

COMPUTATIONAL CHEMISTRY OF ZIGZAG AND ARMCHAIR SITES IN CARBON OXIDATION

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Introduction

While the mechanism of the carbon/oxygen reaction is reasonably well understood, important mechanistic details and the ensuing kinetic quantification are still lacking. These are unlikely to be resolved easily in experimental studies, including those using transient methods. Fortunately, computational chemistry has come of age.

The reactivity difference between zigzag and armchair edge sites can be used as a litmus test for validating the computational chemistry studies. While such studies are increasingly popular, this key issue has not been addressed thoroughly since the pioneering investigations of Coulson [1] and Stein [2]. We report here our initial analysis of electronic structures of zigzag and armchair sites and of their role in adsorption and desorption of oxygen.

Computational Approach

The Gaussian 98 package [3] was used, with HF/6-31G(d) for geometry optimization and frequency calculations, and B3LYP/6-31G(d) for the self-consistent-field (SCF) energies. The bond energies were calculated according to the procedures introduced by Chen and Yang [4].

Results and Discussion

Model A1 cluster (Figure 1a) was assumed to represent well the essential features of zigzag edge sites. At the minimum on the potential energy surface (PES), its number of imaginary frequencies is 0 when spin multiplicity is 3; in contrast, when spin multiplicity is 1, there are two imaginary frequencies, implying a 2nd order saddle point. Therefore, as expected, there are two unpaired electrons in model cluster A1. The atoms-in-molecule (AIM) analysis provides additional evidence that the unpaired electrons are largely localized on the two edge sites. Analysis of molecular orbitals also suggests that 1-14 is a double bond, while 14-15 is a single bond.

Model cluster B1 (Figure 1b) was used to study the electronic structure of armchair sites. The minimum energy was obtained when spin multiplicity is 1, i.e., there are no unpaired electrons in model cluster B1. Bond 23-24 is essentially a triple bond, in agreement with previous studies [1].

The adsorption of O₂ on zigzag edge sites is also shown in Figure 1a. The formation of each C=O bond requires the

localization of an electron from the graphene π system. The associated energy change is shown in Figure 2: 408 kJ/mol is released upon non-dissociative chemisorption, while only additional 50 kJ/mol is released upon subsequent oxygen dissociation.

Adsorption on armchair sites is shown in Figure 1b: formation of C=O bonds here requires no participation of the graphene π system and the energies released in the two stages are of the same order (210 and 310 kJ/mol).

The model cluster shown in Figure 3 was used to study the desorption processes. There are four o-diketone oxygens on armchair sites (34, 35, 37 and 38) and one semiquinone (36) on a zigzag site. Because of the symmetric structure, we focus on bonds 28-35 and 30-36. The bond energy for CO release from o-diketone is 231 kJ/mol, 26% lower than for CO release from semiquinone. The C-C bond 27-28, saturated by O atoms on both ends, is indeed weaker than the C-C bond 28-29 with only one end connected to a semiquinone oxygen; accordingly, the length of the armchair C-C bond was calculated to be 0.1545 nm (significantly greater than 0.141 nm for a single C-C bond).

The ease of dissociative chemisorption of O₂ is thus expected to depend on the degree of delocalization of π electrons in the graphene layer. In particular, because of the different electronic structures of armchair and zigzag sites, chemisorption over the latter sites should be much more structure- (or cluster size-) sensitive. Our calculations do confirm this (Figure 4): more heat is released as the zigzag graphene layer size increases, while there is no such trend for the armchair structures.

These results may be yet another manifestation of the well documented compensation effect in carbon oxidation: while adsorption may occur more readily on the zigzag sites, desorption is clearly easier from the armchair sites.

References

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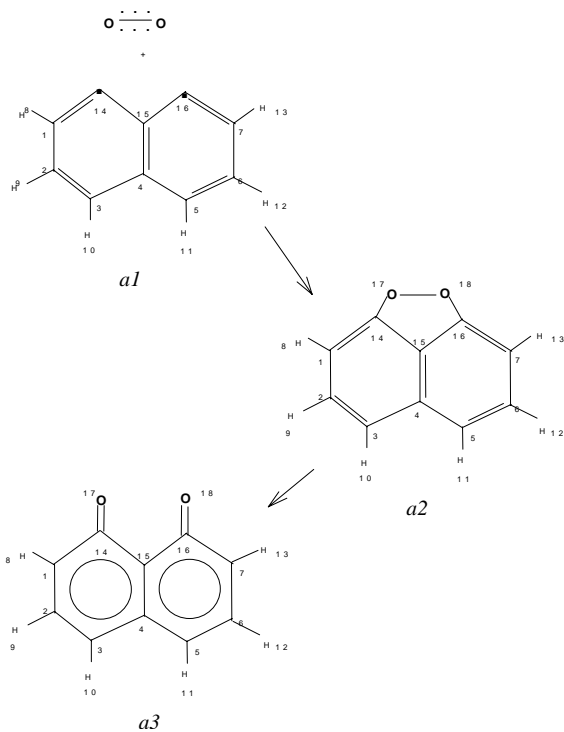


Figure 1 Adsorption of O_2 on zigzag (a) and armchair (b) model cluster.

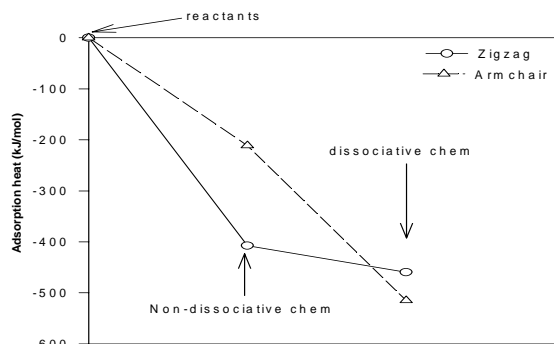
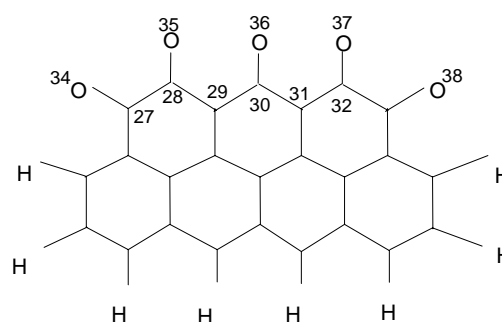


Figure 2 Heats of O_2 adsorption for model clusters (a) and (b).



O(36) - semiquinone oxygen

O(34), O(35), O(37), O(38) - o-diketone oxygen

model C

Figure 3 Model used to investigate oxygen desorption from o-diketone and semiquinone

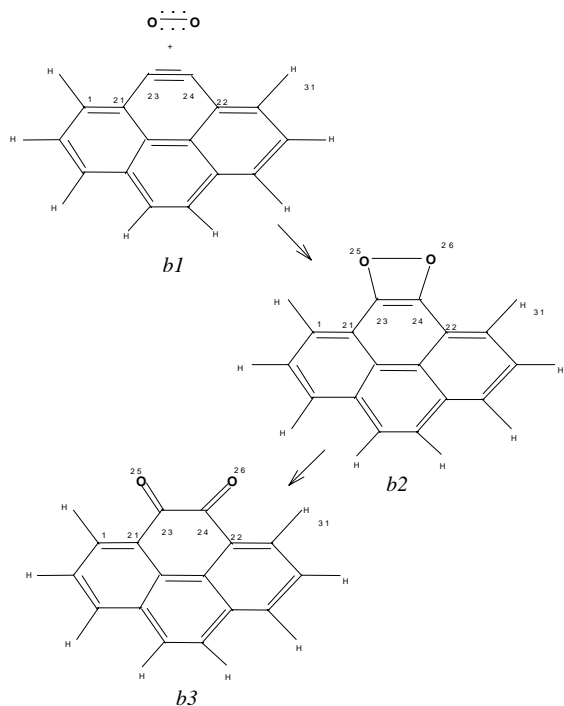


Figure 4 Dissociative O_2 adsorption heats for armchair and zigzag model clusters of different sizes