Sawyer and co-workers\(^1\) pioneered work on superoxide ion (\(O_2^-\)), particularly the direct electrochemical reduction of dissolved oxygen gas in aprotic solvents to form \(O_2^-\) according to the following reaction

\[
\text{O}_2 + e^- \rightarrow O_2^-
\]  

A comprehensive review of superoxide ion chemistry is given by Sawyer et al.\(^4\) Superoxide ion can be formed directly from solvation of \(K_2O\) in aprotic solvents, or electrochemically via direct cathodic reduction of dioxygen (typically \(E = -1.0 V \text{ vs. \ SCE}\)),\(^5\) \(O_2^-\) is a strong nucleophile and disproportionate in water to \(O_2\) and hydroperoxide

\[
2O_2^- + H_2O \rightarrow O_2 + HOO^- + HO^- \]  

For this reason, generation and utilization of \(O_2^-\) must be done in aprotic solvents. Acetonitrile (MeCN), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) are commonly used. The superoxide ion can degrade poly(chlorinated aromatics) and poly(chlorinated biphenyls) (PCBs) to bicarbonates and chlorides.\(^2\)\(^,\)\(^3\)\(^,\)\(^6\)

Room-temperature ionic liquids (RTILs) are stable mixtures of an organic cation/anion salt with an inorganic salt.\(^2\) They are directly related to more familiar high-temperature molten salts that are used, for example, as heat transfer media. Early work on RTILs in electrochemistry focused on their use as an electrolyte for advanced battery systems. Certain RTILs are electrically stable over a range of 2-4 V and higher, are thermally stable, and are resistant to oxidation. Various electrochemical syntheses have been attempted, including polymerization of arenes to form conducting polymers,\(^7\) polymerization of benzene to poly(p-phenylene),\(^8\)\(^,\)\(^9\) oligomerization of anthracene,\(^10\) and preparation of silane polymer films.\(^11\) More fundamental studies on redox reaction kinetics and behavior in RTILs have been done for anthracene,\(^12\) methylanthracene,\(^12\) and other aromatics.\(^13\)\(^-\)\(^18\) It is clear that some RTILs can be used to support electrochemistry. Osteryoung et al.\(^19\) showed that superoxide ion could be generated by the reduction of dioxygen in imidazolium chloride-aluminum chloride molten salt. However, the resulting superoxide ion was unstable and thus cannot be used as a reagent in subsequent reactions.

In this paper, we also show that superoxide ion can be generated via Reaction 1 in RTIL solvents. In addition, we show, using cyclic voltammetry (CV), that in the absence of impurities, the superoxide ion is stable in these solvents. As far as we are aware, this is the first time the generation of stable superoxide ions in ionic liquids is reported. Blanchard and Brennecke\(^20\) showed that halogen-carbon compounds are soluble in RTILs. These findings offer promise that electrochemical oxidation of chlorinated compounds in ionic liquid media may be an environmentally acceptable route for destruction of these pollutants.

**Experimental**

CV tests were performed on the aprotic solvent system tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile (MeCN) and in the ionic liquids 1-n-butyl-3-methylimidazolium hexafluorophosphate, \([\text{bmim}]\text{[HFP]}\), and 1,2-dimethyl-3-n-butylimidazolium hexafluorophosphate, \([\text{dmbim}]\text{[HFP]}\). TEAP (GFS Chemicals) was dried overnight in a vacuum oven at 40°C, HPLC grade MeCN (Fisher Scientific) was used as provided, and \([\text{bmim}]\text{[HFP]}\), \([\text{dmbim}]\text{[HFP]}\) (SACHEM), both with a stated purity of 97%, were dried overnight in a vacuum oven at 50°C. The electrochemistry was performed using an EG&G 263A potentiostat/galvanostat controlled by computer and data acquisition software. The electrode configuration was a glassy carbon working (BASE, 3 mm diam) and a platinum mesh counter (Aldrich) using SCE and Ag/AgCl references (both Fisher Scientific) for the experiments in MeCN and \([\text{bmim}]\text{[HFP]}\), \([\text{dmbim}]\text{[HFP]}\), respectively. The MeCN sample was sealed or handled under nitrogen sparge to prevent water contamination. All \([\text{bmim}]\text{[HFP]}\) and \([\text{dmbim}]\text{[HFP]}\) experiments were performed in a dry glove box under an argon atmosphere. The systems were sparged prior to electrochemical experiments with ultrahigh purity (UHP) nitrogen or oxygen fitted through a Drierite gas purification column (W. A. Hammond).

Prior to superoxide ion generation, a nitrogen sparge was used while obtaining a background voltammogram. Oxygen was then bubbled through the system for 30 min to allow sufficient solubilization. Between consecutive CV runs, oxygen was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients. Nitrogen or oxygen sparging was discontinued during the CV data acquisition.

**Results and Discussion**

Figure 1 shows CVs in (a) 0.1 M TEAP/MeCN and (b) \([\text{bmim}]\text{[HFP]}\). Reduction currents are positive throughout this paper. The CVs were run with nitrogen and oxygen sparging. In MeCN, the presence of oxygen results in a faradic reduction and oxidation peaks at \(-1.00\) and \(-0.72 V \text{ vs. \ SCE}\), respectively. This CV is consistent with that obtained by Sawyer et al.\(^3\) They concluded that the reduction peak is due to the generation of superoxide ion according to Reaction 1 and the oxidation peak due to the reverse of Reaction 1. The negligible background current in the presence of nitrogen indicates that the solvent is stable under these conditions.
In [bmim][HFP], Fig. 1b, the presence of oxygen showed a reduction peak at approximately \(-0.86\) V and an oxidation peak at \(-0.54\) V vs. Ag/AgCl. Sawyer et al.\(^4\) showed that the solvent and electrode materials can effect the reversibility and peak separation of the CVs. The reduction potential for \(\text{O}_2/\text{O}_2^-\) couple shifts to more negative values as the solvating properties of the solvent decrease. The variation in the peak potential for \(\text{O}_2/\text{O}_2^-\) in MeCN and [bmim][HFP] is small enough that the peaks seen in the two solvents are consistent with Reaction 1. The current density for the \(\text{O}_2/\text{MeCN}\) system, however, is more than an order of magnitude larger than that in the \(\text{O}_2/\text{bmim}\) system. The background currents in the two reaction medium are comparable, which indicates that the ionic liquid is also electrochemically stable.

To further quantify the difference in magnitude of the currents in Fig. 1, CVs were run in 0.1 M TEAP/MeCN and [bmim][HFP] for several scan rates, 9, 16, 25, 36, 49, 64, 81, and 100 mV/s. Four of the scans in [bmim][HFP] are shown in Fig. 2. In both solvents, the peak currents and peak potentials are proportional to the square root and the log of the sweep rate, respectively. This is consistent with the electrochemistry of a kinetically irreversible soluble redox couple.\(^2\) Plotting the peak potential vs. the log of the sweep rate gives a cathodic transfer coefficient for Reaction 1 of \(\alpha_c \approx 0.31\). This is then used, along with the solubility of oxygen in MeCN of 8.1 mM\(^4\) and the peak current data, to obtain an \(\text{O}_2\) diffusion coefficient of \(D_{\text{O}_2} = 2.1 \times 10^{-4}\) cm\(^2\)/s. A similar procedure in [bmim][HFP] gives \(\alpha_c = 0.42\) and \(D_{\text{O}_2} = 2.2 \times 10^{-6}\) cm\(^2\)/s (the solubility of oxygen in [bmim][HFP] at room temperature is 3.6 mM\(^2\)). The two orders of magnitude difference in diffusion coefficient is consistent with the fact that the viscosity of MeCN (0.345 cp\(^2\)) is an order of magnitude lower than that of [bmim][HFP] (312 cp\(^2\)).

The cathode scan in Fig. 1b shows that \(\text{O}_2^-\) can be generated in RTILs, and the reverse scan shows that \(\text{O}_2^-\) is stable. Figure 3 shows CVs at 37°C in [bmim][HFP] and [dmbim][HFP]. An elevated temperature was chosen for these CVs because [dmbim][HFP] has a melting point of 30°C. The nitrogen background shows comparable currents, indicating both RTILs are electrochemically stable. For oxygen in [bmim][HFP], the elevated temperature caused a slight shift in the reduction and oxidation peaks toward more positive potentials, but the qualitative features of the CV are not affected by temperature. That is, Reaction 1 produces a...
observed. In addition, the scans showed no reverse peak. This indicates that the superoxide ion generated in the forward scan was Ag/AgCl, and the scan rate was 100 mV/s. (1) Nitrogen, (2) nitrogen with 3.2% by weight water, (3) oxygen without water, and (4) oxygen with 3.2% by weight water.

Figure 4. Effect of water on the stability of superoxide ion in MeCN (0.1 M TEAP). The working electrode was glassy carbon, the reference electrode was Ag/AgCl, and the scan rate was 100 mV/s. (1) Nitrogen, (2) nitrogen with 3.2% by weight water, (3) oxygen without water, and (4) oxygen with 3.2% by weight water.

Figure 5. Structure of (a) 1-n-butyl-3-methylimidazolium and (b) 1,2-dimethyl-3-n-butylimidazolium cations.

routes for electrochemical oxidation of chlorinated compounds in ionic liquid media. The presence of impurities can have a dramatic effect on the stability of the superoxide ion in the ionic liquid. Therefore, work is continuing on controlling the levels of impurities in the RTILs.

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Conclusions

Preliminary experiments with the RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][HFP], showed promise that this solvent was capable of supporting the electrochemical generation of a stable superoxide ion. This finding may lead to new applications for the RTILs.