# OXYGEN ADSORPTION ON NITROGEN CONTAINING CARBON SURFACES

*Alejandro Montoya‡, Jorge O. Gil‡, Fanor Mondragón‡ and Thanh, N. Truong**

‡Institute of Chemistry, University of Antioquia, Medellin, Colombia, A.A 1226, *Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

## Introduction

The reaction of $O_2$ with carbonaceous surfaces has been widely studied due to its important application in industry. In general, $O_2$ is first chemisorbed on an electron-rich site of the carbon basal plane of graphite and then, it dissociates into oxygen atoms.[1,2] Oxygen will diffuse on the surface until finds a structural defect to form covalent bonds. If temperature is appropriated, CO can be released to the gas phase. In char and open nanotubes structures, unsaturated carbon atoms at the edge of the carbon surface can form covalent bonds with oxygen. These sites can chemisorb directly molecular oxygen to form stable carbon-oxygen complexes with a high exothermicity.[3] Several ab initio molecular studies have been performed on the $O_2$-carbon reaction. For instance, Kyotani et al[4] studied the reaction of $O_2$ to the edge of a zigzag carbon structure at the DFT//HF level and found that the $O_2$ side-on adsorption mode is the most exothermic adsorption configuration. The same result was obtained by zhu et al[5] in the reaction of $O_2$ with single wall carbon nanotubes at the DFT level of theory and several carbon-oxygen complexes were found. Although studies on the $O_2$-carbon system abound, the reaction of $O_2$ with nitrogen containing carbonaceous surfaces is less known. The importance of nitrogen oxides in global warming and in stratospheric ozone depletion has motivated the study of NO and $N_2O$ evolution in the combustion and gasification. Therefore, our objective is to carry out oxygen adsorption on nitrogen containing carbonacesous surfaces. As a case study, we compare the thermodynamics of this reaction with the $O_2$-carbon reaction. As a tool we employed electronic structure calculations to get insight into the nature of nitrogen-oxygen complexes.

## Computational Details

We analyzed oxygen adsorptions to the edge of a carbon and a pyridine-type structure. The in-plane $O_2$ side-on approach was used to characterize the nature of carbon and nitrogen-oxygen complexes. Proposed carbon structures have several unsaturated carbon atoms at the edge of a graphene sheet to simulate chemisorption sites. A seven-six member ring structure in zigzag was used in both cases. Reactants, intermediates and products of reaction were fully optimized at the B3LYP density functional[6] using the 6-31G(d) basis set. Electronic calculations were done using the Gaussian 98 program.[7]

## Results and Discussion

**Formation of Surface Oxygen Complexes.** Initially, we studied the $O_2$-carbon reaction. Adsorptions on the carbon structure were carried out on the ground state. After approaching the $O_2$ molecule to the edge of the carbon model, two stable carbon-oxygen complexes were identified. First, the $O_2$ is adsorbed on two adjacent top sites forming a five member ring with an exothermicity of -112 kcal/mol, Figure 1a. Selected optimized geometrical parameters and Mulliken charges on selected atoms are shown in the same figure. As can be seen, a charge transfer from the carbon structure to the adsorbed gas molecule occurs. Therefore, due to the excess of Mulliken charge on the $O_2$, the O-O bond is activated and can be expanded from 1.50 to 2.25 Å to form two adjacent semiquinone groups with an exothermicity of -49 kcal/mol, Figure 1b. This is the most stable carbon-oxygen group identified. The total $O_2$ adsorption process was found to be -161 kcal/mol exothermic. We found an energy barrier of 1.4 kcal/mol to open the five member ring and form the two semiquinone groups. Notice that the energy barrier is very low and the second intermediate is the most stable. Hence, concentration of the five member ring structure should be low compared with the semiquinone structure at high temperatures.

For adsorption of $O_2$ on the pyridine-type structure, calculations were also conducted on the ground state. Oxygen adsorption was carried out over a nitrogen atom located at the edge of the carbon model and three stable nitrogen-oxygen groups were identified. First, after approaching the $O_2$ molecule, an stable structure is found where the N-O distance is longer than the C-O bond distance as depicted in Figure 1c. The adsorption is -46 kcal/mol exothermic. Then, if the N-O distance is further decreased, a stronger bond is obtained forming a five member ring with and endothermicity of 24 kcal/mol, Figure 1d. We found an energy barrier of 25 kcal/mol for this process. Though the energy barrier is large, the total adsorption process is –22 kcal/mol exothermic. Next, the five member is activated by a charge transfer and the O-O bond can be expanded from 1.512 to 2.630 Å to form a semiquinone and a pyridine-N-oxide group with an exothermicity of -73 kcal/mol, Figure 1e. This is the most stable nitrogen-oxygen group identified. We found an energy barrier of 2.9 kcal/mol to open the five member ring. The total $O_2$ adsorption process was found to be -95.6 kcal/mol exothermic. Then, pyridine-N-oxide complex can be a plausible NO precursor because of the small energy barrier and high exothermicity.

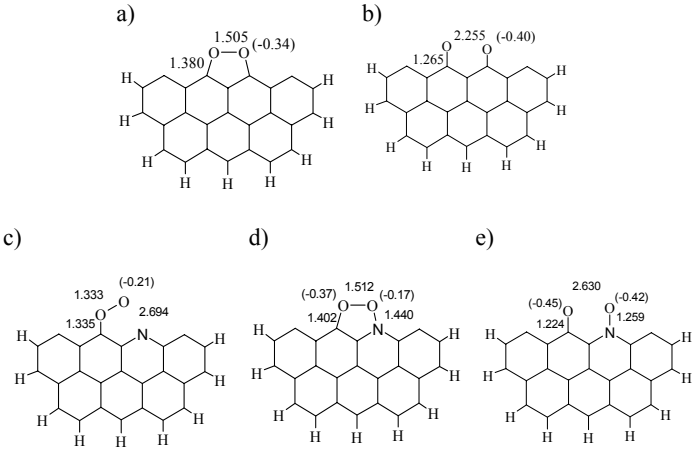


**Figure 1.** Adsorption of $O_2$ to the edge of a carbon and a pyridine-type structure. Structures (a) and (b) are intermediates on the $O_2$-carbon reaction. Structures (c) to (e) are intermediates on the $O_2$ pyridine-type reaction. Numbers are selected optimized bond lengths in Å. Numbers in parenthesis are Mulliken atomic charges in units of electrons.

**NO and CO Desorption.** Because of the unpaired electrons located at unsaturated carbon atoms representing the active sites, the molecular system has several low lying electronic states. As molecules desorb from the carbon surface, these electronic states can cross.[8] Careful examinations of such crossing allow us to correctly determine the potential energy profile. In a previous study we analyzed the desorption mechanism and kinetics of NO from a "clean" carbon structure and in fact electronic crossing occurs as NO

desorb.[9] The word "clean" is in the sense that no other oxygen groups different than those involved in the desorption process were present. Here, we studied the desorption of CO and NO in the presence of other oxygen groups making emphasis on the electronic states of the reactant molecules. Desorption is modeled from the most stable $O_2$ complexes obtained in the preceding section, namely the semiquinone and the pyridine-N-oxide structures, Figure 1b and 1e. The carbon and nitrogen atoms of the CO and NO groups, respectively, were pulled along the z axis and the remaining degrees of freedom of the carbonaceous surfaces are optimized, details of the procedure can be found elsewhere.[8] It was found in both desorbing structures that the carbon surface is relaxed to let CO and NO break away and then closes up to form a five-member ring as seen in Figure 2a-b.

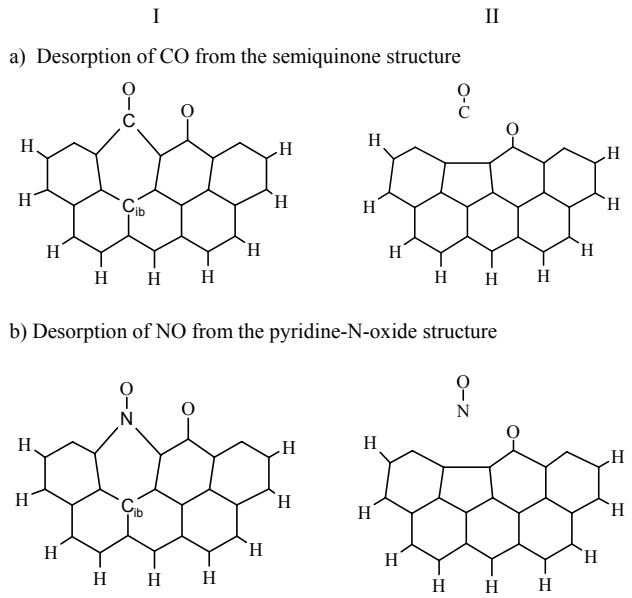


**Figure 2.** Desorption structures for CO and NO from a semiquinone and pyridine-N-oxide structures. I: The activated complex has a N-Cib and C-Cib distance of 3.8 Å. II: Reaction product.

The desorption energy has its maximum on the activated complex and it decreases as the desorbed specie distance increases from the carbon structure. As low lying electronic states can exist on the reactant molecules, the desorption energy barrier depends on the initial spin multiplicity selected. As comparison purposes, we have optimized the reactant and the activated complex at the two lowest electronic energies. Therefore, the energy difference between the two electronic states can be determined. Table 1 depicts the energy difference due to the change in spin multiplicity of the reactants and activated complexes. For reactants, it is seen that the energy difference between the two lowest electronic states is small. Then, one can expect that both electronic states are populated. As the desorbed molecule start to release, there is a change in the ground state from doublet to quartet and from singlet to triplet for CO and NO desorption structures, respectively. Notice that the energy difference in the activated complexes are larger than those of the reactants.

**Table 1. Calculated Electronic Energy Difference for Reactants and Activated Complexes. ***

| oxygen complex | | Reactant | Activated complex |
|---|---|---|---|
| Semiquinone | Ground state | Doublet | Quartet |
| | ΔE(GS-CES) | 5 | 18 |
| Pyridine-N-oxide | Ground state | Singlet | Triplet |
| | ΔE(GS-CES) | 0.02 | 21 |

* ΔE(GS-CES): Energy (kcal/mol) difference between the ground state and the closest electronic state

From the data in Table 1 it is seen that the spin multiplicity has an important effect on the desorption energy barrier. The difference can be as greater as 20 kcal/mol or higher. Electronic crossing not only is limited to clean carbon surfaces, it is also observed in the presence of other oxygen groups on the carbon surface and careful analysis should be done when considering the desorption patterns to obtain first principle kinetics data. Detailed analysis of the activation energies will be further discussed.

## Conclusion

Using density functional theories, the nature and the dynamic transformation of different carbon and nitrogen-oxygen complexes were analyzed. pyridine-N-oxide structure seems to be a plausible NO precursor during combustion of carbonaceous materials.

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