

MOLECULAR MODELING OF CARBON REACTIONS: SOME EFFECTS OF SURFACE CHEMISTRY AND GASEOUS REACTANT

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Introduction

There is increasing interest in modeling the structure and reactivity of carbons using first principles. Computational chemistry has certainly come of age [1, 2] and there is a rapidly accumulating literature even in carbon science [3-7]. Much uncertainty remains, however, regarding the relevance of the selected model structures and the ability of theory to address the truly important issues, especially those whose experimental clarification is either very difficult or too tedious. As part of an ongoing effort to use quantum chemistry to first elucidate the exact nature of carbon active sites and then quantify their concentration, here we focus our attention on the origin and structure of chemisorbed CO₂ on the zigzag sites.

In a recent study, Montoya et al. [8] concluded that the “adsorption energy depends strongly on the type of the local active site rather than on the size of the molecular model [structure].” Abundant experimental and some theoretical evidence does exist in support of this assessment, but much additional research is deemed necessary before we can confidently claim that “[t]hree stable carbon-oxygen complexes are formed due to the interaction of CO₂ with a clean carbon model, i.e., lactone, heterocyclic and furan-type complexes” [8]. For example, it is a well known fact that CO₂ chemisorption under the most relevant conditions (those of concomitant carbon gasification) is overwhelmingly dissociative [9, 10], producing gas-phase CO and a C—O surface complex (e.g., a semiquinone), and this should guide our theoretical analyses.

The objective of the present communication is to discuss the existence of structure A in Figure 1, in which the adsorbed CO₂ molecule occupies a single zigzag site. I explore the circumstances under which such outcome is thermodynamically favorable, especially in comparison with structures B and C, also shown in Figure 1; it is of interest that Montoya et al. [8], as well as Zhu et al. [11], do postulate its existence, but then dismiss it on the basis of the finding that it has “at least one imaginary frequency and thus do[es] not correspond to local equilibrium structure” [8]. In doing so, my broader objective is to illustrate the sensitivity of the results obtained to the assumptions made regarding the electronic configuration of the graphene layer; I will also argue here that insufficient attention has been paid to the latter point [12], with too many theoretical studies neither stating nor justifying such assumptions. Thus, for example, simply removing H atoms from the graphene edge as a means of

'creating' carbon active sites, without *critically* examining the resulting spin multiplicity (M) issues, is convenient but it may be both unrealistic and misleading; rather than using as a criterion the adoption of M values that result in the most energetically stable *final* structures [13], here we pay special attention to the *initial* structures. It is questionable whether such reactive free radical sites exist on the carbon surface in the initial stages of chemisorption and reaction; thus, for example, it is well known that they would not survive room-temperature air exposure and would be stabilized by O₂ chemisorption [14].

Theoretical Analysis

The Gaussian *ab initio* quantum chemistry software, either on a single personal computer or a cluster of PCs, was used to analyze the fate of an adsorbed CO₂ molecule when one or two adjacent zigzag sites are available for reaction. Density functional theory (B3LYP) and the 6-31G(d) basis set was used in most cases for geometry optimization, vibrational frequency analysis and calculation of thermochemical properties; this combination has been shown in many studies to be currently a very reasonable compromise between CPU demand and model realism. In particular, it incorporates electron correlation at a moderate cost of computer time; furthermore, spin contamination of open-shell systems (M>1) is much less of an issue than when the alternative Hartree-Fock formalism is used.

Results and Discussion

The results presented here are relevant to the initial stage of the CO₂ gasification mechanism, some of whose possibilities are illustrated in Figure 1. The following key points are to be noted. (1) We agree with Montoya et al. that "[f]ormation of the lactone carbon-oxygen group is the most exothermic reaction" [8]; it is intriguing to note, however, that in all cases the presence of two unpaired electrons in the model graphene layer (M=3) results in a *lower* adsorption exothermicity. (2) Single-site CO₂ adsorption (structure A) is not thermodynamically favored when two adjacent zigzag sites are free: the optimized structure reverts to either structure B or structure C.

In order to explore the reasons for these findings and their implications, the following optimized geometries were analyzed in more detail: (1) C₁₈H₁₀—CO₂, M=1, with both C10 and C14 as free sites; (2) C₁₈H₁₀—CO₂, M=1, with C10 and C7 as free sites, the latter representing a carbene-type carbon atom; (3) C₁₈H₉O—CO₂, M=2, with C10 and C14 as free sites; (4) C₁₈H₈O₂—CO₂, M=1, with C10 and C14 as free sites, the latter being a carbene-type carbon atom. Analysis of vibrational frequencies (typically in the range 50-3000 cm⁻¹) showed that none of these model structures represent saddle points or transition states.

Rather convincing evidence for CO₂ dissociation will be provided. The consequent Occam's razor argument – contrary to what one might infer from Figure 1 and from the conclusions of Montoya et al. [8] is that single-site dissociative adsorption is the dominant pathway for CO₂ chemisorption on zigzag sites. This is illustrated in Figure 2. The corresponding reaction enthalpies (see

also Figure 1) are favorable: -18.9 kcal/mol (M=2) for reaction (a) and -43.9 (M=1) and -34.8 (M=3) kcal/mol for reaction (b). It will be interesting to test the intuitively appealing assumption that the former reaction is more important in advanced stages of CO₂ gasification (when bond-breaking desorption processes can generate such intermediate reactive radicals), whereas the latter is dominant in its initial stage. Structures B and C in Figure 1 would then be relegated to CO₂ chemisorption in the absence of gasification and/or the formation of a stable complex, which is known to temporarily inhibit the reaction rather than serve as a reactive intermediate and which is typically not as important, from a kinetic standpoint, as it is in O₂ gasification [15].

These results are also thought to provide further evidence for the proposed importance of carbene-type edge sites in carbon materials [12, 16]. The consequences of this proposal will be examined further as part of our comprehensive modeling studies of both singlet and triplet carbene structures and their key roles in carbon gasification.

Conclusion

A principal channel for CO₂ chemisorption on the zigzag graphene edge appears to be the dissociative adsorption on carbene-type active sites.

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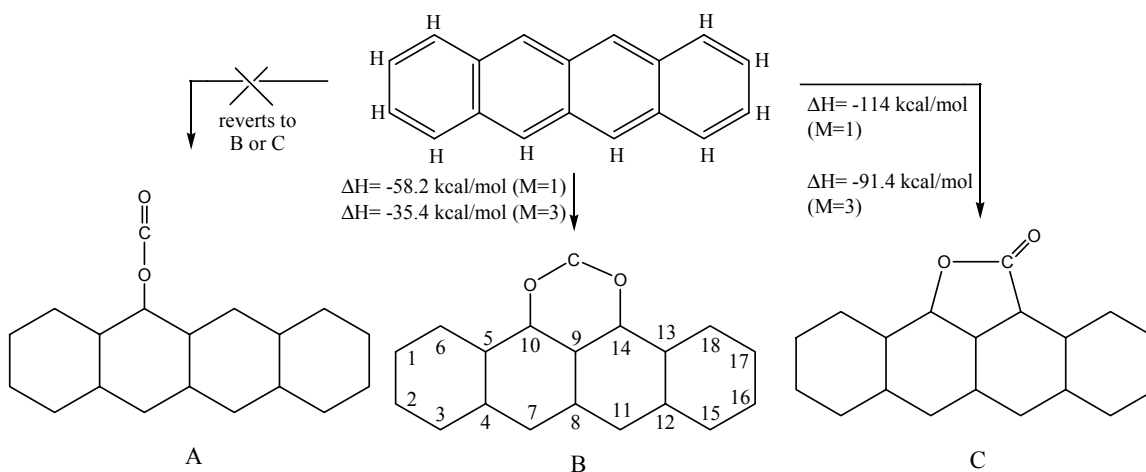


Figure 1. Three hypothetical pathways for chemisorption of CO₂ on the graphene layer having two free and adjacent zigzag sites.

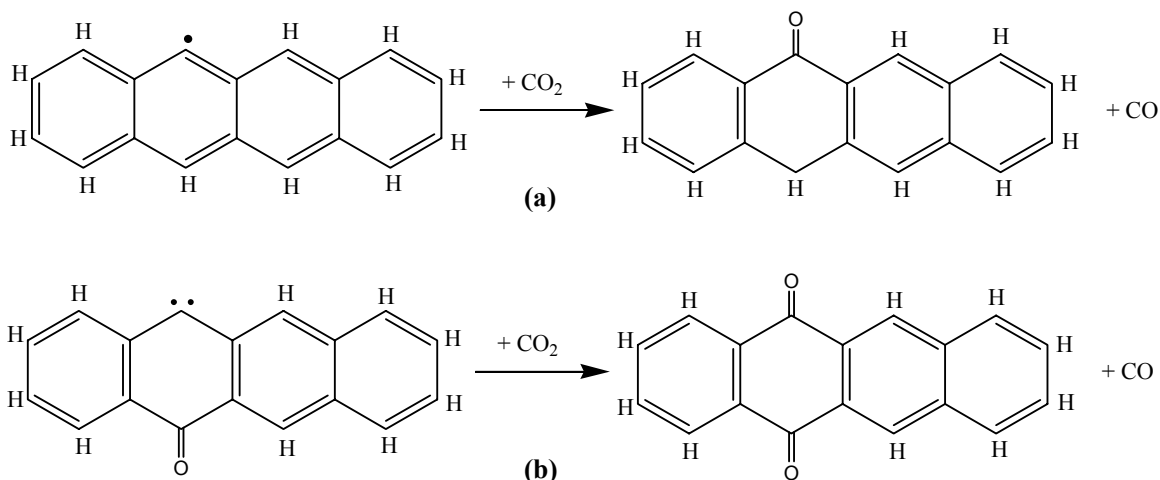


Figure 2. Proposed principal pathway for CO₂ chemisorption on zigzag sites in a graphene layer: (a) advanced stages of gasification (burnoff level > 0%); (b) initial stage of gasification (burnoff level = 0%).

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