at 200 mTorr. and 625°C and 675°C obtained were rather erratic, probably because of the instability of the oxide formed under these conditions. They have, therefore, been discarded. It was, of course, important that the product ratio used should be that obtained during the period of first order kinetics.

From these graphs, interpolations were made, at 2, 5, 10, 15, 20 and 25 per cent burn-off. The values obtained for 20 per cent burn-off are shown in Table 1. It can be seen that at each temperature, increasing initial O₂ pressure causes an increase in surface oxide formation and a decrease in the product ratio. These same values are plotted in Fig. 1, which shows graphs of product ratio against surface oxide formation for different temperatures for 20 per cent burn-off. Similar graphs were also drawn for other burn-offs. These graphs allowed a direct comparison

of product ratios for the different reaction temperatures, but with identical surface conditions, i.e. the same burn-off and the same surface oxide formation. As previous workers had found an exponential relationship between the product ratio and the reaction temperature, graphs were drawn of $\log(\text{CO}/\text{CO}_2)$ against $1/T$, for constant burn-off and surface oxide formation. These graphs for 20 per cent burn-off are shown in Fig. 2. Parallel straight lines were obtained indicating a relationship between product ratio and absolute temperature as follows:

$$\text{CO}/\text{CO}_2 = A \cdot \exp(-E/RT)$$

The activation energy E was found to be independent both of burn-off and surface oxide formation (i.e. independent of the condition of the surface). The pre-exponential factor ' A ' was found to be a function of the surface. The value of E

Table 1. Interpolations for surface oxide formation and product ratio at 20 per cent burn-off

Temperature (°C)	Initial pressure (mTorr.)	Surface oxide* μ moles O ₂ /g	Product ratio
525	10	14.0	3.4
	25	25.0	3.1
	50	37.0	3.0
	100	46.0	2.8
	200	52.0	2.5
575	10	9.0	4.6
	25	15.0	4.3
	50	25.5	4.0
	100	36.5	3.9
	200	48.0	3.5
625	10	8.1	5.6
	25	11.7	5.4
	50	17.0	5.1
	100	25.0	5.0
675	25	9.7	6.7
	50	12.8	6.6
	100	15.0	6.5

*Type I surface is equivalent to 35 μ moles O₂/g.

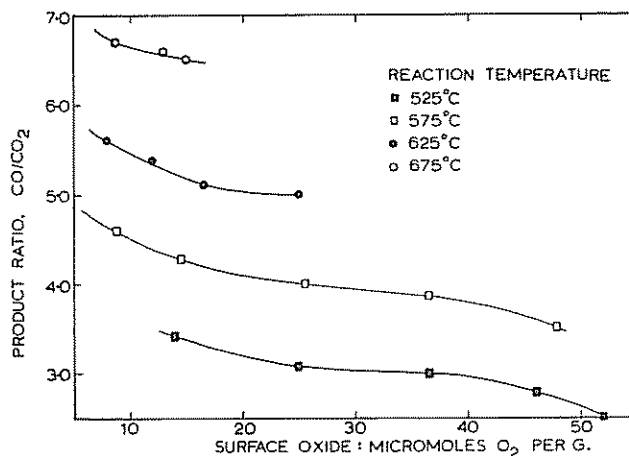


Fig. 1. Relationship between product ratio CO/CO₂ and surface oxide formation for various reaction temperatures for 20 per cent burn-off Graphon.

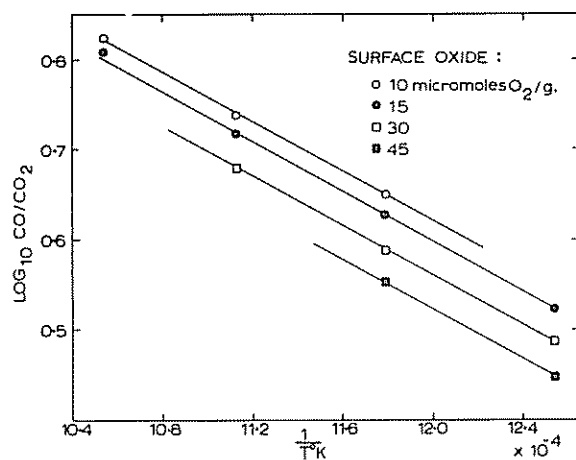


Fig. 2. Arrhenius plots between product ratio and temperature at various levels of surface oxide formation for 20 per cent burn-off Graphon.

measured was 6.4 kcal/mole, a value which agrees well with that obtained for a variety of widely differing carbons by Bonnetain and his coworkers [4, 5].

It may be that the value of E is independent of the types of carbon and is a measure of the difference in activation energy between the decomposition of CO generating complex and the decomposition of CO₂ generating complex.

The values of E obtained by Arthur [1] and Rossberg [2] are much higher, and this may be at least partly due to their high O₂ pressures and their wide temperature range. At the lower end of the temperature range, surface oxide formation would be very much higher than at the higher end of the range, so that their values of E reflected not only a temperature effect but also the effect of a radical change in the state of the surface.

Figure 3 shows how ' A ' depends on burn-off and surface oxide formation. It can be

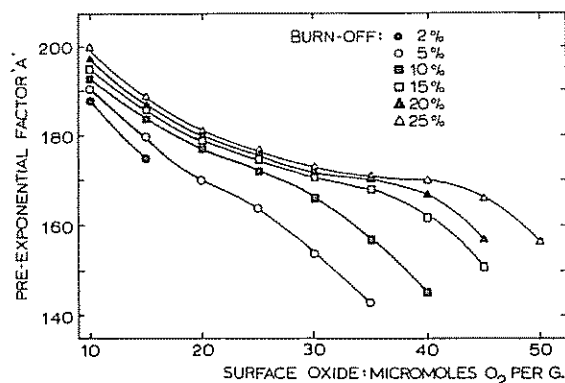


Fig. 3. Dependence of the pre-exponential factor ' A ' on the extent of Graphon burn-off and surface oxide present.

seen that as the active surface is progressively covered by surface oxide, ' A ' decreases, because CO generating sites are being deactivated more rapidly than CO₂ generating sites. It can also be seen that the curves exhibit a point of inflection for a value of ' A ' of about 170. These points of inflection also (except for 2 per cent burn-off) lie at a value of surface oxide formation equivalent to the coverage of the Type I surface [10]. At this point of inflection, a transition is taking place between reaction predominantly on the Type I surface to reaction predominantly on the Type II surface.

When the points in Fig. 3, which corresponded to reaction on the Type I surface, are compared, it appears that the value of ' A ' was a function of the percentage of the Type I surface available for reaction.

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