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Dynamics and Reactivity Patterns***

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Ionic Liquids: Radiation Chemistry, Solvation Dynamics and Reactivity Patterns

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Program Definition

Ionic liquids (ILs) are a rapidly expanding family of condensed-phase media with important applications in energy production, nuclear fuel and waste processing, improving the efficiency and safety of industrial chemical processes, and pollution prevention. ILs generally have low volatilities and are combustion-resistant, highly conductive, recyclable and capable of dissolving a wide variety of materials. They are finding new uses in chemical synthesis, catalysis, separations chemistry, electrochemistry and other areas. Ionic liquids have dramatically different properties compared to conventional molecular solvents, and they provide a new and unusual environment to test our theoretical understanding of primary radiation chemistry, charge transfer and other reactions. We are interested in how IL properties influence physical and dynamical processes that determine the stability and lifetimes of reactive intermediates and thereby affect the courses of reactions and product distributions. We study these issues by characterization of primary radiolysis products and measurements of their yields and reactivity, quantification of electron solvation dynamics and scavenging of electrons in different states of solvation. From this knowledge we wish to learn how to predict radiolytic mechanisms and control them or mitigate their effects on the properties of materials used in nuclear fuel processing, for example, and to apply IL radiation chemistry to answer questions about general chemical reactivity in ionic liquids that will aid in the development of applications listed above.

Very early in our radiolysis studies it became evident that the slow solvation dynamics of the excess electron in ILs (which vary over a wide viscosity range) increase the importance of pre-solvated electron reactivity and consequently alter product distributions and subsequent chemistry. This difference from conventional solvents has profound effects on predicting and controlling radiolytic yields, which need to be quantified for the successful use under radiolytic conditions. Electron solvation dynamics in ILs are measured directly when possible and estimated using proxies (e.g. coumarin-153 dynamic emission Stokes shifts or benzophenone anion solvation) in other cases. Electron reactivity is measured using ultrafast kinetics techniques for comparison with the solvation process.

Methods. Picosecond pulse radiolysis studies at BNL's Laser-Electron Accelerator Facility (LEAF) are used to identify reactive species in ionic liquids and measure their solvation and reaction rates. IL solvation and rotational dynamics are measured by TCSPC and fluorescence upconversion measurements in the laboratory of E. W. Castner at Rutgers Univ. Diffusion rates of anions, cations and solutes are obtained by PGSE NMR in S. Greenbaum's lab at Hunter College, CUNY and by Castner's group at Rutgers. Professor Mark Kobrak of CUNY Brooklyn College performs molecular dynamics simulations of solvation processes. In collaboration with J. Davis (U. South Alabama) we are characterizing the radiolytic and other properties of boronium ionic liquids, which could be used to make fissile material separations processes inherently safe from criticality accidents.

Ionic liquid synthesis and characterization. Our work often involves novel ILs that we design to the requirements of our radiolysis and solvation dynamics studies and are not commercially available. We have developed in-house capabilities and a network of collaborations (particularly with S. Lall-Ramnarine of Queensborough CC and R. Engel of Queens College) to design, prepare and characterize ILs in support of our research objectives. Cation synthesis is done with a CEM microwave reactor, resulting in higher yields of purer products in much shorter time than traditional methods. We have assembled an instrumentation cluster including DSC, TGA, viscometry, AC conductivity, Karl Fischer moisture determination and ESI-mass spec (for purity analysis and radiolytic product identification). The cluster

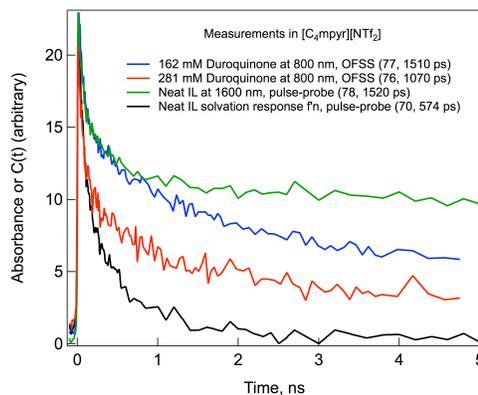
serves as a resource for our collaborators in the New York Regional Alliance for Ionic Liquid Studies and other institutions (Penn State, ANL). Our efforts are substantially augmented by student internships from the BNL Office of Educational Programs, particularly the FaST program, which brings collaborative faculty members and their students into the lab for ten weeks each summer. Since 2003, a total of 29 undergrads, two graduate students, one pre-service teacher, one high school student and four junior faculty have worked on IL projects in our lab, many of them for more than one summer.

Recent Progress

Electron solvation and pre-solvated reactivity in ionic liquids. The reactivity of excess electrons is of prime importance to the radiation chemistry of virtually all liquids. In ionic liquids, the relatively slow relaxation dynamics bestows particular significance to the reactivity of pre-solvated electron states, which occurs in competition with electron solvation processes. On a practical level it is necessary to quantify these effects in order to predict and effect control over the distributions of radiolysis products. On a fundamental level, not enough is understood about how pre-solvated electron scavenging mechanisms operate, including the nature of pre-solvated electron species and how they vary in different media.

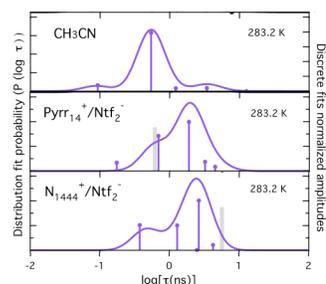
Ionic liquids are well suited for these investigations because their relaxation dynamics at room temperature extends comfortably through the picosecond regime and even into the nanosecond time scale. Thus, pre-solvated electron states can be easily detected using the picosecond pulse radiolysis instrumentation of BNL's Laser-Electron Accelerator Facility. In previous work we have used electron pulse-laser probe time delay transient absorption methods to measure the solvation process of the excess electron in the pyrrolidinium ionic liquid $C_4\text{mpyr}^+\text{NTf}_2^-$ and two related ILs. We are now in the process of using the optical fiber single-shot spectroscopy (OFSS) detection developed at LEAF by Andrew Cook to observe the electron scavenging kinetics of a wide variety of solutes in the same $C_4\text{mpyr}^+\text{NTf}_2^-$ IL in which we have characterized electron solvation. The solubility characteristics of ionic liquids will permit direct comparison of inorganic and organic scavengers that are not normally soluble in the same solvent system at high enough concentrations to scavenge pre-solvated electrons. The OFSS results show that the various solutes have different reactivity profiles with respect to particular solvated or pre-solvated excess electron species. That much had been inferred a long time ago from extrapolations of nanosecond kinetics to "time zero", but the distinction is that the combination of ionic liquids and OFSS permits us to directly observe the solvation and scavenging processes and thus obtain mechanistic insights.

A case in point is the electron scavenger duroquinone (2,3,5,6-tetramethyl-1,4-benzoquinone, DQ). When DQ is added to $C_4\text{mpyr}^+\text{NTf}_2^-$, a rapid (~ 76 ps) decrease in excess electron absorption at 800 nm is observed. When the DQ concentration is low (~ 40 mM) the amplitude of that decay process is small, but it becomes a dominant feature as the concentration is increased, although the time constant remains the same. (In the absence of DQ, the absorbance at 800 nm actually increases slightly in this time frame due to solvation-induced blue shift of the electron spectrum.) The observed electron scavenging process coincides with the 74-ps feature associated with electron solvation (see adjacent figure to compare the electron decay at two DQ concentrations with the profile of the solvation process as indicated by the red-edge, 1600 nm absorption trace or the solvation function obtained via SVD analysis). In this case, it appears that the pre-solvated may react with DQ molecules in its proximity, perhaps by tunneling, much more efficiently than fully solvated electrons. Effectively, the solvation process shuts down the scavenging pathway. Other solutes, such as nitrate anion, have different kinetic behavior and do not show the prompt decay feature.



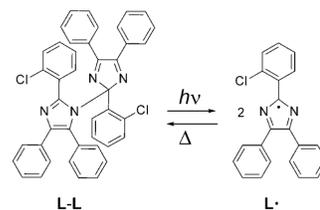
By quantitative measurement of the scavenging profiles of many reactants, we seek to provide a mechanistic basis for understanding excess electron scavenging that can be applied to real-world applications such as predicting radiolytic product distributions during the processing of radioactive materials and guiding the deliberate addition of reactants to reduce radiolytic damage, or conversely, to maximize yields of desired products.

Electron transfer in ionic liquids. (In collaboration with Heather Lee and Ed Castner of Rutgers University) Photoinduced electron-transfer reactions in a system comprised of an *N,N*-dimethyl-1,4-phenylenediamine donor, proline bridge and coumarin 343 acceptor were studied by TCSPC as a function of temperature and viscosity and analyzed using multi-exponential nonlinear least squares fitting (dots and bars) and maximum entropy methods (curves). In two ionic liquids the ET kinetics was broadly distributed, while the distributions were narrow in neutral organic solvents, demonstrating the intrinsic heterogeneity of IL systems.



Future Plans

Cage escape and recombination in ILs. Slow dynamics and diffusion in ionic liquids have significant consequences for photoinduced reactions, where product quantum yields often depend on cage escape rates in competition with back reaction. In ILs, cage escape may be slowed by sluggish displacement of the solvent cage, affording greater opportunity for recombination and consequent reduction in quantum yield. In previous work, we observed such effects in the photolysis of *ortho*-chloro-hexaaryl-bisimidazole (*o*-Cl-HABI, L-L in the adjacent scheme) where quantum yields of the lophyl radical ($L\bullet$) were much lower in three ILs than in DMSO. We intend to examine the early stages of cage escape of lophyl radical pairs on the picosecond to nanosecond time scale using the OFSS detection (see above). The OFSS system is critical to this effort because the diffusive recombination of lophyl radicals takes many seconds in ILs and in ordinary solvents, making typical repetitive pump-probe experiments completely impractical. In contrast, OFSS provides picosecond-resolution, 5-nanosecond-range transient absorption data using relatively small numbers of shots that can be collected at arbitrarily long delays in-between. With this advantage, we will examine the kinetics of cage escape and recombination in ILs of different viscosities, and the effects of slow IL relaxation dynamics on the planarization of the lophyl radical, which provides the very large reorganization barrier for radical dimerization on longer time scales. (Collaboration with Prof. V. Strehmel (U. of Applied Sci., Krefeld, Germany) and A. Cook and D. Polyanskiy (BNL))



Studies of structure and reaction dynamics in ionic liquids using EXAFS and femtosecond spectroscopy. In a collaboration with R. Crowell, R. Musat and D. Polyanskiy, photoionization of Br^- anion in neat and diluted bromide ionic liquids is being used to probe the dynamics of excess electrons and excited states. Static and time-resolved Br EXAFS is employed to study the structure of the ionic liquid and the dynamics and reactivity of the Br atom formed by the photoionization. The results can be applied to understanding analogous iodide systems of interest in solar photoconversion.

Development of Vibrational Spectroscopies at LEAF. Until recently the detection of short-lived species generated by pulse radiolysis at LEAF has relied primarily upon absorption or emission spectroscopy in the UV-visible-NIR regions. Although these methods afford excellent kinetic information, structural identification of intermediates for the elucidation of reaction pathways can be inconclusive in many cases. Time-resolved vibrational spectroscopic (TRVS) detection methods (both IR and Raman) offer highly specific molecular and structural characterization. We are therefore in the

process of implementing time-resolved infrared (TRIR) and time-resolved resonance Raman (TR³) detection systems for pulse radiolysis. The successful coupling of these techniques with pulse radiolysis will add a powerful new dimension to our research and enable a wide variety of investigations (in collaboration with D. Grills, J. Preses, A. Cook, D. Polyansky and K. Iwata).

Publications on ionic liquids

1. *Recombination of Photogenerated Lophyl Radicals in Imidazolium-Based Ionic Liquids* V. Strehmel, J. F. Wishart, D. E. Polyansky, and B. Strehmel, *ChemPhysChem* **10**, 3112-3118 (2009).
2. *The radiation chemistry of ionic liquids and its implications for their use in nuclear fuel processing*, J. F. Wishart and I. A. Shkrob in "Ionic Liquids: From Knowledge to Application," Rogers, R. D.; Plechkova, N. V.; Seddon, K. R., Eds. *ACS Symp. Ser.* **1030**, Amer. Chem. Soc.: Washington, (2009) Ch. 8, pp 119-134.
3. *Radiation Chemistry and Photochemistry of Ionic Liquids*, K. Takahashi and J. F. Wishart in "Charged Particle and Photon Interactions with Matter" Y. Hatano, Y. Katsumura and A. Mozumder, Eds. Taylor & Francis, (2010) Ch. 11, pp 265-287.
4. *Heavy Atom Substitution Effects in Non-Aromatic Ionic Liquids: Ultrafast Dynamics and Physical Properties* H. Shirota, H. Fukazawa, T. Fujisawa, and J. F. Wishart, *J. Phys. Chem. B*, **114**, 9400-9412 (2010)
5. *Ionic Liquids and Solids with Paramagnetic Anions*, B. M. Krieger, H. Y. Lee, T. J. Emge, J. F. Wishart, E. W. Castner, Jr., *Phys. Chem. Chem. Phys.*, **12**, 8919-8925 (2010)
6. *Exploring the Effect of Structural Modification on the Physical Properties of Various Ionic Liquids*, S. I. Lall-Ramnarine, J. L. Hatcher, A. Castano, M. F. Thomas, and James F. Wishart in "ECS Transactions - Las Vegas, NV, Vol. 33, Molten Salts and Ionic Liquids 17" Fox, D., *et al.*, Eds.; The Electrochemical Society, Pennington, NJ, (2010) pp. 659 - 665.
7. *Electron solvation dynamics and reactivity in ionic liquids observed by picosecond radiolysis techniques* J. F. Wishart, A. M. Funston, T. Szreder, A. R. Cook and M. Gohdo, *Faraday Discuss.* **154**, submitted.

Publications on other subjects

8. Book: "Recent Trends in Radiation Chemistry," J. F. Wishart and B. S. M. Rao, Eds.; World Scientific, Singapore, (2010). (ISBN 978-981-4282-07-9)
9. *Ultra-fast pulse radiolysis methods*, J. Belloni, R. A. Crowell, Y. Katsumura, M. Lin, J.-L. Marignier, M. Mostafavi, Y. Muroya, A. Saeki, S. Tagawa, Y. Yoshida, V. De Waele, and J. F. Wishart in "Recent Trends in Radiation Chemistry," J. F. Wishart and B. S. M. Rao, Eds. Ch. 5, pp 121-160, World Scientific, Singapore, (2010).
10. *Application of External-Cavity Quantum Cascade IR Lasers to Nanosecond Time-Resolved Infrared Spectroscopy of Condensed-Phase Samples Following Pulse Radiolysis*, D. C. Grills, A. R. Cook, E. Fujita, M. W. George, J. M. Preses, and J. F. Wishart, *Appl. Spect.* **64**, 563-570 (2010), cover publication.