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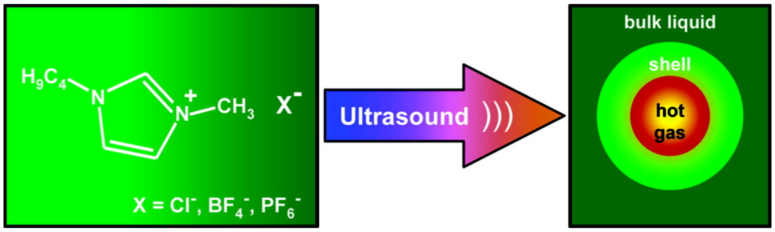

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Sonochemistry and Sonoluminescence of Room-Temperature Ionic Liquids

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Room-temperature ionic liquids have emerged as unique solvents for a variety of applications, including liquid−liquid extraction, electrochemistry, ionic liquid crystals, and biphasic catalysis.[1−4] Recent research has focused on air-stable, room-temperature ionic liquids composed of asymmetric *N*,*N*′-dialkylimidazolium cations with a variety of bulky anions such as PF_6^- and BF_4^-. These ionic liquids exhibit unique properties, including high thermal stability, large liquid range, and negligible vapor pressure.[5] These properties also make ionic liquids potentially attractive for use in sonochemical reactions. Very recently, ionic liquids have been used in sonochemical accelerations of Heck and Suzuki cross-coupling reactions and to produce ionic liquids.[6,7] No prior studies, however, have examined the effects of acoustic cavitation on such ionic liquids. We report here the sonochemical and sonoluminescent properties of several ionic liquids.

Sonochemistry and sonoluminescence are a result of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid.[8] The collapse of such bubbles creates hot spots with temperatures as high as 5000 K, pressures up to 800 atm, and cooling rates in excess of 10^{10} K/s.[9,10] These conditions are responsible for a variety of chemical and physical effects. For example, volatile organometallic precursors have been sonochemically decomposed into nanostructured materials with unique morphology and catalytic activity.[11,12]

The chemical effects of cavitation are highly dependent on the contents of the collapsing bubble and hence on the choice of solvent. To minimize participation of the solvent vapor and to maximize the temperatures reached within the bubbles during cavitation, high-boiling hydrocarbon solvents have traditionally been used for the sonochemical preparation of materials.[13,14] The two main disadvantages associated with these types of solvents are carbon contamination from sonochemical decomposition of the solvent and an upper limit on the bulk temperatures at which sonochemical reactions can be effectively run.[15] Both of these effects are directly proportional to the vapor pressure of the solvent, which makes ionic liquids especially enticing.

We have examined the effects of acoustic cavitation on a number of ionic liquids, including butylmethylimidazolium chloride (BuMeImCl), butylmethylimidazolium tetrafluoroborate ($BuMeImBF_4$), butylmethylimidazolium hexafluorophosphate ($BuMeImPF_6$), urea ammonium nitrate (UAN), and decylmethylimidazolium tetraphenylborate ($DecMeImBPh_4$). BuMeImCl and $BuMeImBF_4$ were prepared under anhydrous and inert conditions to produce colorless room-temperature liquids.[16−18] $DecMeImBPh_4$ was prepared using similar conditions.[19] $BuMeImPF_6$ was prepared according to the literature with some additional purification.[16,20] UAN was prepared by mixing equimolar amounts of high purity urea and ammonium nitrate at 80 °C. Sonications were carried out at 20 kHz at ∼60 W/cm^2 for 3 h using 15−35 mL of neat ionic liquid at approximately 85 or 135 °C under an Ar flow.

Table 1. Headgas Composition during Sonication of Ionic Liquids

ionic liquid	T_{dec} (°C)[a]	T_{us} (°C)[b]	rate$_{dec}$ at 135 °C (μmol/min)	headgas components[b]
BuMeImCl	285	85, 135	3.8	chlorobutane (25.6%), chloromethane (51.1%), IDP[c] (23.3%)
$BuMeImBF_4$	450	85, 135	2.5	IDP[c]
$BuMeImPF_6$	290	85, 135	2.5	IDP[c]
$DecMeImBPh_4$	350	85, 135	1.9	benzene (71.6%), toluene (7.8%), cyclopentadiene (1.4%), 1-hexene (0.5%), 2,4-hexadiene (0.7%), IDP[c] (18%)
urea:NH_4NO_3	160	85		CO_2 (85.1%), NH_3 (14.9%)

[a] Decomposition temperatures (T_{dec}) were determined by the onset of mass loss during thermogravimetric analysis. [b] Relative percentages and rates determined during sonication at 135 °C. Similar product distribution observed at 85 °C. [c] Imidazole decomposition products (IDP): 1,3-butadiene (0.4%), 1,3-butadiyne (2.2%), acetonitrile/isocyanomethane (21.9%), 2-methylpropane (60.7%), 2-propenenitrile (7.4%), pent-3-en-1-yne (7.4%).

During sonication, all of the imidazolium ionic liquids darkened from colorless to amber, indicating some decomposition. UAN did not change color during sonication. The IR spectra, ^{13}C NMR spectra, ^{19}F NMR spectra, fast atom bombardment mass spectra (FAB-MS), UV−visible spectra, and elemental analysis of BuMeImCl and $BuMeImBF_4$ contained no significant differences before and after sonication. The ^{1}H NMR spectrum after sonication, however, contained additional peaks in the imidazole region amounting to 0.44% of total hydrogens.

The headgas over each sonication was sampled and analyzed with gas-chromatography mass spectrometry (GC-MS). Table 1 contains a list of the conditions and observed head-gas components. During sonication, all of the imidazolium ionic liquids produced gases/vapors that contained trace amounts of light hydrocarbons and nitriles consistent with the decomposition of imidazoles. The headgas over the sonication of BuMeImCl contained approximately 26% chlorobutane, 51% chloromethane, and 23% various alkyl halides or imidazole decomposition products. The headgas formed during the sonication of $BuMeImBF_4$ and $BuMeImPF_6$ contained no detectable fluoride-containing species. The headgas over the sonication of $DecMeImBPh_4$ contained 72% benzene and trace amounts of other cyclic products. Analysis of the headgas during sonication of UAN revealed small amounts of NH_3 and CO_2. No analytes were detected above the ionic liquids during control runs with the imidazolium ionic liquids at >150 °C without ultrasound.

Further evidence of sonochemical decomposition was observed in the multibubble sonoluminescence (MBSL) spectra of BuMeImCl and UAN (Figure 1). During the sonication of BuMeImCl and UAN, light was emitted from the cloud of bubbles formed in the ultrasonic field, a phenomenon observed and studied with many

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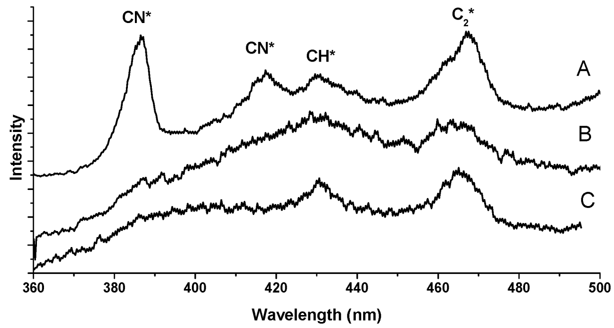

Figure 1. MBSL spectra of (A) 1-methylimidazole, (B) 1-methylimidazole with 1.5% *n*-butyl chloride, and (C) BuMeImCl.

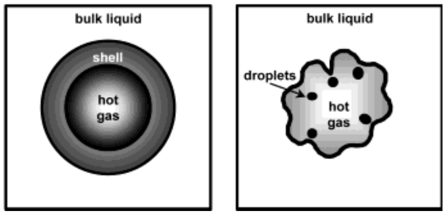

Figure 2. Two-site model of sonochemical reactivity.

other systems to determine the temperature of collapsing bubbles and their contents.[21] Spectroscopic analysis of the MBSL from BuMeImCl contained molecular emission from excited states of C_2 and CH. For comparison, we analyzed the MBSL spectra of 1-methylimidazole and a 1.5% mixture of 1-chlorobutane in 1-methylimidazole. The MBSL spectrum of neat 1-methylimidazole shows excited-state emissions from CH, C_2, and CN. The addition of 1.5% 1-chlorobutane to 1-methylimidazole quenches the CN* emission and results in a spectrum that closely resembles the MBSL spectrum of BuMeImCl. The MBSL of UAN is dominated by excited-state CN emission.

The products detected in the ^1H NMR, headgas, and MBSL spectra are a result of the ultrasonic decomposition of both the ionic liquids themselves and of their primary sonolysis products. The primary decomposition products for the imidazolium ionic liquids are *N*-alkylimidazoles and 1-alkylhalides. A previous thermolysis study of *N*,*N*′-dialkylimidazolium salts reports that the decomposition is an S_N2 process that results in a mixture of *N*-alkylimidazoles and 1-alkylhalides.[22]

One might have assumed that the negligible vapor pressure of ionic liquids would have very little susceptibility to sonochemical degradation. Our observed sonolysis of these ionic liquids, however, is consistent with the two-site model of sonochemical reactions: the first (and dominant site) is the bubble's interior gas-phase, while the second is an initially liquid phase.[23] The latter corresponds either to heating of a shell of liquid around the collapsing bubble or to droplets of liquid ejected into the hot spot by surface wave distortions of the collapsing bubble, as shown in Figure 2. The second initially liquid reaction site has a measured temperature of ~1900 K, well above the decomposition temperatures of these ionic liquids. Secondary products are also apparent from the more volatile primary sonolysis products, which have sufficient vapor pressure to diffuse into the interior of bubbles. It is likely that the presence of emission from excited states of C_2 and CH in the MBSL spectrum for BuMeImCl results from secondary processes.

In conclusion, we have shown that ionic organic liquids do decompose under ultrasonic conditions. The presence of various organic products in the headgas and the observation of emission from excited states of C_2 in the MBSL spectra confirm the decomposition of the ionic liquids during sonication.

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Supporting Information Available: H^1 NMR spectra of BuMeImCl before and after sonication and multibubble sonoluminescence spectrum of UAN. This material is available free of charge via the Internet at http://pubs.acs.org.

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