

# ON SOME KEY QUESTIONS IN THE APPLICATION OF COMPUTATIONAL CHEMISTRY TO CARBON REACTIVITY

Ljubisa R. Radovic<sup>1</sup> and Bradley Bockrath<sup>2</sup>

<sup>1</sup>Department of Energy and Geo-Environmental Engineering, The Pennsylvania State University, University Park, PA 16802

<sup>2</sup>National Energy Technology Laboratory, U. S. Department of Energy, Pittsburgh, PA

## Introduction

There is no question that computational chemistry has come of age, even for the analysis of complex gas-solid interaction issues such as carbon reactivity. Thus, for example, on March 28, 2001 the Web of Science (Institute of Scientific Information, www.webofscience.com) listed hundreds of scientific papers that report the use of the commercially available Gaussian 98 software package. What has become the main challenge is to steer this budding research toward answers to “legitimate” questions, answers that have been difficult to obtain by experimental means, answers that are of greatest interest to carbon researchers. It is quite tempting to take from the commercially available programs the information that they routinely provide and thus offer answers to uninteresting, hard-to-understand or even irrelevant questions.

The reactivity difference between zigzag and armchair edge sites is a case in point. Elsewhere at this Conference we argue that this issue can, and indeed should, be used as a litmus test for the potential usefulness of computational chemistry in furthering both our qualitative and, especially so, our quantitative understanding of carbon reactivity. Here we address the following two issues:

(a) How does carbon site reactivity depend on the nature of the graphene layer edges?

(b) Which computational parameters can be used for an a priori quantification of site reactivity?

In previous experimental studies [1] we have provided indirect evidence for the existence of partially stabilized radical sites at graphene layer edges. Contrary to the statement by Stein [2] that they involve “stabilization by *delocalization*” (emphasis added), the postulated stabilization is thought to involve *localization* of itinerant  $\pi$  electrons, presumably by virtue of formation of “in-plane  $\sigma$  pairs,” i.e.,  $\pi$ - $\sigma$  electron pairs, perhaps analogous to those existing in divalent carbenes. It is of course not surprising that Stein [2] had not “found [any] basis for [the existence of these] sites”: Hückel molecular

orbital (HMO) theory does not analyze  $\sigma$  electrons explicitly. So we must revisit this neglected issue using *ab initio* methods.

## Computational Methods and Model Structures

The Gaussian 98W software package [3] was used in most calculations. Figure 1 shows the structures [2] that were selected for closer scrutiny. A comparison with the aromatic carbene structures is of special interest. Comparison of Mulliken spin densities, atomic charges and dipole moments obtained using HF/3-21G\* and B3LYP/6-31G(d) vs. a method that includes configurational interaction (e.g., CASSCF) should lend confidence in the ability of the former two approaches to deal with unpaired electrons at free carbon sites.

## Results and Discussion

The most fundamental expression for carbon reactivity, which at the same time describes the practically relevant mass loss rate (the mass of carbon consumed per unit residual mass and per unit time), is the following one:

$$R = \{ \text{Site reactivity} \} \{ \text{Number of reactive sites} \}$$

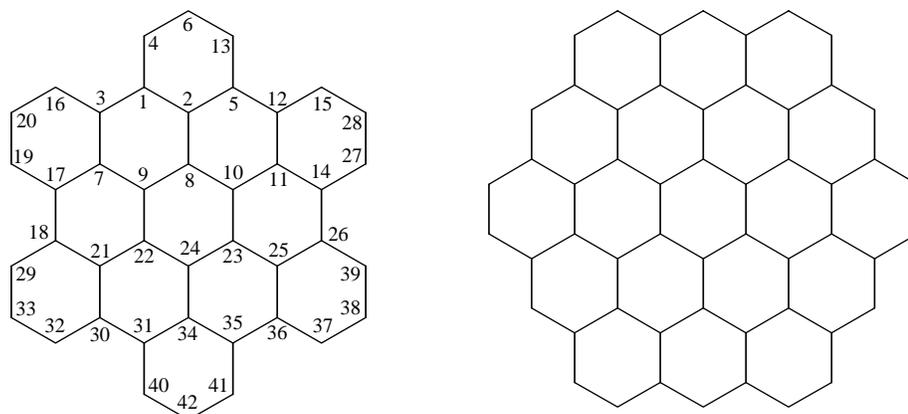
In experimental studies the number of reactive sites has been measured by transient kinetics and temperature-programmed desorption techniques. The intrinsic site reactivity (or turnover frequency) is then inferred, and analyzed for its dependence on temperature or carbon type, from the ratio of chemically controlled reaction rate to the number of reactive sites. A more direct theoretical method to determine turnover frequencies is desirable. For example, we used a combination of HMO theory and Monte Carlo simulation to study carbon reactivity profiles, and free valence indices were used to quantify site reactivity [4]. Our objective here is to use a unique set of more fundamental indices – such as electron density (in the case of adsorption) and bond strength (in the case of desorption) – to evaluate both parameters directly and simultaneously. In such an approach, the number of reactive sites is

automatically determined by the threshold level of site reactivity. Three basic cases will be discussed: (a) termination with H-atoms; (b) termination with O-atoms; and (c) termination with free carbon (stabilized radical?) sites. Figure 2 shows how the degree of  $\pi$ - $\sigma$  coupling in the orbital population of carbon atoms changes as a function of their distance from the graphene layer edge.

## References

1. Menendez, JA, Xia B, Phillips J, Radovic LR, *Langmuir* 1997; 13; 3414-20.
2. Stein SE, *Acc. Chem. Res.* 1991; 24: 350-6.
3. Frisch MJ et al., Gaussian 98, Gaussian, Inc., Pittsburgh, PA, 1998.
4. Kyotani T, Ito K-I, Tomita A, Radovic LR, *AIChE J.* 1996; 42: 2303-9.

**Figure 1.** Model structures used: left, armchair edges (A); right, zigzag edges (B).



**Figure 2.** Distribution of charge in model structure A (RHF 3-21G\*/6-31G(d)): upper graph, from left to right, carbon atoms 19, 17, 7, 9, 8; lower graph, from left to right, carbon atoms 6, 2, 8.

