

Picosecond Radiolysis of Ionic Liquids

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Ionic liquids (ILs) have potentially important applications in nuclear fuel and waste processing, energy production, improving the efficiency and safety of industrial chemical processes, and pollution prevention. Successful use of ionic liquids in radiation-filled environments will require an understanding of ionic liquid radiation chemistry. For example, characterizing the primary steps of IL radiolysis will reveal radiolytic degradation pathways and suggest ways to prevent them or mitigate their effects on the properties of the material. A second reason to study ionic liquid radiation chemistry is to use our knowledge of primary species reactivity to conduct pulse radiolysis studies of general chemical reactivity in ILs, which will aid in the development of energy production, chemical industry and environmental applications. Our main approach has been to conduct picosecond pulse radiolysis studies at BNL's Laser-Electron Accelerator Facility (LEAF)¹ to identify reactive species in ionic liquids and measure their reaction rates. In addition, we develop new ionic liquids to facilitate radiolysis studies and characterize their physical properties.

Ionic liquids have dramatically different properties compared to conventional molecular solvents. We have been studying how these properties influence physical processes that determine the stability and lifetimes of reactive intermediates and thereby affect the course of chemical reactions and product distribution. Pulse radiolysis of [R₄N][NTf₂], [R₄N][N(CN)₂], and [R₄P][N(CN)₂] ionic liquids produces solvated electrons that absorb over a broad range in the near infrared and persisting for hundreds of nanoseconds. Systematic cation variation shows that solvated electron's spectroscopic properties depend strongly on the lattice structure of the ionic liquid. The rate constants of solvated electron reactions with O₂, CO₂ and aromatic acceptors (e.g.; pyrene) measured in several ionic liquids indicate that the diffusion rate for the solvated electron in ionic liquids can be significantly lower than those of small neutral molecules or radicals such as the H-atom, in contrast to the situation in molecular solvents. These results support the contention that the diffusion constants of charged and neutral reactants differ considerably in ionic liquids, which could lead to a means of controlling reactivity through rational selection of ionic liquid properties.

Measurements of excess electron solvation processes by picosecond NIR pulse-probe radiolysis and of excited-state emission dynamics (Stokes shift and polarization anisotropy decay) of solvatochromic coumarin-153 show that the reorganization dynamics of ionic liquids occur on much longer timescales (nanoseconds) than in conventional polar solvents (picoseconds). This phenomenon profoundly influences the reactivity and energetics of radiolytically-generated excess electrons. Scavenging of the excess electron before it becomes fully solvated is a significant facet of the overall radiation sensitivity of ionic liquids, possibly due to less competition from slower electron solvation processes. Studies are underway to probe that relationship.

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