Theoretical Framework for Modeling Soot Oxidation

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The demand combustion processes place on the environment will almost certainly grow in the coming decade. This issue places a great demand on the need to understand and control the byproducts of fossil fuel combustion. One particularly detrimental byproduct is soot, which makes efforts to mitigate its production of fundamental interest. It has been established that soot is largely composed of polycyclic aromatic hydrocarbons (PAH) and that oxidation of these species is the current primary pathway by which it is destroyed. However, experimental data for these processes is often difficult or impossible to obtain for various reasons. The development of theoretical models for assessing the stability of these oxidized species is critical for understanding and controlling processes that involve these materials. Additionally, these systems are believed to serve as models for graphene oxidation. Graphene has recently been identified as a promising object of materials science research and development.

The following hierarchy of models has been adopted for graphene research: single-layer PAH models a saturated zigzag graphene edge; multi-layer PAH models sections (patches) of a graphene surface with various combinations of zigzag and armchair edges; graphene patches model constituent parts of soot. Therefore, the relationship between structure and reactivity of soot can be described using structure/property relationships established for PAHs and can be validated or disqualified by studying graphene.

For the linear oxyradicals of PAH (PAHO), we have established a simple connection between local electronic structure and overall stability of the system. The resulting intuitive chemical model based on the concepts of delocalized bonding and aromaticity rationalizes properties of a graphene edge with oxygen at different positions. The model can be applied to the description of multi-layer PAHO. In addition, it is anticipated that fundamental concepts of reactivity may be applied to explain the behavior of the PAHO in CO abstraction. The important result in this direction is establishing reaction pathways of the rearrangement of oxyradical moiety and subsequent loss of CO.

A related direction is the establishment of a computational framework that can be used over the range of model objects from linear PAH to interacting graphene moieties in soot. We have benchmarked several quantum chemical methods for these systems. These include density functional (DFT) methods, Moller-Plesset perturbation theory, and quantum Monte Carlo. The latter will ensure very accurate energy profiles along the reaction pathways for the systems at a level of treatment of electron correlation not accessible with the other methods.

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