From PAHs to Soot: A Theoretical Exploration of Molecular Growth and Reactivity

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Persistent organic pollutants (POPs) are a major class of environmental contaminants, with polycyclic aromatic hydrocarbons (PAHs) being a particularly toxic subclass. PAHs primarily form through incomplete combustion processes, including coal burning, incineration, waste burning, and fuel combustion. Structurally, they consist mainly of fused benzene rings, though some also incorporate pentagonal rings. A key characteristic of PAHs is their ability to grow into larger and more complex structures through successive reactions, ultimately leading to soot formation.

The environmental and health risks associated with PAHs stem from their ability to form increasingly toxic compounds via radical-mediated mechanisms. These reactions typically begin with hydrogen abstraction, generating reactive radical sites that facilitate further molecular growth. To systematically identify potential reaction initiation points, the C-H bond dissociation enthalpy (BDE) values of 16 priority PAHs were determined. Six density functional theory (DFT) methods (B3LYP, B3LYP-D3, B97D3, M06-LD3, M06-2X-D3, and ωB97X-D) were applied in combination with four basis sets (6-31G(d), 6-31+G(d,p), 6-311++G(d,p), and def2-TZVP), and the most suitable combination was selected. The BDE values and corresponding bond lengths helped pinpoint the most reactive sites. It was found that the most reactive sites are predominantly armchair and peak hydrogen positions, with fluorene exhibiting the lowest BDE and acenaphthylene the highest, where hydrogens were aliphatic and in peak positions, respectively.

Hydrogen abstraction reactions were further investigated for 10 parent PAHs using the ωB97XD/6–31+G(d,p) level of theory, with hydrogen (•H), hydroxyl (•OH), and methyl radicals (•CH3) as reaction partners. Quantum theory of atoms in molecules (QTAIM) analysis provided insights into electron density at bond critical points, revealing a correlation between BDE values and activation energy. These findings enhance the understanding of PAH growth mechanisms, their environmental persistence, and their role in air pollution and human health risks.