

THE ORIGINATION OF SOOT FORMATION: A STUDY ON ETHYL-LINKED NAPHTHALENE DIMERS

DANIEL M. HEWETT, VICTORIA M. BOULOS, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN, USA.*

Combustion is the main source of power worldwide. This makes understanding combustion pathways and byproducts vital to optimizing power output and minimizing the unwanted byproducts. One of the main byproducts of the combustion process is soot, which can be accurately described as a large aggregate of polyaromatic hydrocarbons (PAHs). While the general process by which soot particles grow in size have been laid out, the incipient steps by which individual PAH molecules begin to aggregate is still a mystery. Current models of soot formation require individual PAH molecules to dimerize and π stack in PAHs significantly smaller than are thermodynamically capable of doing so. One largely untested possibility is that PAHs linked together by short chemical linkages could be responsible for the initial steps of aggregation. In particular, we propose that resonance-stabilized benzylic-like radicals could recombine to form ethyl-linked PAH dimers that are responsible for the initial stages of aggregation and π stacking. These covalently-linked dimers could withstand the high energies present in the combustion flame and provide a seed for soot aggregation. This brings us to the following question: At what sized PAH will these ethyl-linked aromatics be capable of π stacking, and if they can, will conformations leading to π stacking compete with other, more extended geometries? We begin to answer this question by studying a series of ethyl-linked naphthalene dimers in which the ethyl linkage bridges the two unique sites of substitution (shown below). These molecules are brought into the gas phase by heating, and cooled in a supersonic expansion. LIF excitation, IR-UV holeburning, fluorescence-dip infrared spectroscopy, and dispersed fluorescence are used to record conformer-specific UV and IR spectra. These dimers also have fascinating electronic spectroscopy associated with the presence of two UV chromophores that are in identical or nearly identical environments, leading to extensive vibronic coupling. The experimental results will be compared with a multi-mode theoretical model of near-resonant vibronic coupling.

