Arene-Thioether Mixed Complex Radical Cations

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Studies of radiolytically generated radical cations in aromatic hydrocarbon solvents have led to the first direct characterization of monomeric thioether radical cations in liquid solution. Observation of these very reactive chemical intermediates is made possible by the great sensitivity of fluorescence-detected magnetic resonance (FDMR) and by solvent stabilization of the thioether radical cations via electron donation. Monomeric thioether radical cations in arene solvents such as toluene exist as arene-thioether mixed complex radical cations — the first π -lone pair mixed complex radical cations ever observed. Such orbital interactions are of fundamental importance for open-shell intermediates as they have consequences for both electronic structure and reactivity. Thioether radical cations provide a valuable test system to probe the chemical influence of orbital interactions that are generic to all π -type and heteroatom-containing organic radical cations, and magnetic resonance provides unsurpassed structural resolution for condensed-phase paramagnetic intermediates. This research was carried out by D. W. Werst of the Radiation and Photochemistry Group at ANL. Support was provided by the DOE Division of Chemical Sciences.

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ARENE-THIOETHER MIXED COMPLEX RADICAL CATIONS

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Studies of radiolytically generated radical cations in the condensed phase are demonstrating the prevalence of intermolecular electronic interactions, and the consequent effects on the chemical reactivity, of these fundamentally important open-shell intermediates. Interactions between the frontier molecular orbitals of species with open electronic shells and those with closed shells can result in significant covalent bonding and stable complexes. Weaker electronic interactions can still be manifested by changes in reactivity. The structure and dynamics of transient radical ions are investigated in the Radiation and Photochemistry Group at ANL in organic liquids and solids on the nanosecond time scale via time-resolved magnetic resonance.

Radical cation intermediates are important in electrochemistry, organic photochemistry, and photosynthesis, to name just a few of the diverse areas of chemistry in which they are encountered. Their study has become critical for the development of many promising new technologies such as organic conductors and solar energy converters. Radical cations are primary species in high-energy chemistry involving ionizing or photoionizing radiation, and thus radical cation reaction mechanisms must be elucidated in order to understand the damage mechanisms in materials that are exposed to ionizing radiation. Exposure to ionizing radiation can be a useful tool in industrial applications and/or an undesired environmental hazard to living organisms.

An essential experimental advance in recent years has been the development of novel time-resolved magnetic resonance methods that allow the direct observation of transient paramagnetic species in chemically reactive systems. In particular, the double-resonance method known as fluorescence-detected magnetic resonance (FDMR) selectively detects the EPR spectra of condensed-phase radical ions with unsurpassed sensitivity. FDMR allows transient radical cations to be observed in real time and simultaneously provides well-resolved structural information.

The hyperfine structure and g-factors obtained from FDMR give precise information about the spin-density distribution in radical cations and are excellent diagnostics of structure and bonding in radical cation complexes. Electron donation to the singly occupied molecular orbital (SOMO) of a radical cation results in the transfer of spin to the donor. The sharing of spin density is reflected by the decrease in the hyperfine coupling to the acceptor (original radical cation) and an increase of hyperfine coupling to the magnetic nuclei of the donor species. In the case of a symmetric dimer the spin is shared equally and coupling to equivalent nuclei on the constituent molecules is the same. Two types of examples are olefin dimer radical cations and thioether dimer radical cations. The former are π -type radical cation complexes and the latter are σ -type three-electron-bonded complexes.

The donor molecules with which radical cations interact can be the solvent itself. For example, monomeric sulfide radical cations in aqueous solutions are monosolvated three-electron-bonded heterocomplexes, $\text{R}_2\text{S}^{\bullet+} \cdot \text{OH}_2$. We have recently shown that thioether radical cations can be stabilized by electron donation from π orbitals in arene solvents such as toluene. Arene-thioether complex radical cations generated radiolytically in toluene/thioether mixtures are examples of π -lone pair mixed complex radical cations that had not previously been observed.

Complex formation between arene molecules and thioether radical cations is deduced from the g factors of thioether radical cations in aromatic hydrocarbon solvents and the relative magnitude of the hyperfine coupling to the thioether protons. Hyperfine coupling to the solvent protons is not resolved in the FDMR spectra, which implies that the solvated thioether radical cations interact with two or more solvent molecules. Hyperfine coupling constants for thioether radical cations in aromatic solvents are approximately a third smaller than for the fully oxidized species, and a

FDMR spectrum observed at 205 K in toluene containing 3×10^{-3} M thietane and 10^{-3} M anthracene- d_{10} . The sulfide radical cation signal (quintet which matches the stick spectrum simulated with $a(4H) = 20.8$ G) clearly indicates hyperfine coupling to one thietane molecule.

concomitant reduction in the g factors is observed due to the decreased spin-orbit coupling to sulfur. As expected, the hyperfine coupling constants and g factors vary systematically with the thioether ionization potential in a given solvent. Likewise, a given thioether is less fully ionized in arene solvents with lower ionization potentials.

Thus the FDMR experiments give direct information about the effects of orbital interactions on the electronic structure of radical cations, and they give additional information about the pervasive influence of orbital interactions on radical cation reactivity. Thioether radical cations are an illustrative example. Thioether radical cations in *n*-hexane solvent are not solvent stabilized because alkanes do not possess π or lone-pair orbitals capable of overlapping with the SOMO of the thioether cation. The uncomplexed thioether radical cations are very reactive. In *n*-hexane, thioether radical cations that are not rapidly coordinated to a neutral sulfide molecule decay instead via deprotonation (i.e., α -C-H bond scission). The rate of proton transfer to *n*-hexane is at least comparable to the rate of deprotonation reactions of thioether radical cations in water. The surprising result that deprotonation occurs with similar rates in *n*-hexane and water is due to the fact that

the uncomplexed R_2S^{*+} is more reactive than the monosolvated species, $R_2S^+ \cdot OH_2$, found in aqueous solutions.

The lesson taught by the FDMR studies is that comparisons of radical cation reactivity in different systems are far more meaningful when the structure of the radical cation has been fully elucidated in each system. Uncomplexed radical cations and variously solvated radical cations that arise due to electron donation from solvent orbitals in different solvents are distinctly different species with expectedly distinct properties.

Orbital interactions are equally important for positive holes in pure materials, although they have been less thoroughly investigated. Current FDMR studies in alkene liquids are revealing that the structure of radical cations in pure alkenes cannot be predicted by extrapolation from dilute solution behavior. A striking example is tetramethylethylene (TME). The TME radical cation is a prototypical example of the propensity of alkene radical cations in dilute solutions (e.g., alkane solvents) to react with their neutral parent molecules to form complex radical cations - dimer, and even oligomer, radical cations. However, TME radical cations in pure TME exist as localized, monomolecular radical cations. The hyperfine coupling constant is slightly smaller in pure TME (15.4 G) than for the isolated TME monomer radical cation (17.1 G) and attests to a small residual coupling between the positive hole and surrounding TME solvent molecules.

The amazing transition from charge delocalization in small TME aggregates to localized radical cations in pure TME is just one illustration of the intriguing behaviors of positive holes in pure materials. FDMR studies in pure liquids and solids can reveal much about charge distribution following ionization. FDMR studies of solids are especially relevant to damage mechanisms in materials exposed to ionizing radiation. The disposition of positive charge, positive-charge mobility in the absence of diffusion, migration of holes to lower potential traps and charge recombination are all important questions ultimately concerning the distribution of damage sites in irradiated materials. FDMR studies are showing that one way of approaching a systematic understanding of the diverse behavior of radical cations in different materials is by understanding the fundamental ways orbital interactions influence charge/spin distribution and radical cation reactivity.

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