SPECTROSCOPY AND IONIZATION THRESHOLDS OF ISOELECTRONIC 1-PHENYLALLYL AND BENZYLALLENYL RESONANCE STABILIZED RADICALS

JOSHUA A. SEBREE, NATHAN KIDWELL, EVAN BUCHANAN, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; MAREK ZGIERSKI, *National Research Council Canada, Ottawa, ON*.

In recent years it has been proposed that resonance-stabilized radicals (RSRs) may play an important role as intermediates in the formation of polycyclic aromatic hydrocarbons (PAHs). RSRs gain extra stability by delocalizing the unpaired electron through a neighboring conjugated π-system. Because of this extra stability, RSRs are able to build up in concentration, allowing for the creation of larger, more complex systems through their recombination with other RSRs. Mass-selective two-color resonant two-photon ionization spectra of two RSRs, phenylallyl and benzylallenyl radicals, have been recorded under jet-cooled conditions. These two radicals, while sharing the same radical conjugation, have unique properties. The phenylallyl and benzylallenyl radicals were respectively produced via discharge of trans-β-methylstyrene and benzylallene in argon prior to supersonic expansion. The D_0-D_1 origin of the phenylallyl radical was found at 19204 cm^{-1} and was found to have a strong vertical ionization energy of 6.905(2) eV. By comparison, the benzylallenyl radical has an origin at 19703 cm^{-1} and, while showing similar Franck-Condon activity to phenylallyl, has an IP curve indicative of a large geometry change between the ground state and the ion 7.50(2) eV. Visible-visible holeburning was used to show that each radical exists in one conformeric form in the expansion. The CH stretch region of each radical was taken using D_0-Resonant Ion Dip Infrared Spectroscopy in a novel four laser experiment. A combination of this and DFT calculations was used to show that each radical exists in a trans geometry.