A Combined Crossed Molecular Beams and Electronic Structure Study on the Gas Phase Formation of Prototype Aromatic and Polycyclic Aromatic Hydrocarbons (PAHs)

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Chemical reaction networks modeling the formation of PAHs in combustion flames imply that the phenyl radical (C_6H_5) presents one of the most important transient species involved in the formation of PAHs. However, despite impressive kinetic data, the reaction products formed in bimolecular collisions of phenyl radicals with unsaturated hydrocarbons have remained elusive. Therefore, we engaged a systematic research program to investigate the reaction dynamics of phenyl radicals with unsaturated hydrocarbons under single collision conditions as provided in crossed molecular beam experiments over a wide range of collision energies up to about 50 $kJmol^{-1}$. These crossed beam experiments focused on the reaction dynamics of phenyl radicals with hydrocarbon molecules accessing the C_9H_x (x=8,10) and $C_{10}H_x$ (x = 6, 8,10) PESs and, hence, investigating the formation of bicyclic aromatic species holding the *indene* and *naphthalene* carbon skeletons. This was achieved by crossing supersonic beams of phenyl radicals with allene (H_2CCCH_2), methylacetylene (CH_3CCH), and propylene ($CH_3C_2H_3$) (*indene core*) as well as diacetylene (HCCCCH), vinylacetylene ($HCCC_2H_3$), and 1,3-butadiene ($C_2H_3C_2H_3$) (*naphthalene core*). The crossed beam experiments of phenyl with methylacetylene (CH_3CCH) and allene (H_2CCCH_2) as well as with vinylacetylene (C_2H_3CCH) depicted for the very first time that ***polycyclic aromatic hydrocarbons indene (C_9H_8) and naphthalene ($C_{10}H_8$) are formed as a result of a single collision event between the aromatic phenyl radical and a hydrogen-deficient hydrocarbon molecule***. These lower collision energies lead to an enhanced life time of the initial collision complex allowing the latter to isomerize via hydrogen migration(s) and/or cyclization ultimately leading to PAH formation such as indene and naphthalene through hydrogen loss involving a tight exit transition state. The reaction with vinylacetylene was shown to be barrier-less thus establishing that PAH formation is facile even at temperatures as low as 10 K as present in cold molecular clouds.