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Early Events in Ionic Liquid Radiation Chemistry

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EARLY EVENTS IN IONIC LIQUID RADIATION CHEMISTRY

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Abstract: Ionic liquids are interesting and useful materials whose solvation time scales are up to thousands of times longer than in conventional solvents. The extended lifetimes of pre-solvated electrons and other energetic species in ionic liquids has profound consequences for the radiolytic product distributions and reactivity patterns. We use a newly developed, multiplexed variation of pulse-probe spectroscopy to measure the kinetics of the early dynamical and reactive events in ionic liquids.

1. Introduction

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 [1-3]. ILs 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 [4-11]. 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.

2. Experiment / Methods

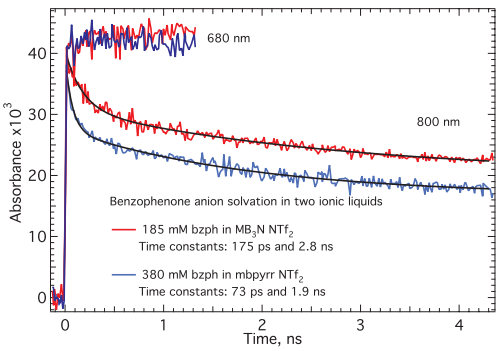
Picosecond pulse radiolysis studies at BNL's Laser-Electron Accelerator Facility (LEAF) are used to identify reactive species in ionic liquids and measure their solvation and reaction rates [12]. Recently we have begun to use the Optical Fiber Single-Shot (OFSS) optical detection technique, which recently developed at LEAF by Andrew Cook [13], to directly examine the competitive kinetics of pre-solvated electron scavenging and electron solvation in ionic liquids using a broad range of scavengers and liquids of widely different viscosities [11]. The OFSS technique is

excellent for these studies, which require many samples of high solute concentrations in liquids too viscous to flow for pulse-probe kinetics work. Material consumption can be limited to 0.125 mL per sample. Complementary TCSPC measurements of IL solvation and rotational dynamics using solvatochromic dyes are performed in the laboratory of E. W. Castner, Jr. at Rutgers Univ [6]. EPR spectroscopic investigations of radical species in irradiated ILs are carried out at ANL by I. Shkrob, T. Marin and S. Chemerisov [3,14,15].

3. Results and Discussion

In preliminary experiments, we used OFSS to monitor electron capture by benzophenone, Cd^{2+} and NO_3^- at varying concentrations in C_4mpyrr NTf_2. As the concentrations of benzophenone or Cd^{2+} increase, the spectral blue shift associated with the electron solvation process disappears, indicating that these scavengers react efficiently with pre-solvated electrons. In contrast, NO_3^- does not show that effect. The observations resemble those obtained by Jonah and coworkers for a series of scavengers in flowing cold 1-propanol (-60 ˚C) [16] except that in ionic liquids these measurements can be made at room temperature with static, small volume samples thanks to the OFSS technique. 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.

Solvation phenomena in ionic liquids are also being investigated through the time-resolved absorption spectral shift of the highly solvatochromic benzophenone anion [17,18]. The spectral range of the presently



operational OFSS system is well suited for the benzophenone experiments, whereas electron solvation is best observed in the NIR, for which we do not yet have the necessary cameras. We used OFSS to follow benzophenone anion solvation in C_4mpyrr NTf_2 and $MeBu_3N$ NTf_2 at selected wavelengths. The trend of solvation being slower in the higher-viscosity ionic liquid is seen in the neighboring graph, but quantification of the solvation dynamics requires a full spectral analysis, which is underway.

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