

# ON THE MOLECULAR MODELING OF CARBON GASIFICATION KINETICS

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## Introduction

In almost all gasification reactions the key to the understanding of the kinetics is the quantitative and qualitative analysis of the fate of carbon-oxygen surface complexes. While it is well known that a distribution of desorption (and adsorption) energies exists for CO and/or CO<sub>2</sub>, as a function of both the nature of the carbon material and its burnoff level, it is often sufficient [1] to divide the surface complexes into two groups, denoted C–O and C(O). The C–O ‘spectators’ accumulate on the surface during reaction; they are temporary inhibitors because their turnover is much inferior to the ‘average’ turnover frequency. The C(O) complexes are true reaction intermediates because their residence time on the surface is much shorter. An additional complication is the now well established induced heterogeneity effect: the presence of C–O complexes destabilizes the adjacent free carbon active sites and/or the desorption of products leads to the formation of highly reactive, though transient, ‘nascent’ active sites [2,3].

These phenomena have been the focus of carbon gasification research for the last four decades [4]. The principal tools in this research have been experimental: analysis of rates vs. heat-treatment conditions [5,6], rates vs. burnoff levels [1], temperature-programmed desorption [7], and transient kinetics [1,8]. With the advent of readily available molecular modeling software, computational tools can now complement, and in some cases replace, some of these experiments. However, the reliability of the conclusions obtained with these tools has yet to be demonstrated; the temptation to treat them as “black boxes” is often irresistible.

Here we begin to address one of the crucial issues: How do the various commercially available computational tools deal with the fundamental problem of oxygen coverage on the carbon surface? Several two-dimensional approximations of graphene layers are adopted and the effects of their

burnoff and surface oxygen accumulation are scrutinized. Simple Hückel molecular orbital (HMO) theory, several semi-empirical models (e.g., AM1 and PM3), as well as an *ab initio* approach are considered [9].

## Model Structures

Figure 1 shows some of the model structures under consideration. The key features are (a) the presence of increasing amounts of surface oxygen, which is invariably detected as carbon burnoff increases [1,6,10], and (b) the mobility of surface oxygen on the basal plane.

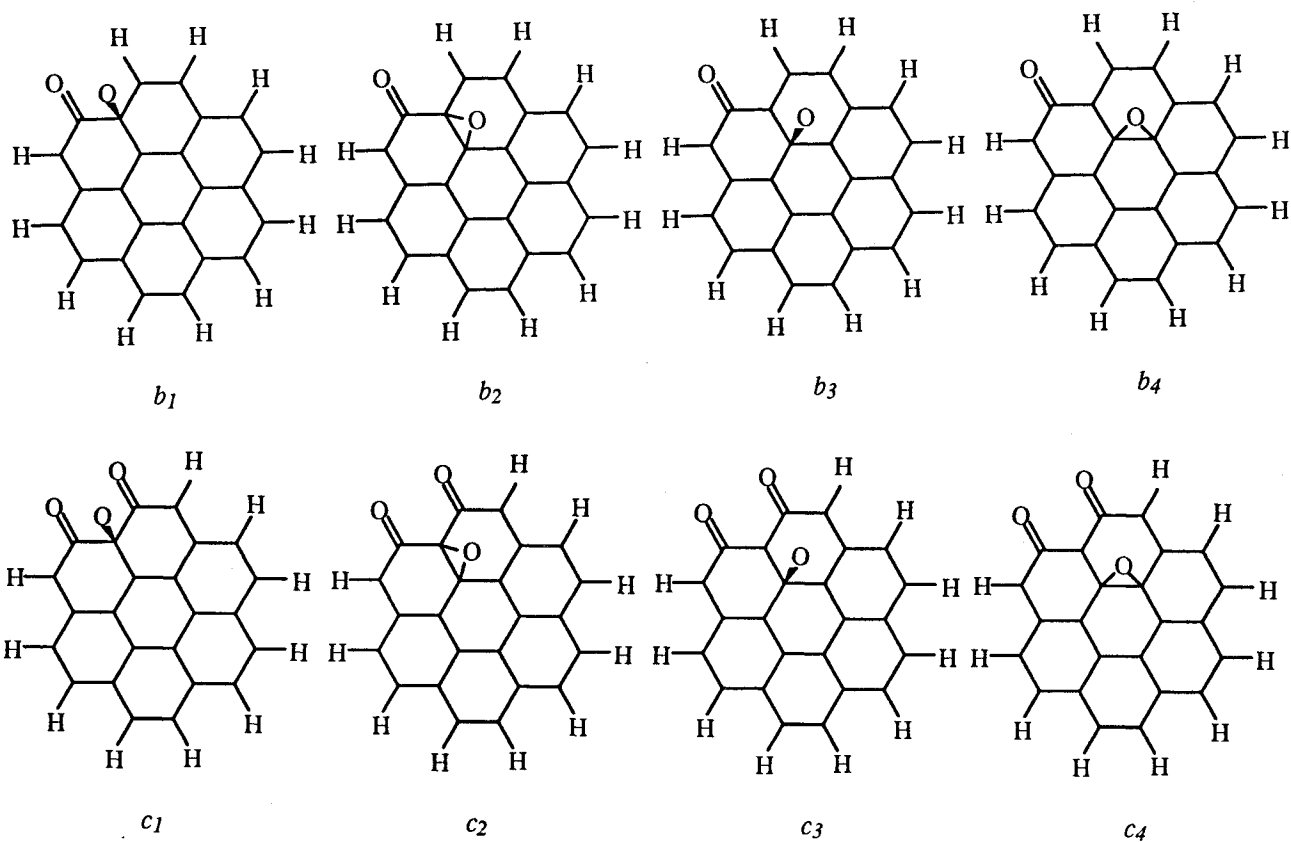
## Preliminary Results

The relative roles of edge and basal-plane oxygen in carbon gasification are of primary interest here. Previous applications of molecular orbital theory have not only confirmed the *presence* of surface oxygen on the basal plane (to be distinguished from *chemisorption* of oxygen onto the basal plane) but have also suggested that this oxygen is mobile (with an activation energy of ~11 kcal/mol) [10]. It remains to be shown how sensitive this conclusion is to the electronic configuration of the graphene edges and to explore its kinetic consequences.

Table 1 summarizes the bond energies of an oxygen atom on the graphene layers shown in Figure 1. The most stable position appears to be between two carbon atoms. The energies are seen to depend on both the position of oxygen with respect to the edge carbon atoms and the amount of edge C–O complexes. In particular, they increase when surface oxygen is closer to the graphene layer edge and as the concentration of edge C–O complexes increases. This means that, as gasification proceeds and the population of surface oxygen increases, the basal-plane oxygen becomes an increasingly stable configuration on the surface. The dependence of these and other trends on model selection will be reported.

## References

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**Figure 1.** Model carbon structures with oxygen atoms on the basal plane in different positions (structures a1-a4 are identical to b1-b4, except that hydrogen is bound to the C1 carbon instead of oxygen).

**Table 1.** Bond energies of an oxygen atom on the basal plane (kcal/mol, PM3 semiempirical method).

Structure	Position of oxygen on the basal plane			
	Above C2	Between C2 & C3	Above C3	Between C3 & C4
a	29.0	39.7	25.8	35.9
b	38.6	45.8	26.5	37.1
c	68.6	63.6	37.7	49.3