

Mechanisms of PAH growth and oxidation in combustion

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The presentation will overview results of ab initio calculations of potential energy surfaces combined with RRKM-Master Equation calculations of reaction rate constants, carried out in order to unravel reaction mechanisms of the growth of polycyclic aromatic hydrocarbons (PAHs) as well as oxidation of their radicals with molecular oxygen at temperatures and pressures relevant to combustion. In particular, we will compare the oxidation mechanism and rate constants of the phenyl and naphthyl radicals with those for the pyrenyl radical, which reacts consequently with two O₂ molecules oxidizing a six-member ring first and a five-member ring second. We will also describe our recent efforts directed toward the development of a comprehensive mechanism of PAH growth in combustion and will consider possible formation routes to two-ring PAHs, naphthalene and indene. The reactions potentially leading to naphthalene involve C₁₀H_x (x = 6-11) surfaces and include variations of the HACA mechanism, recombination of two cyclopentadienyl radicals, C₆H₅ (phenyl) + C₄H₄ (vinylacetylene)/C₄H₆ (1,3-butadiene), C₉H₇ (indenyl) + CH₃, and C₇H₇ (benzyl) + C₃H₃ (propargyl). Alternatively, the reactions leading to indene occur on C₉H_x (x = 6-11) potential energy surfaces and include C₆H₅ + C₃H₄ (allene and propyne), benzyl + C₂H₂ (acetylene), C₆H₅ + C₃H₆ (propene), C₆H₅ + C₃H₅ (allyl), and C₆H₅ + C₄H₆ (1,2-butadiene). While modeling is required to compare contributions of different reactions to the formation of naphthalene and indene, a number of interesting qualitative conclusions on the role of various mechanisms will be presented based on the computed temperature and pressure-dependent rate constants.