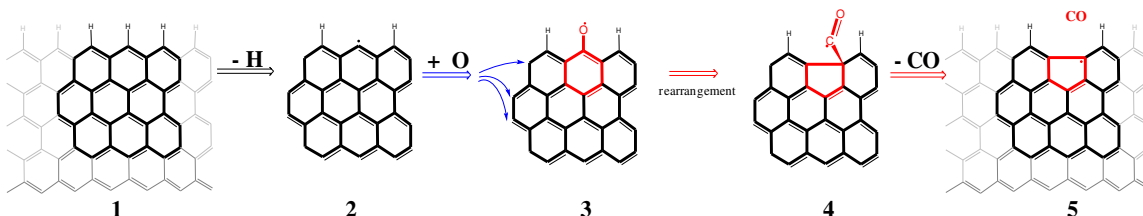


## Reaction Pathways of Soot Oxidation: Simple Models

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Graphene has recently provided scientists and engineers with enormous opportunities for materials science applications. Graphene can be found as a single sheet or folded in various shapes, most notably as nanotubes. Our interest in graphene lies in deciphering its processes of growth and fragmentation. In particular, we seek understanding of the oxidation initiated fragmentation process; illustrated in the figure below. It is a localized event that makes possible the treatment, without loss of generality, of a subsystem rather than an entire graphene sheet.



We have benchmarked several commonly used DFT methods and variants of the MP2 method at all stages of oxidation. These methods were chosen because of their relatively low cost and consistent quality of reported geometries and energies of structures. The goal is to establish a modeling approach that gives consistent results at least for single- and multi-layer PAHs. The B3LYP approach was found adequate for quality of geometries, energies, and topography of potential energy surfaces. Currently, research is proceeding in the following directions: establishment of where O atom prefers to bond to a graphene edge and mapping rearrangement pathways of the phenoxy-radical moiety with subsequent loss of CO. These steps have been achieved for systems consisting of one to six benzene rings in all isomeric variations. The approach is currently being extended to larger motifs such as graphene patches of 3x3 (above), 4x4 up to 7x7 with both zigzag and armchair edges. These systems require more extensive theoretical analysis because the ground states of large PAHs are often polyradical. Once we have characterized the larger systems, established the thermodynamic stability of the oxygenated systems, and revealed the pathways of molecular rearrangements, we shall carry out quantum Monte Carlo calculations to obtain accurate energies to facilitate validation of the oxidation mechanism.

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