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Ultrafast transient absorption spectrum of the room temperature Ionic liquid 1-hexyl-3-methylimidazolium bromide: Confounding effects of photo-degradation

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HIGHLIGHTS

- Charge transfer in the ionic liquid HMIIm⁺/Br⁻ was investigated.
- Transient absorption spectroscopy shows the criticality of refreshing the samples.
- Eliminating the degradation effects, a new chemistry in HMIIm⁺/Br⁻ is revealed.
- Little evidence exists to support the formation of esol – absorbing in the NIR.

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ABSTRACT

The photochemistry of the charge transfer (CT) band of the room temperature ionic liquid (RTIL) 1-hexyl-3-methylimidazolium bromide (HMIIm⁺/Br⁻) is investigated using near-IR to vis ultrafast transient absorption (TA) and steady-state UV absorption spectroscopies. Continuous irradiation of the CT band at 266 nm results in the formation of photo-products that absorb strongly at 266 nm. It is shown that these photo-products, which are apparently very stable, adversely affect ultrafast TA measurements. Elimination of these effects reveals at least two transient species that exist within the TA detection window of 100 fs to 3 ns and 500–1250 nm. One of the components is a short-lived (< 1 ps) species that absorbs at 1080 nm. The second band exhibits a multicomponent spectrum that is very broad with an absorption maximum around 600 nm and a lifetime that is longer than the 3 ns window of our TA spectrometer. Within the signal to noise ratio of the TA spectrometer little to no solvated electron is generated by the CT mechanism.

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ABBREVIATIONS: RTILs, Room Temperature Ionic Liquids; CT, charge transfer; CTTS, charge transfer to solvent; TA, transient absorption; DFT, density functional theory; HMIIm⁺/Br⁻, 1-hexyl-3-methyl imidazolium bromide; HMIIm⁺/NTf₂⁻, 1-hexyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide; BMIM⁺/Cl⁻, 1-butyl-3-methylimidazolium chloride; BMIm⁺/PF₆⁻, 1-butyl-3-methylimidazolium hexa-fluoro-phosphate; BMIm⁺/BF₄⁻, 1-butyl-3-methylimidazolium tetra-fluoroborate; TPA⁺/NTf₂⁻, N,N,N-trimethyl-*n*-propylammonium bis(trifluoromethanesulfonyl)imide; [X:e⁻], halogen:electron pair

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1. Introduction

Due to their unique characteristics: low vapor pressures, wide electrochemical windows and remarkable solvent properties, room temperature ionic liquids (RTILs) have been proposed for use in a wide variety of industrial applications (Castner and Wishart, 2010; Plechkova and Seddon, 2008; Wishart, 2009). Accordingly, RTILs have received considerable attention in both fundamental and applied research over the past decade. One class of these compounds, the imidazolium salts, has been shown to have numerous potential uses in many areas, especially in energy related technologies such as photoelectrochemical cells, (Grätzel, 2001) nuclear fuel reprocessing, (Harmon et al., 2001) energy storage devices, (Simon and Gogotsi, 2008) separation science (Luo et al.,

2006; Pandey, 2006) and carbon dioxide sequestration (Gurkan et al., 2010; Jutz et al., 2011). Two issues that are common to almost all of the potential applications of imidazolium based ILs are the need to understand the fundamental aspects of the initial physico-chemical processes that involve charge transfer (CT) from the anion to cation and the solvation structure and dynamics of the anion (this is especially important for the use of ILs in separations and solar cell applications); (Dupont and Suarez, 2006; Maroncelli, 1993; Maroncelli et al., 2012).

Unfortunately, this class of ILs has been shown to be unstable under exposure to UV, (Brands et al., 2007; Katoh and Takahashi, 2009) ionizing radiation (Berthon et al., 2006; Le Rouzo et al., 2009) and elevated temperatures (Awad et al., 2004; Del Sesto et al., 2009). In order to design robust ILs that can fulfill their potential applications it is necessary to study the fundamental processes that lead to their degradation which begin with the dynamics of the initial CT process.

As a result there have been numerous ultrafast studies of halide-based imidazolium ionic liquids (for a recent review see reference (Chandrasekhar and Unterreiner, 2010 and references therein). In particular is the pioneering work of the Unterreiner group using femtosecond transient absorption (TA) spectroscopy to study the ultrafast dynamics following excitation of the CT band of a series of chloride- and iodide-based imidazolium ILs (Brands et al., 2007; Chandrasekhar et al., 2006, 2008; Chandrasekhar and Unterreiner, 2010). The CT band was excited at 266 nm and probed over the region of 555–1556 nm. For the halide-based imidazolium salts they observed an instrument-response-limited rise followed by a bi-exponential decay with time constants of about 2 ps and several hundred picoseconds. The spectra taken at 400 fs (iodide) and 10 ps (chloride) after excitation exhibit a very broad (> 1 eV) absorption peak that is centered near 1500 nm. They attributed the fast component to a caged halogen:electron pair ($[X:e^-]$) and the longer lived specie to a solvated electron. They suggested that one possibility to analyze the results was in terms of the Staib and Borgis (1996) model in which the initial excitation immediately generates the metastable $[X:e^-]$ pair. The electron either escapes to become solvated or recombines with the halogen atom or a neighboring imidazolium ring. As an alternative explanation they offered the possibility that the excess electrons are generated via ionization of the imidazolium to form a dication. However, as they point out it has been shown that their excitation wavelength of 257 nm (4.8 eV) is not energetic enough to ionize the imidazolium cation. During the course of their measurements they observed that both the iodide- and chloride-based imidazolium salts “turn yellow upon continuous irradiation”. Based upon steady-state UV absorption measurements they attributed the yellow color to the formation of di- and tri-halide species. Furthermore, they go on to show that the TA kinetics observed at a single wavelength strongly depend upon the scan rate, suggesting possible contributions from stable photo-products. (Brands et al., 2007) In earlier work (Shkrob et al., 2013) part of our team observed that in dilute solutions of C_nMIm^+/Br^- in C_nMIm^+/NTf_2^- , the released halogen atom very rapidly abstracts H from the aliphatic arms of the IL cations, forming HBr, the dimer radical, $C_2^{\bullet+}$, and the H-loss radical, $C(-H)^{\bullet+}$. Consequently, the dihalide or trihalide radicals are not produced under these conditions.

In this letter we focus on the photochemistry of the anion-cation CT process in the RTIL 1-hexyl-3-methyl imidazolium bromide ($HMIm^+/Br^-$). We show that the interpretations of previous ultrafast studies (Brands et al., 2007; Chandrasekhar et al., 2006; Chandrasekhar et al., 2008; Nese Chandrasekhar and Unterreiner, 2010) are questionable due to the rapid buildup of stable photo-products that possess a strong absorption cross section at the pump wavelength (266 nm) and also exhibit emission in the visible region (the emission goes away when the sample is

refreshed). By eliminating the effects of photo-degradation, new absorption features connected to the initial photochemical events in imidazolium based RTILs are revealed and it now becomes possible to begin to unravel these complex processes. The new results indicate that the initial CT events may include contributions from excited states, caged halogen:electron pairs, and radical cation dimers. The experimental details can be found in the [supplemental information section](#).

2. Materials and methods

2.1. Sample preparation

All chemicals used were of commercial grade and used without purification: 1-Methylimidazole and 1-bromohexane were purchased from Sigma Aldrich; lithium bis(trifluoromethylsulfonyl) imide was obtained from IoLiTech; acetonitrile and ethyl acetate were purchased from Mallinckrodt Chemicals. Ultrapure Millipore Milli-Q water with a resistivity of 18.2 M Ω and less than 10 ppb organic carbon was used. $HMIm^+/Br^-$ and $HMIm^+/NTf_2^-$, with the structures presented in Fig. 1, were synthesized according to the method presented in the [Supplementary information](#).

The sample cell used for the steady state measurements is a 12 μ m pathlength commercial (Harrick) IR cell using 2 mm thick CaF_2 windows. The transient absorption measurements use the same cell with a 12 μ m pathlength and 56 μ m pathlength when flowing the sample. The samples were prepared under controlled Ar atmosphere in order to avoid contamination or hydration. For the transient absorption measurement, a dual pump syringe (New Era Pump Systems Inc.) system is used to refresh the sample, which allows continuous flow of the sample at a 2 ml/min rate. During the steady state and transient absorption measurements, without sample flow, a fast emission buildup is observed, which increases with the exposure time; this emission disappears when flowing the samples.

Details about the steady state and transient absorption measurements are presented in the [Supplementary information](#).

3. Results and discussion

Static spectra under different 266 nm irradiation exposures are shown in Fig. 2. For comparison, the dashed line is the spectrum of the bromide-free RTIL 1-hexyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide ($HMIm^+/NTf_2^-$) without UV photolysis. Based on the similarity to imidazole, the absorption below 230 nm (peak at 210 nm) is assigned to the $\pi-\pi^*$ transition originating from the C=C bond of the imidazolium cation (Katoh 2007) (note: $[NTf_2^-]$ absorbs at $\lambda < 210$ nm). Substitution of $[NTf_2^-]$ with bromide produces an additional absorption feature that has been shown to be a CT band (Katoh et al., 2008). Fig. 2 shows the buildup of the absorption in the UV as a function of exposure to

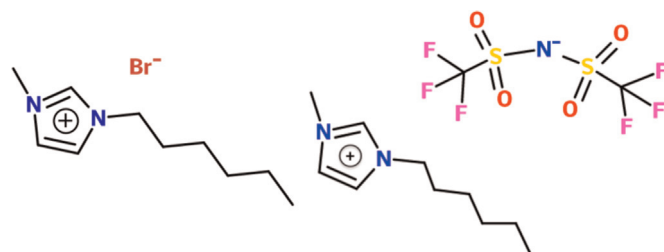


Fig. 1. Molecular structure of the $HMIm^+/Br^-$ (left image) and $HMIM^+/NTf_2^-$ (right image).

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