Mechanisms of PAH growth and oxidation in combustion

Alexander M. Mebel

Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida, 33199. E-mail: mebela@fiu.edu

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 O_2 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 $C_{10}H_x$ (x = 6-11) surfaces and include variations of the HACA mechanism, recombination of two cyclopentadienyl radicals, C_6H_5 (phenyl) + C_4H_4 (vinylacetylene)/C_4H_6 (1,3-butadiene), C_9H_7 (indenyl) + CH_3, and C_7H_7 (benzyl) + C_3H_3 (propargyl). Alternatively, the reactions leading to indene occur on C_9H_x (x = 6-11) potential energy surfaces and include C_6H_5 + C_3H_4 (allene and propyne), benzyl + C_2H_2 (acetylene), C_6H_5 + C_3H_6 (propene), C_6H_5 + C_3H_5 (allyl), and C_6H_5 + C_4H_6 (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.