

ANALYSIS OF THE REACTION OF CARBON WITH O₂ USING AB INITIO MOLECULAR ORBITAL THEORY

Takashi Kyotani, and Akira Tomita

Institute for Chemical Reaction Science, Tohoku University,

2-1-1 Katahira, Sendai 980-8577 JAPAN.

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INTRODUCTION

The mechanism of carbon gasification with oxygen has been widely studied. It is generally accepted that oxygen molecules chemisorb on carbon free sites to form surface oxygen complexes, C(O), which then desorb as CO₂ and/or CO. We attempted to clarify the mechanism of such reaction processes on carbon surface with several experimental techniques such as temperature programmed reaction and step response experiments using isotopically labeled reactants [1, 2]. In addition to these experimental approaches, molecular orbital (MO) theory is very helpful for the understanding of reaction mechanism. The usefulness of MO theory in the analysis of catalyzed and uncatalyzed carbon gasification has been demonstrated by many researchers [3-10]. Recently, using ab initio MO theory Yang *et al.* theoretically investigated desorption behavior of semiquinone, carbonyl and epoxy oxygen as surface oxygen complexes and discussed the mechanism of carbon gasification with oxygen-containing gases [11]. Furthermore, we have found that it is possible to simulate several experimental results of carbon-NO reaction when ab initio MO theory is applied [12]. Here, we attempted to analyze and simulate the chemisorption process of oxygen molecule and the formation of surface oxygen complexes on carbon edge sites using ab initio MO theory.

CALCULATION METHOD

Both the Gaussian 94 [13] and Gaussian 98 [14] packages were used to calculate molecular orbitals of model compounds for carbon-O₂ system. For simplicity, two types of single layer polyaromatic compounds with different sizes were employed as models for carbon. Figure 1 illustrates the structure of the two types of carbon models (models A and B) which have zigzag edge site on the upper side of each model. Some of carbon atoms are numbered for convenience. The edge atoms on the upper side are unsaturated and the rest of them are terminated with hydrogen atoms. A single O₂ molecule was put at a given distance from the zigzag edge in two different ways as shown in Figure 2. For side-on mode, the O₂ bond axis is parallel to the edge line. In the case of vertical mode, the bond axis was perpendicular to the plane of carbon model layer.

In order to investigate how O₂ molecule approaches the zigzag edge site of model A, we attempted to determine potential energy surface for each of the two approach modes (side-on and vertical). For such calculation, a grid for the position of the O₂ molecule was constructed near the edge site as shown in Figure 3, where each grid point was set in Y direction varying from 0.10 to 0.19 nm with an increment of 0.01 nm and in X direction from the right-hand C(1) atom to the most left-hand one with an increment of 0.01 nm. Thus, the shape of the mesh became square. The center of a single O₂ molecule was put on one of the points and then the following Energy calculation was done. First, the whole system including model A and the O₂ molecule was subjected to UHF (unrestricted Hartree-Fock) calculation with the basis set of 3-21G(d) with only O₂ bond distance optimized. Then, density functional method using the B3LYP functional with the basis set of 6-31G(d) was applied for single point energy calculation of the whole system with the optimized O-O distance. This energy calculation was done for all the grid points in Figure 3. For each grid point, the heat of adsorption, ΔH , was determined as a difference between the total energy of the calculated system and the sum of the energies of the corresponding carbon model and O₂ molecule. Since only O₂ bond distance was optimized in this grid calculation, the values of ΔH obtained are always a little larger than these determined by a full optimization calculation.

RESULTS AND DISCUSSION

From the grid calculation mentioned above, potential energy surface of O_2 on carbon zigzag site was determined for both side-on and vertical modes. The resultant surface is shown as two contour plots in Figure 4. The abscissa and the ordinate of each plot were defined as the distance in X direction from the right-hand C(1) atom in model A and the distance in Y direction from C(1) atoms, respectively. The coordinates in the horizontal axis correspond to geometrical position of the model drawn just below each contour plot. Since the potential energy surface was plotted in terms of ΔH , the thermal stability of the whole system can be evaluated from this value, i.e., the larger value the ΔH , the more unstable the system. For the potential energy surface in side-on mode, there are two minima located at the abscissas of 0.13 and 0.37 nm and at the ordinate of 0.14 nm. These two abscissas correspond to the positions of the two C(2) carbon atoms. This finding suggests that the center of O_2 molecule which is approaching model A goes toward either of the two C(2) atoms. Then, the O_2 molecule reaches the minimum at the ordinate of 0.14 nm to form surface oxygen species (model a) as illustrated in Figure 5, where O atoms are chemically bound to the C(1) atoms to form a five-membered ring. On the other hand, the result of the vertical approach was quite different from the side-on case. Since the observed three energy minima (Figure 4) are located at the abscissas corresponding to the positions of the C(1) atoms, the center of O_2 molecule is expected to go toward the C(1) atoms. As the result of such approaching, another surface oxygen species (model b) as shown in Figure 5 is formed at the ordinate of 0.12 nm. The species consists of a three-membered ring and from the energy contour map it can be seen that its thermal stability is lower than that of model a. In both the approach modes, the value of ΔH of each minimum in the contour plots is negative, indicating that the chemisorption of O_2 molecule is an exothermic process. This finding accords with the commonly observed feature for O_2 chemisorption on fresh carbon surface.

We put a single O_2 molecule at a distance of 0.13 nm from the zigzag site of model B in either side-on or vertical mode. Then the whole system including model B and O_2 was subjected to the ab initio calculation with all the geometrical parameters optimized. As a result, oxygen-containing species similar to model a is formed in the case of side-on mode and vertical approach gave model b-like structure. The heat of formation, ΔH , for each fully optimized structure was determined. For side-on and vertical approaches, the values were found to be -490 and -270 kJ/mol, respectively, which are not far from the observed one (-410 kJ/mol).

The process simulated in Figure 4 can be regarded as chemisorption of O_2 on fresh carbon surface without any pre-chemisorbed species. It would be worth elucidating the effect of pre-chemisorbed species on the O_2 chemisorption process. For this purpose, we investigated how the presence of either O or H atom on carbon surface influences the structure and the ΔH of the chemisorbed species on zigzag edge site. As a basic model of the edge site, we employed model B and bound one or two O atoms to the C(1) atoms as a quinone group. In the case of H atom, we terminated one or two zigzag edge carbon atoms by H atom. After the optimization calculation of these pre-chemisorbed models, we put a single O_2 molecule in the side-on mode on the edge sites. The final optimized structures are illustrated in Figure 6. In every case, a five-membered ring species similar to model a is formed upon the O_2 chemisorption. The values of ΔH are tabulated in Table 1, indicating that there is no noticeable change in ΔH , although the presence of a single C(O) increases the ΔH to some extent.

CONCLUSIONS

Potential energy surface of a single O_2 molecule on carbon zigzag site was determined by the ab initio MO calculation. It was concluded from such calculation that the way of how O_2 molecule approaches the zigzag site depends on the relative position of O_2 to the zigzag site, i.e., side-on or vertical mode. Furthermore, the MO theory predicts that the thermal stability of the O_2 -chemisorbed species formed in the side-on mode is higher than that of the vertical case. It was found that the presence of pre-chemisorbed species such as

C(O) or C(H) on zigzag edge site does not influence the structure and the ΔH of O_2 -chemisorbed species.

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Table 1 Heat of adsorption of O_2 -chemisorbed species. (ΔH for model B without any pre-chemisorbed species is -490 kJ/mol.)

Structure	ΔH (kJ/mol)
c	-550
d	-500
e	-480
f	-480

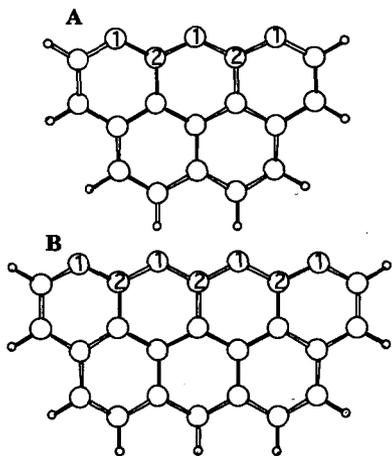


Fig. 1 Selected models of carbon. Large and small circles stand for carbon and hydrogen atoms, respectively.

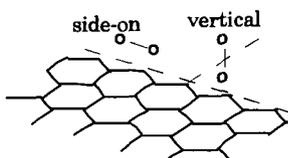


Fig. 2 Two positions of O_2 molecule near carbon edge site

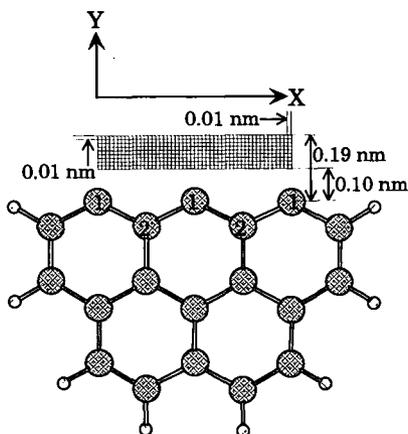


Fig. 3 Grid points for the energy calculation of the system of model A and O_2 molecule.

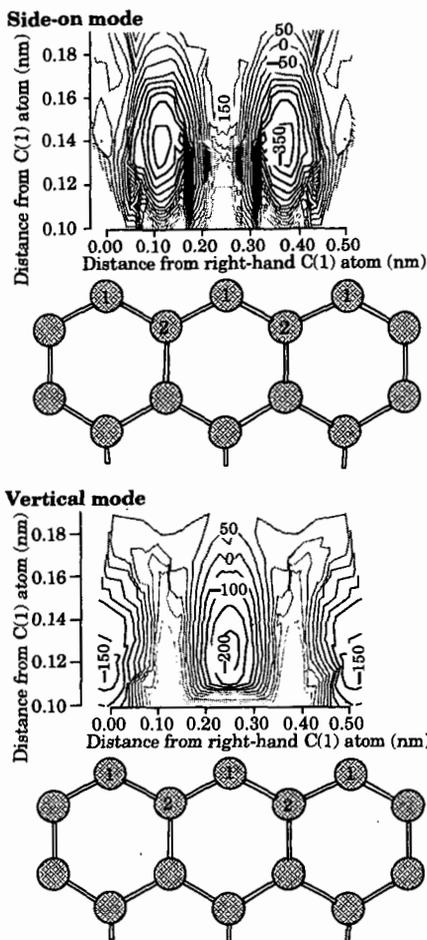


Fig. 4 Energy potential contour map for the carbon-O₂ system. Each contour line corresponds to a heat of reaction for this system and each line is drawn by the step of 50 kJ/mol.

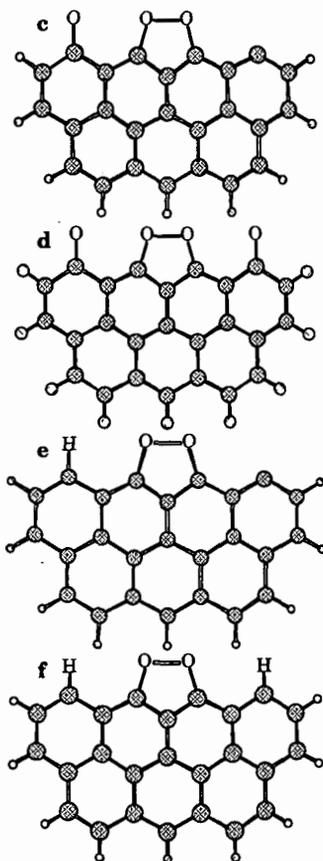


Fig. 6 Surface oxygen complexes formed by O₂ chemisorption on the zigzag site in side-on mode.

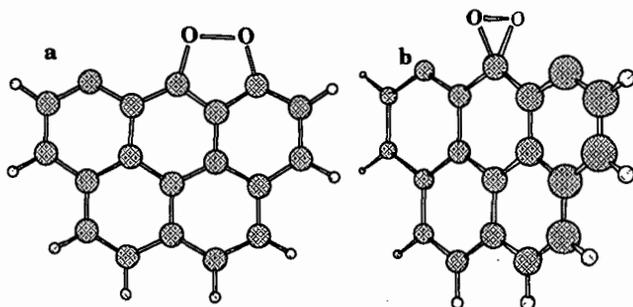


Fig. 5 Surface oxygen complexes formed by O₂ chemisorption on the zigzag site of model A in side-on and vertical modes.