

ON THE ROLE OF CARBON-OXYGEN SURFACE COMPLEXES IN THE CARBON/OXYGEN REACTION MECHANISM

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INTRODUCTION

In the past, attempts to characterize the reactivity of carbon materials have led to conclusions regarding the importance of active sites and carbon-oxygen (C(O)) complexes in the carbon/O₂ reaction mechanism [1,2]. More recently, questions have been raised concerning the possibility of oxygen presence on the basal plane during gasification. Studies with disordered (turbostratic) carbons (e.g., polymer-derived carbons and coal chars) revealed that the quantity of C(O) complexes on the surface at gasification conditions exceeds significantly the quantities formed during low-temperature chemisorption [3-5]. One of the possible mechanistic explanations for this experimental fact is the so-called "spillover effect" whereby oxygen atoms, chemisorbed on the edge sites of carbon crystallites, migrate ("spill over") from the edges to the basal plane [5]. Spillover is the process that occurs when active species, C(O) complexes, are formed on one type of sites (e.g., edges), and are subsequently transferred to another type of sites (e.g., basal plane). Although the basal plane does not participate directly in carbon gasification, it serves as an additional reservoir of oxygen. A larger quantity of oxygen resides on the surface at higher temperatures, because spillover is an activated process.

Since it is rather difficult (or even impossible) to trace the fate of oxygen atoms on the basal plane by experimental techniques, theoretical molecular orbital calculations seem to be very attractive. Results of such calculations [6-11] have shown that there are no obstacles for the presence of oxygen atoms on the basal plane at temperatures at which gasification of carbon takes place.

Yang and Wong [12] were the first to provide experimental evidence for the presence and mobility of oxygen on the basal plane. Pan and Yang [10] have reiterated that basal-plane oxygen should be taken into consideration in the analysis of high-temperature CO desorption spectra. More recently, Chen *et al.* [11] showed that an oxygen atom on the basal plane lowers the binding energy of a neighboring C-C bond by 30%; therefore, it is important for the analysis of carbon reactivity. In our previous paper [13], a reaction mechanism was proposed according to which the quantity of basal-plane oxygen determines the CO/CO₂ product ratio.

The objective of the present communication is to pursue a further understanding of the role of basal-plane and edge C(O) complexes in the formation of CO and, especially, CO₂. Both theoretical and experimental techniques were used.

MECHANISM OF CO AND CO₂ FORMATION

The proposed mechanism of CO and CO₂ formation (Figure 1) follows from the reaction mechanism discussed in Ref. [13]. Carbon monoxide forms *via* decomposition of a C(O) complex at the edge of a carbon crystallite. Carbon dioxide, which is known to be a primary reaction product [14], forms by interaction and simultaneous decomposition of adjacent edge and basal-plane C(O) complexes. Formation of CO requires cleavage of two C-C bonds and is straightforward. The transition-state complex for CO₂ formation is more complicated; it requires the simultaneous cleavage of three bonds (two C-C and one C-O bond) and the formation of one C-O bond.

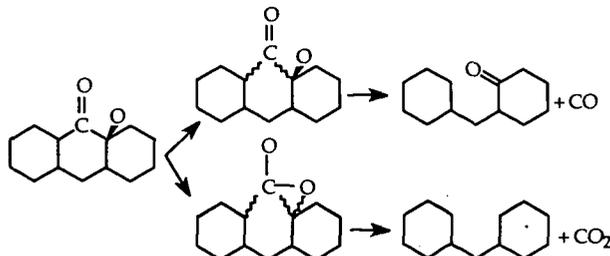


Figure 1. Proposed mechanism for CO and CO₂ formation in the C/O₂ reaction.

MOLECULAR ORBITAL CALCULATIONS

The objective of these computer simulations is to assess how the activation energy for C-C bond dissociation depends on the quantity and nature of surrounding C(O) complexes. The results of such calculations allow us to estimate the relative changes in the rates of CO and CO₂ formation as the concentration of edge and basal-plane oxygen atoms changes. In addition, bond energies for oxygen atoms on the basal plane were calculated in order to show that basal-plane oxygen can indeed exist on the surface at reaction conditions.

The calculations were performed using a molecular orbital theory package (MOPAC 5). The PM3 semiempirical parametric method with unrestricted Hartree-Fock Hamiltonian was used. A seven-ring structure (coronene) was chosen as a model for the carbon surface. The edges were saturated with either hydrogen or oxygen atoms (Figure 2). In addition to the basic structures *a*, *b* and *c*, structures with oxygen on the basal plane in various positions were considered. With the aid of MOPAC, the geometries of each model structure were optimized, and heats of formation of the resulting structures were calculated.

The bond energy of oxygen on the basal plane was calculated as an enthalpy change in the hypothetical reaction of oxygen atom removal from the surface. The resulting bond energies of the basal-plane oxygen in different positions are shown in Table I. It appears that the most stable position of oxygen is between two carbon atoms, rather than right above a carbon atom. This is in agreement with the findings of other authors [6-10]; the absolute values of bond energies are also in agreement with the literature data [7-9]. The rather large bond energies indicate that the basal-plane complex could be present on the surface, and should be included in the reaction mechanism.

Figure 3 shows how the heat of formation of several model structures changes as the distance between carbon atoms 1 and 2 increases and the coordinates of all atoms except 1 and 2 are allowed to relax. The smallest distance corresponds to the unbroken C1-C2 bond, and the largest distance corresponds to the broken C1-C2 bond (zero bond order). The point of maximum energy corresponds to the geometry of a transition-state complex. The difference between the heats of formation of the transition-state complex and the initial structure is equal to the activation energy of the C1-C2 bond cleavage reaction.

As the quantity of both edge and basal-plane C(O) complexes increases, the stability of the C-C bond is seen to decrease. For example, upon addition of a second edge oxygen atom, the activation energy of C1-C2 bond cleavage decreases from 64.7 kcal/mol (structure *b*) to 48.9 kcal/mol (structure *c*); similarly, it decreases from 30.7 kcal/mol for structure *b*₁ to 5.5 kcal/mol for structure *c*₁. More dramatic changes occur when additional basal-plane oxygen accumulates on the surface. The potential barrier diminishes from 64.7 to 30.7 kcal/mol (structures *b* and *b*₁, respectively), and from 48.9 to 5.5 kcal/mol (structures *c* and *c*₁, respectively). This result is in agreement with the important experimental fact that the activation energy for oxygen complex removal decreases as the surface coverage increases [15,16].

As it follows from the reaction mechanism shown in Figure 1, cleavage of the C1-C2 bond is a reaction path for CO formation. Therefore, the above results imply that the activation energy for CO formation decreases and the CO formation rate increases with increasing population of both edge and basal-plane oxygen on the surface.

Unfortunately, because of their complexity, no molecular orbital calculations of the potential barrier for CO₂ formation were done to date, and the influence of C(O) complexes on the rate of CO₂ formation was not determined. However, some speculative conclusions can be made on the basis of stability of the C1-C2 bond. Calculations show that for structures with basal-plane oxygen (*b*₁ and *c*₁), C1-C2 bond cleavage is an exothermic reaction; therefore, it is probably favored thermodynamically. For structure *c*₁, the exothermicity of bond cleavage together with a low activation energy (5.5 kcal/mol) implies that this structure is not very stable, and its transition to the structure with the broken C1-C2 bond is more favorable. This in turn suggests that structure *c*₁ does not give any CO₂ upon its decomposition. This will enhance the above mentioned relative increase in CO formation as the amount of oxygen on the surface increases.

In conclusion, the addition of edge oxygen to structure *b*₁ and addition of basal-plane oxygen to structure *c* both lead to an increase in the CO/CO₂ ratio in the products of decomposition of C(O) complexes present on the surface. In the next section, these predictions are compared with experimental results.

EXPERIMENTAL RESULTS AND DISCUSSION

In this section, the relative amounts of CO and CO₂ in the temperature-programmed desorption (TPD) patterns of two different carbon samples are analyzed as a function of the quantity of C(O) complexes on the surface.

Carbon samples were prepared by carbonization of petroleum pitch and cellulose at 1000 °C. Samples were oxidized at 600 °C in a mixture of 20% O₂/80% Ar until ~20% burnoff, and then cooled to room temperature at the fastest possible rate (~100 °C/min in the beginning of cooling) either in O₂ or in Ar. After cooling and without any exposure to air, the samples were analyzed by TPD. The products of surface oxygen complex decomposition were monitored by a quadrupole mass spectrometer.

The procedure of cooling the samples in different atmospheres allows one to prepare samples with different surface concentrations of C(O) complexes, while preserving the same total surface area; so the effect of surface area variations is minimized. During the cooling stage in O₂, chemisorption of oxygen produces additional C(O) complexes on the surface. Since gasification is not taking place, these complexes remain on the surface and are revealed in the subsequent TPD analysis. During the cooling stage in the inert gas, no additional oxygen chemisorption occurs; instead, desorption of the least stable (reactive) C(O) complexes takes place.

The TPD spectra of two pitch-based carbon samples are presented in Figure 4. In agreement with the work of Ranish and Walker [17] and Lizzio *et al.* [4], the sample cooled in O₂ has a much higher amount of oxygen on the surface; it also has a higher amount of CO in the decomposition products. Very similar results were obtained for two cellulose-based samples (Figure 5); although the total amount of C(O) complexes is much less dependent on the manner of cooling, the CO/CO₂ ratio is again higher for the sample that was cooled in O₂.

Therefore, the CO/CO₂ ratio in the products of TPD increases as the quantity of surface oxygen increases. This result is in excellent agreement with the results of molecular orbital calculations. An increasing amount of oxygen on the surface would lead to a larger proportion of structures of type *c*₁ relative to *b*, *b*₁ and *c*, of structures *c* relative to *b*, and of structures *b*₁ relative to *b*. According to the molecular orbital calculations discussed previously, all of this would lead to an increasing quantity of CO in the products of decomposition of these complexes.

It is important to emphasize that the observed increase in the CO/CO₂ ratio (in the products of TPD) with increasing quantity of C(O) complexes is exactly the opposite to what is commonly observed during carbon gasification in O₂. In agreement with the literature data [2], we have found that the CO/CO₂ ratio decreases as the total amount of C(O) complexes increases during gasification in O₂. In order to explain these different trends, which are thought to contain important mechanistic clues [18], further investigation of the effects of surface oxygen on O₂ chemisorption vs. C(O) complex decomposition is needed.

REFERENCES

1. Laine, N. R., Vastola, F. J., and Walker, P. L., Jr., *J. Chem. Phys.* **67**, 2030 (1963).
2. Phillips, R., Vastola, F. J., and Walker, P. L., Jr., *Carbon* **7**, 479 (1969); **8**, 205 (1970).
3. Taylor, R. L., Ph.D. Thesis, Penn State University (1982).
4. Lizzio, A. A., Jiang, H., and Radovic, L. R., *Carbon* **28**, 7 (1990).
5. Walker, P. L., Jr., Taylor, R. L., and Ranish, J. M., *Carbon* **29**, 411 (1991).
6. Bennett, A. J., McCarroll, B., and Messmer, R. P., *Phys. Rev. B* **3**, 1397 (1971).
7. Hayns, M. R., *Theoret. Chim. Acta* **39**, 61 (1975).
8. Barone, V., Lelj, F., Iaconis, E., Illas, F., Nino, R. and Jounou, A., *J. Mol. Struct.* **136**, 313 (1986).
9. Fromherz, T., Mendoza, C., and Ruetter, F., *Mon. Not. R. Astron. Soc.* **263**, 851 (1993).
10. Pan, Z., and Yang, R. T., *Ind. Eng. Chem. Res.* **31**, 2675 (1992).
11. Chen, S. G., Yang, R. T., Kapteijn, F., and Moulijn, J. A., *Ind. Eng. Chem. Res.* **32**, 2835 (1993).
12. Yang, R. T., and Wong, C. J., *J. Chem. Phys.* **75**, 4471 (1981).
13. Skokova, K., and Radovic, L. R., Proc. 22nd Biennial Conference on Carbon, 1995, San Diego, CA, p. 608.
14. Hart, P. J., Ph.D. Thesis, Penn State University (1966).
15. Vastola, F. J., Hart, P. J., and Walker, P. L., Jr., *Carbon* **2**, 65 (1964).
16. Ahmed, S., and Back, M. H., *Carbon* **23**, 513 (1985).
17. Ranish, J. M., and Walker, P. L., Jr., *ACS Preprints (Div. Fuel Chem.)* **32**(4), 132 (1987).
18. Ranish, J. M., and Walker, P. L., Jr., *Carbon* **31**, 135 (1993).

Table I. Bond energies of oxygen atom on the basal plane in different positions, in kcal/mol.

Structure	Position of oxygen on the basal plane			
	above C2	between C2 & C3	above C3	between C3 & C4
<i>a</i>	29.0	39.7	25.8	35.9
<i>b</i>	38.6	45.8	26.5	37.1
<i>c</i>	68.6	63.6	37.7	49.3

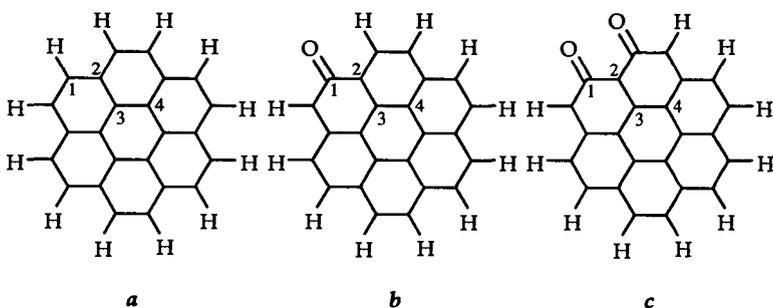


Figure 2. Model carbon structures used for molecular orbital calculations.

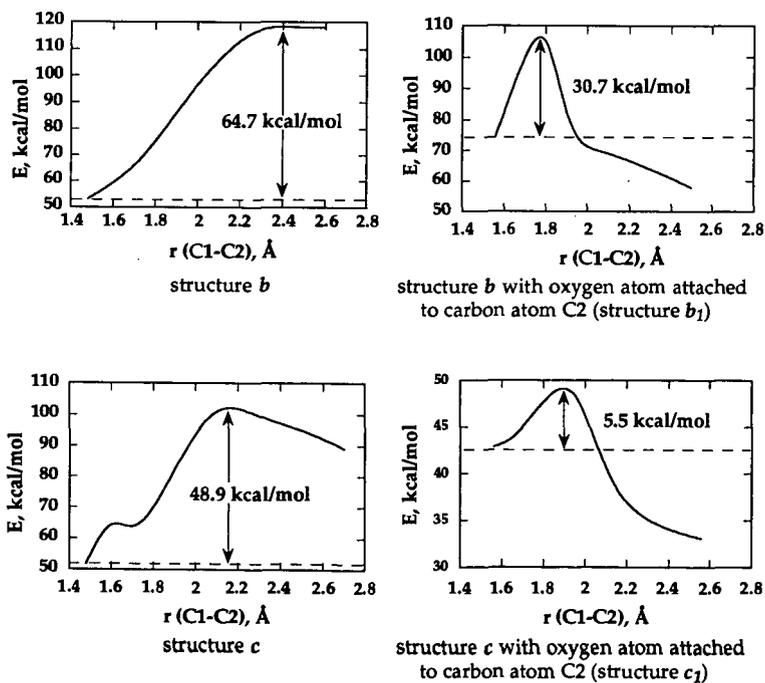


Figure 3. Potential curves for the reaction of C1-C2 bond cleavage.

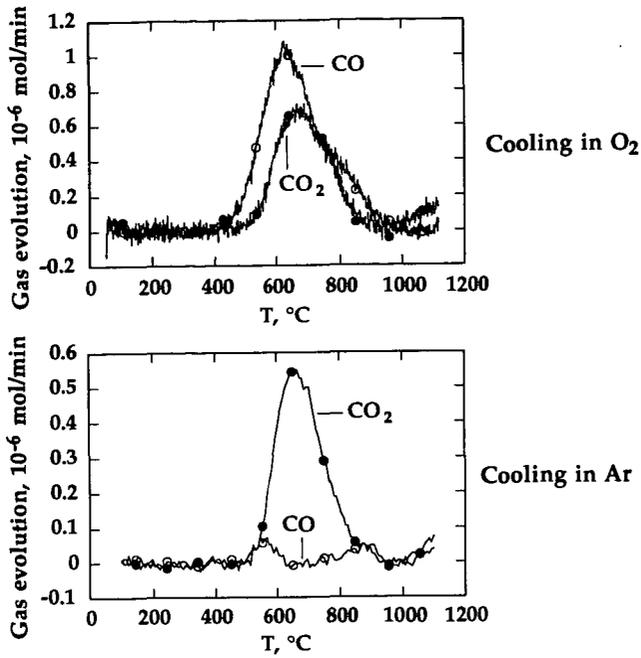


Figure 4. TPD profiles of petroleum pitch-derived carbon after gasification in O₂ until 20% burnoff followed by cooling in O₂ or Ar.

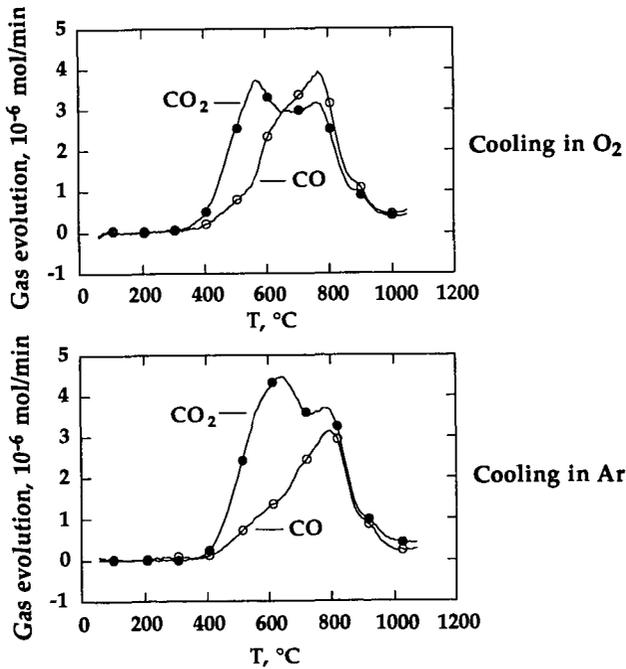


Figure 5. TPD profiles of cellulose-derived carbon after gasification in O₂ until 20% burnoff followed by cooling in O₂ or Ar.