

# Soot Formation in Fuel Combustion – the Role of Aromatic Diradicals

Enoch Dames and Hai Wang

Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089-1453, USA

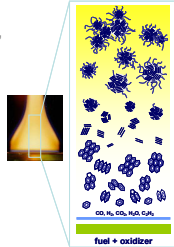
**Background:** A generally undesired byproduct of fossil fuel combustion, soot is one of the most prevalent anthropogenic aerosols, affecting atmospheric visibility, global climate, and human health. Soot formation in flames is a highly reversible process driven, in part, by two competing thermodynamic forces: enthalpy release from chemical bond formation and entropy increase due to release of gas phase species accompanying particle formation. This poster presents our current understanding of soot formation in flames and describes the potential role of aromatic polyradicals in filling key knowledge gaps.

## Impacts of Soot



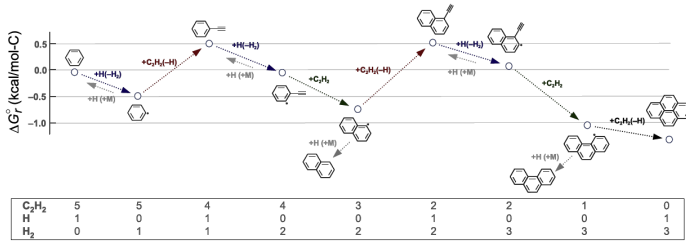
sources: vehicular exhaust, power generation, cooking, volcanism

- atmospheric visibility
- deleterious effects on human health
- bioaccumulation in flora and fauna
- climate impact through positive and negative radiative forcing

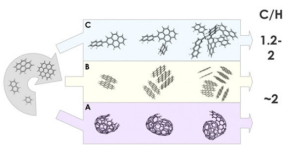


## Aspects of Soot Formation

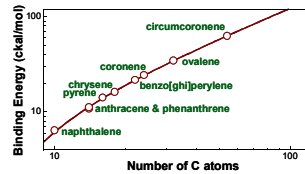
Soot nucleates from polycyclic aromatic hydrocarbons. In this example,<sup>1</sup> standard Gibbs function per carbon atom is plotted relative to an initial system with benzene : acetylene : H atom = 1 : 5 : 1 at 1800 K. The molecular growth process is seen to be highly reversible and kinetically controlled.



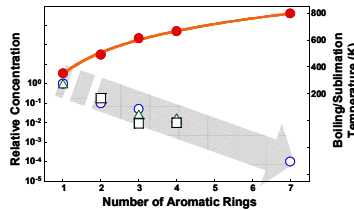
Three conceptual mechanisms of soot particle nucleation:



The van der Waals self-binding energies of many PAHs are known:<sup>2</sup>

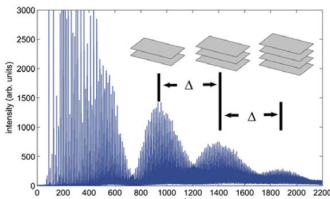


As indicated by their boiling/sublimation temperatures, only larger PAHs are capable of dimerizing within the hot temperature environment inherent to flames:



Relative concentrations and normal boiling/sublimation temperatures of selected PAHs in the HACA sequence of reactions (1-, 2-, 3-, 4- and 7-numbered aromatic rings are benzene, naphthalene, phenanthrene, pyrene, and coronene, respectively): circles: 90-Torr burner-stabilized acetylene flame<sup>3</sup>; triangle: 30-Torr toluene flame ( $\phi = 1.9$ );<sup>4</sup> 30-Torr benzene flame ( $\phi = 1.78$ , relative to naphthalene).<sup>5</sup>

Above a certain size, PAHs interact with each other to form stacked structures, but the way in which they do so is still uncertain.



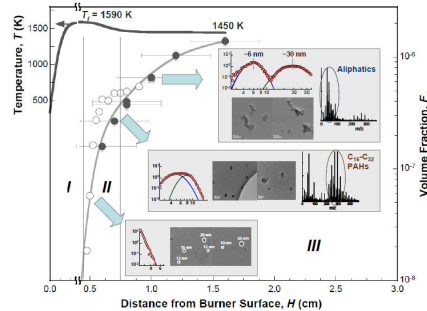
Mass spectrum of high-molecular weight species extracted from a 100-Torr acetylene-oxygen flame ( $\phi = 3.25$ ) by molecular beam mass spectrometry with 193 nm laser ionization (Courtesy of H.-H. Grotheer).

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## Unresolved Aspects of Soot Formation

- current models cannot predict soot mass growth in post-flame regions, where growth can occur without the presence of H atoms
- formation of aromatic core/aliphatic shell in nascent soot



Temperature profile and soot volume fraction of a burner-stabilized laminar premixed ethylene-oxygen-argon flame ( $\phi = 2.5$ ).

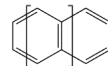
Experimental evidence supporting the above points:

- Particle sizes determined from mobility scanning<sup>6</sup> and TEM<sup>7</sup>
- Chemical composition determined by photoionization aerosol mass spectrometry<sup>8</sup>
- Soot volume fraction by small angle neutron scattering<sup>9</sup> and thermocouple particle densitometry<sup>6,9</sup>

Zone I – Flame region  
Zone II – Onset of soot nucleation  
Zone III – Particle aggregation and bimodality; soot volume fraction continues to increase

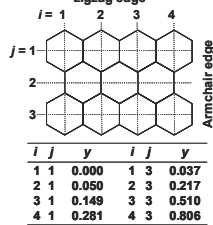
## Possible Role of Aromatic Radicals

Although various forms of soot (and even coal) are well documented to harbor persistent free radicals,<sup>10-12</sup> their role in the evolution of soot size and composition remains largely unknown. Within the framework of PAHs, a large body of evidence points towards  $\pi$ -electronic poly-radical ground states:



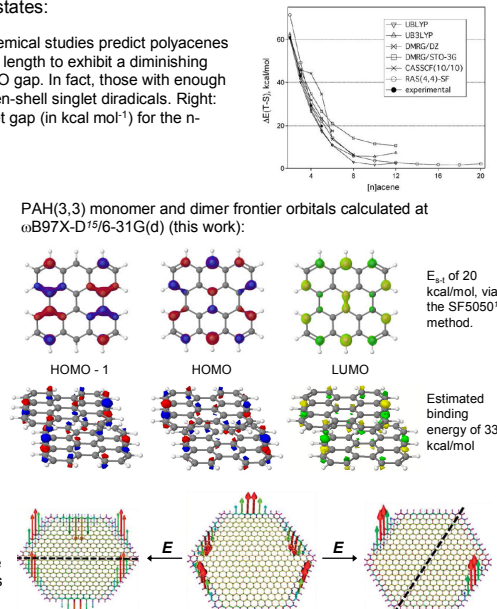
The n-ace series

Graphenes of varying size also have open-shell singlet ground states:



PAH( $i, j$ ) and radical character ( $0 \leq y \leq 1$ ) based on UBHandHLYP/6-31G(d) calculations<sup>14</sup>

Spin density distributions (arrows) of a singlet polyradical ground state and the first two lowest triplet states in a large PAH:<sup>17</sup>



The characteristics of such  $\pi$  radicals makes them good candidates for exploring significantly enhanced binding and stacking in PAH clusters, and the general hydrophilicity of freshly made soot. However, practical computational tools for such large systems, beyond density functional theory, are necessary to provide accurate answers for this problem.

## Acknowledgements

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