On the mechanism of soot nucleation

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The mechanism of carbon particulate (soot) inception has been a subject of numerous studies and debates. We critically reviewed prior proposals, analyzed factors enabling the development of a meaningful nucleation flux, and then introduced new ideas that lead to the fulfillment of these requirements. In the new proposal, a rotationally-activated dimer is formed in the collision of an aromatic molecule and an aromatic radical; the two react during the lifetime of the dimer to form a stable, doubly-bonded bridge between them, with the reaction rooted in a five-member ring present on the molecule edge. Several such reactions were examined theoretically and the most promising one generated a measurable nucleation flux. The consistency of the proposed model with known aspects of soot particle nanostructure is discussed. The foundation of the new model is fundamentally the H-Abstraction-Carbon-Addition (HACA) mechanism with the reaction affinity enhanced by rovibrational excitation. In particular, by carrying out molecular dynamics simulations of dimerization of midsize polycyclic aromatic hydrocarbons (PAH), which is the presumed critical step in formation of carbonaceous particles in terrestrial and extraterrestrial environments, we have discovered non-equilibrium precursor mediated kinetics for reactions of gaseous molecules at high temperatures. The non-equilibrium precursor state originates from inelastic collisional dynamics of two PAH monomers, with low-frequency modes acting as a sink for translational energy in the reaction coordinate. Owing to the prolonged lifetime of the non-equilibrium physical dimer, the probability of chemical dimerization increases by an order of magnitude. This phenomenon brings us closer to a solution for the carbon-particle inception puzzle and should prove useful for the fundamental understanding of gas-phase chemical reactions involving large molecules.