Exploring gas-phase reactivity of aromatic σ,π-type biradicals and *closo*-Borane Radicals

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Carbon-centered σ-type radicals and oxygen-centered π-type radicals are of interest in organic synthesis and improved understanding of biological activity of analogous natural products. Elucidation of the gas-phase reactivity of many organic σ-type mono-, bi-, and polyradicals has been accomplished by linear quadrupole ion trap mass spectrometric (LQIT-MS) analysis. However, aromatic molecules containing both σ- and π-type radical sites have not been explored. Their reactivity is expected to be unique, based on the spin delocalization of the π-type radical sites throughout the aromatic π-system and the spin localization of the σ-type radical site. Though these radical orbitals are orthogonal, spin delocalization of the π-type radical is hypothesized to influence reactivity. Mono- and biradical ions in these studies were generated in an LQIT-MS in positive mode using atmospheric pressure chemical ionization, protonating pyridine molecules substituted with iodine and methoxy groups. The relative locations of the iodine and methoxy groups varied between isomers. Methoxy groups were used to generate the oxyl π-type radical site on protonated pyridine by collision-activated dissociation (CAD) of the methyl group. Cleavage of the carbon-iodine bond by CAD generated the σ-type radical site. Ion-molecule reactions were studied with neutral reagents cyclohexene, cyclohexane and dimethyl disulfide. Low reactivity of the σ,π-type biradicals toward each neutral reagent was observed in comparison to their σ- or π-type monoradical analogs. The triplet ground states of these biradicals, compared to the singlet ground states of their monoradical analogs, may explain their reduced reactivity.

A second research focus involved *closo*-borane clusters, of significant interest in treatment of cancer using boron neutron capture therapy, as well as in materials chemistry and organic catalysis. Highly symmetrical *closo*-borane polyhedral doubly-charged anions were compared with smaller cluster sizes of lower symmetry. These anions were ionized using negative mode electrospray ionization with LQIT-MS to produce singly-charged anions and doubly-charged anionic radicals. Reactions of neutral reagent allyl iodide with each ion suggested an electrophilic behavior of the boron free binding site, an unusual observation for anions. Further investigation of the gas-phase reactivity of these *closo*-borane cluster anions is ongoing to characterize this interesting class of electrophilic anions.