Electrogenerated Radical Anions in Room-Temperature Ionic Liquids

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The sequential two-electron reduction of benzaldehyde to the radical anion and dianion species in 1-butyl-3-methylimidazolium triflimide and 1-butyl-1-methylpyrrolidinium triflimide is reported. In 1-butyl-1-methylpyrrolidinium triflimide, the heterogeneous electrochemistry and follow-up chemical reactivity are essentially equivalent to that in conventional molecular-solvent-based electrolytes where no interaction with the media is observed. In 1-butyl-3-methylimmidazolium triflimide, reduction occurs via the same two heterogeneous processes; however, the apparent heterogeneous rate constants are smaller by ca. 1 order of magnitude which leads to quasi-reversible electrochemical behavior. Since the bulk viscosities of the liquids are similar, the slower heterogeneous kinetics are attributed to local interfacial viscosity due to local ordering in the imidazolium-based medium. Also, a dramatic anodic shift in the reduction potentials is observed in 1-butyl-3-methylimidazolium triflimide media that is attributed to a stabilizing interaction of the radical anion and dianion species with the imidazolium cation.

Introduction

So-called room-temperature ionic liquids (RTILs)[1−3] are molten salts that are generally comprised of an organic cation (e.g., 1-butyl-3-methylimidazolium) and an inorganic anion such as nitrate or triflimide ([NTF$_2$]). Although this genre of molten salts was initially developed as electrolytes in electrochemical devices,[4,5] their use as molecular-solvent-free reaction media for organic synthesis applications has evolved dramatically over the past decade.[1−3,6] Recently, their application as reaction media for organic electrochemical reactions has emerged[7−10] because they are inherently conducting liquid media within which electrochemistry can be performed in the absence of both molecular solvent and extraneous electrolyte. Also, their redox robustness, nonvolatility, and generally "green" credentials[1−3] render RTILs, in principle at least, a superior reaction media for preparative-scale organic electrochemical transformations compared with conventional molecular solvents such as acetonitrile or tetrahydrofuran in which extraneous organic electrolytes are dissolved and where product recovery is frequently difficult.[11]

Although RTILs are used principally as "inert" reaction media for classical organic chemical reactions, it is becoming apparent that their rich physiochemical properties (e.g., Lewis and/or Brønsted acidity/basicity, hydrogen-bonding ability, $\pi-\pi$ interactions, etc.) influence chemical reactivity.[12,13] Considering that organic electrochemical processes involve the generation of highly reactive species, the possible involvement of these types of interactions has specific relevance for organic electrochemistry because species such as radical anions are known to interact with their supporting medium under certain conditions.[14] Therefore, the transfer of known electrochemical reactions from conventional noninteracting media to RTIL environments is not necessarily a straightforward task.

Obviously, the ability of an RTIL to influence heterogeneous electron-transfer and/or homogeneous chemical processes is a function of its chemical composition; therefore, RTILs of varying composition should be expected to attenuate chemical reactivity for specific chemical reactions, which, indeed, has been shown to be the case for chemical reactions.[12] This is one of the bases for the emerging concept of "task-specific" ionic liquids,[15,16] i.e., the deliberate design of RTILs to effect some specific function, e.g., to control the outcome of chemical reactions.

In light of this, a recent study[9] examining the effect of RTIL composition (imidazolium and quaternary ammonium cations with triflimide and PF$_6^-$ anions) on the heterogeneous electrochemistry and homogeneous reactivity of electrogenerated radical cations (from durene, naphthalene, anthracene, etc.) has shown that the post-electron-transfer homogeneous chemistry is effectively unaltered in various RTIL environments relative to a conventional molecular solvent (acetonitrile) insofar as the mechanism remains unchanged while the kinetics of follow-up chemical reactions are only slightly affected. However, the kinetics of the heterogeneous electron-transfer processes are slower by about 1 order of magnitude. The slow heterogeneous kinetics were attributed to slow solvent-reorganization dynamics in the viscous RTIL media. A similar rationale was used by Evans et al.[17] in their study of the oxidation of *N,N,N′,N′*-tetraalkyl-*para*-phenylenediamines to the corresponding radical cation and dication species in a series of [NTF$_2$]-containing ionic liquids where the RTIL cations were either imidazolium or quaternary ammonium species. These authors report little change in $k°$ with respect to cation type, i.e., $k°$ ranged from 1.0×10^{-3} cm s^{-1} to 0.025 cm s^{-1} ($k°$ is the heterogeneous electrochemical rate constant).

Also, preliminary results in this laboratory[8] have shown that electrochemical radical anion generation by the one-electron reduction of benzaldehyde in 1-butyl-1-methylpyrrolidinium triflimide ([Bmpyr][NTF$_2$]) RTIL and its follow-up chemical reactivity are essentially unaffected as compared to noninteracting conventional media such as alkaline methanol.

The reduction of benzaldehyde has been investigated extensively in a number of different media[18−20] where it is known

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that under neutral or alkaline conditions the primary reduction process involves a one-electron reduction of the carbonyl group to form the radical anion that, in turn, can be reduced in a one-electron process to the dianion at more cathodic potentials. The heterogeneous electrochemical rate constants ($k°$) for both processes is ≥ 0.1 cm s^{-1};[18,19] therefore, these processes are considered electrochemically reversible. The one-electron reduction of benzaldehyde is a useful model reaction for the assessment of the interaction of radical anions with their environment because the pK_a for the formation of its conjugate acid (the neutral α-hydroxybenzyl radical) is 8.4,[18] i.e., in the absence of a proton source, the electrogenerated species will remain the radical anion; therefore, the decay of its interfacial population will be solely due to the well-known radical anion dimerization reaction.[18−21] Significantly, the relatively small second-order rate constant (k_2) for the dimerization reaction ($k_2 \cong 10^4$ mol^{-1} dm^3 s^{-1}) is such that the reversible electrochemistry for the benzaldehyde/radical anion redox is easily accessible voltammetrically using microelectrodes and fast voltammetry.[18−21,22]

This paper reports the two-step reduction of benzaldehyde in 1-butyl-3-methylimidazolium triflimide ([Bmim][NTF$_2$]) and [Bmpyr][NTF$_2$] RTILs at Pt microelectrodes using fast cyclic voltammetry. It will be shown that the heterogeneous electrochemistry is dependent on the type of RTIL employed, whereas the follow-up chemical reactivity is not significantly affected by RTIL type. The differing behavior is interpreted as being a function of the differing physiochemical properties of the RTILs. In particular, a large stabilization of the radical anion by interaction with the imidazolium cation is evident.

Experimental Section

[Bmim][NTF$_2$] and [Bmpyr][NTF$_2$] were synthesized and prepared for use according to the literature.[23,24] Benzaldehyde was obtained from Aldrich and was used without further purification. The RTILs were sparged with Ar prior to measurements, and all solutions were kept under Ar during measurement. Benzaldehyde solutions of known concentration were prepared by the direct addition of a known volume of the substrate into an electrochemical cell that contained a known volume of the appropriate ionic liquid.

Electrochemical measurements were made with a CH Instruments CH600B potentiostat in the two-electrode configuration using full positive feedback *iR* compensation. The working electrode was a 10 μm diameter Pt microdisk electrode (sealed in soft glass), which was polished with 0.05 μm alumina prior to use. The pseudo-reference electrode was a Pt wire (Goodfellow). All potentials are quoted with respect to the potential for ferrocene redox (Fc/Fc$^+$) in the respective ionic liquid. Voltammograms were recorded at potential sweep rates up to 5000 V s^{-1}. All measurements were carried out at room temperature. Digital simulations were performed using VirtualCV, which is a C++ version of Grosser's CVSim.[25] Also, here, we report cathodic currents as being positive.

Results and Discussion

Figure 1 (solid line) shows a cyclic voltammogram for the reduction of benzaldehyde at the Pt microelectrode in [Bmpyr]-[NTF$_2$] ionic liquid recorded at 1000 V s^{-1}. It is clear that two reversible one-electron reduction processes occur with half-wave potentials ($E_{1/2,1}$) of -1.73 V vs Fc/Fc$^+$ and ($E_{1/2,2}$) -2.33 vs Fc/Fc$^+$. These processes can be assigned to the primary reduction of benzaldehyde to the radical anion and the subsequent reduction of the radical anion to the dianion species.[18,19]
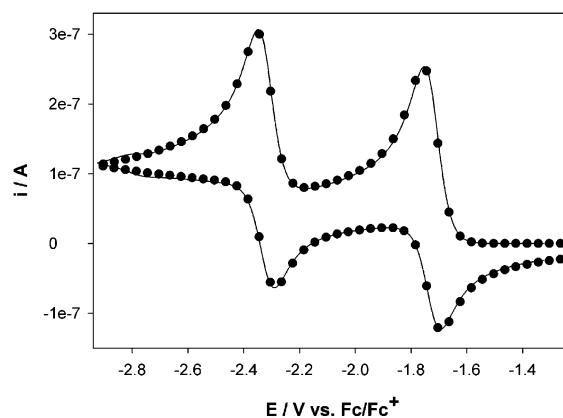

Figure 1. Cyclic voltammogram for benzaldehyde ($C = 15.6 \times 10^{-3}$ mol dm^{-3}) reduction at 1000 V s^{-1} (solid line) and a simulated voltammogram (filled dots) with $k_{2,\text{Bmpyr}} = 1.4 \times 10^4$ mol^{-1} dm^3 s^{-1} and $k_{1,\text{Bmpyr}} = 1000$ s^{-1}.

The peak-to-peak separation (ΔE_p) of the individual waves are 0.074 and 0.072 V, which remain constant from 500 to 5000 V s^{-1}. Considering that ΔE_p values remain constant, this suggests that the voltammetric data correspond to a reversible (fast) redox process that is slightly contaminated with a residual uncompensated solution resistance (*iR* drop), i.e., the $\Delta E_p > 2.303RT/nF$ observation is not due to heterogeneous kinetic control. Notwithstanding, it is useful to adopt the approach of Nicholson and Shain[26] to estimate the *apparent* heterogeneous rate constants for both the primary and secondary processes ($k_1^{0,\text{app,Bmpyr}}$ and $k_2^{0,\text{app,Bmpyr}}$, respectively), since these values represent the *minimum* values that these rate constants can be. This analysis yielded $k_1^{0,\text{app,Bmpyr}} = 0.8$ cm s^{-1} and $k_2^{0,\text{app,Bmpyr}} = 0.7$ cm s^{-1}, which is in keeping with values reported by Saveant et al.[18,19] It can also be seen that the potential separation between the primary and secondary processes is 0.6 V, which is in direct agreement with the observation of Saveant et al.[18] under ethanol/pH 12/tetrabutylammonium perchlorate conditions, which, in turn, indicates that the radical anion does not interact to any electrochemically measurable extent with the quaternary ammonium [Bmpyr] cation or the triflimide anion. Noninteraction is the usual observation for radical anion generation for quaternary ammonium electrolytes in conventional solvents.[27] It is also noticeable that there is no trace of a reduction process at intermediate potentials (between the primary and secondary processes), which is a clear indication of the absence of the neutral α-hydroxybenzyl radical as expected for the aprotic RTIL environment.[18]

Digital simulation of the voltammograms yields the second-order rate constant for the radical anion−radical anion dimerization reaction (k_2) and the pseudo-first-order rate constant for the stabilization of the dianion species (k_1). It is presumed that the dianion is stabilized by the formation of an alcoholate−[Bmpyr] adduct in a dissimilar fashion to the stabilization of radical anions in chloroaluminate molten salt.[28] It is also assumed that all diffusion coefficients are equal to that for benzaldehyde (3.0×10^{-7} cm^2 s^{-1}) as measured by microelectrode voltammetry and that α = 0.5 for both processes. Figure 1 (filled dots) is the best fit simulation overlaid on the experimental voltammogram where $k_{2,\text{Bmpyr}} = 1.4 \times 10^4$ mol^{-1} dm^3 s^{-1} and $k_{1,\text{Bmpyr}} = 1000$ s^{-1}. Significantly, the $k_{2,\text{Bmpyr}}$ value is in keeping with that of other media.[18−21] No literature value for $k_{1,\text{Bmpyr}}$ is available, but its magnitude indicates a relatively long lifetime for such a reactive species.

Figures 2a and 2b (solid lines) show cyclic voltammograms for the reduction of 18.8×10^{-3} mol dm^{-3} benzaldehyde in

[Bmim][NTF$_2$] ionic liquid at potential sweep rates of 1000 and 500 V s^{-1}, respectively. It is immediately obvious that the electrochemistry is very different from that observed in the [Bmpyr]-based RTIL. It is clear that two quasi-reversible reduction processes occur at −0.75 V vs Fc/Fc$^+$ and −1.80 V vs Fc/Fc$^+$, respectively. These processes again correspond to the initial formation of the radical anion and the subsequent reduction of the radical anion to the dianion species. The peak-to-peak separation (ΔE_p) at a potential sweep rate of 1000 V s^{-1} for the primary and secondary process are 0.215 and 0.277 V, respectively. Significantly, for both processes, the ΔE_p values decreased with decreasing potential sweep rates. For example, at 500 V s^{-1}, ΔE_p for the primary process is 0.172 V, while for the secondary process ΔE_p is 0.234 V. These data clearly indicate the quasi-reversible nature of both reduction processes, which is in direct contrast to that observed in [Bmpyr]-based RTIL (vide supra). Through the use of these ΔE_p values, in conjunction with the theory of Nicholson and Shain as above,[26] the *apparent* heterogeneous rate constants for both redox processes in the [Bmim] molten salt ($k_1{}^{0,\text{app,Bmim}}$ and $k_2{}^{0,\text{app,Bmim}}$) can be calculated. Again, in this calculation, it was assumed that all diffusion coefficients (D) were equal ($D = 3.0 \times 10^{-8}$ cm^2 s^{-1} as measured by microelectrode voltammetry) and that $\alpha = 0.5$ for both processes. The values obtained are $k_1{}^{0,\text{app,Bmim}} = 0.015$ cm s^{-1} and $k_2{}^{0,\text{app,Bmim}} = 0.009$ cm s^{-1} for the first and second reduction processes, respectively. This apparently indicates that the heterogeneous process is slow in [Bmim]-based RTIL. However, it is well-known that both benzaldehyde reduction processes are reversible (fast), where $k°$ for the first process is at least 0.1 cm s^{-1}.[18,19] Also, the results pertaining to benzaldehyde reduction in [Bmpyr][NTF$_2$] show that $k°$ for the first redox and second processes are ≥ 0.7 and ≥ 0.8 cm s^{-1}, respectively (vide supra). Considering that both RTILs have a common anion, this observation is interesting insofar as the [Bmim] cation seems to inhibit the heterogeneous electron-transfer process since the effect is common to both radical anion and radical cation generation.[9,17]

Hapiot et al.[9] argued that the slow heterogeneous electron-transfer kinetics observed in their studies for the generation of radical cations is due to slow solvent-reorganization dynamics in the viscous RTIL media. Considering that the bulk dynamic viscosity (η) of the [Bmpyr] and [Bmim] RTILs used here are similar (at 298 K, $\eta = 0.080$ and 0.057 km m^{-1} s^{-1} for [Bmpyr] and [Bmim], respectively), the large difference in $k°$ in the similarly viscous liquids seems unlikely to be solely a function of bulk liquid viscosity. However, what is known about imidazolium-based RTILs is their ability to form highly organized "layers" at solid interfaces.[29] This behavior will give rise to local interfacial physiochemical properties (e.g., local density, viscosity, and dielectrics) that may differ significantly from the bulk RTIL properties. This will have two possible consequences. First, Marcus-type solvent reorganization (which occurs during electron transfer) will be slow, as suggested by Hapiot et al.[9] (vide supra), and is observed in other viscous systems such as polymers.[30] Also, significantly, upon potential perturbation, relaxation of the electrical double layer will require reorganization of a highly ordered purely ionic interfacial region, which may also be slow due to the breakdown of the strong intermolecular forces that give rise to the organized structure. Therefore, the actual electrode potential, at short times at least, will not keep pace with the potentiostatic sweep or step.[22] Both scenarios will give rise to apparent quasi-reversible behavior as observed here and by others for [Bmim]-based ionic liquids.[9,17] Figures 3a and Figure 3b show the chronoampero-
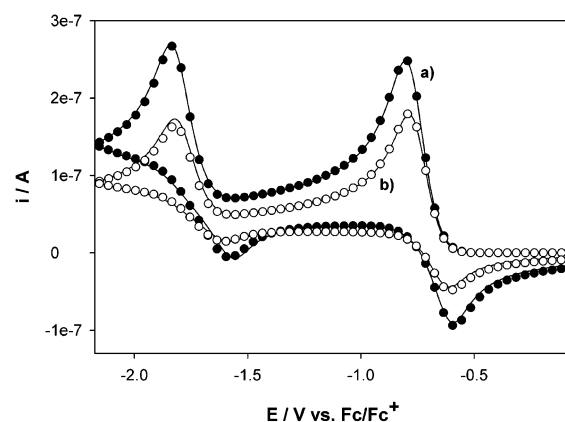

Figure 2. Cyclic voltammograms for benzaldehyde ($C = 18.8 \times 10^{-3}$ mol dm^{-3}) reduction at (a) 1000 V s^{-1} and (b) at 500 V s^{-1}. Filled dots and open circles represent the simulation at 1000 and at 500 V s^{-1}, respectively, where $k_{2,\text{Bmim}} = 1.0 \times 10^4$ mol^{-1} dm^3 s^{-1} and $k_{1,\text{Bmim}} = 1600$ s^{-1}.
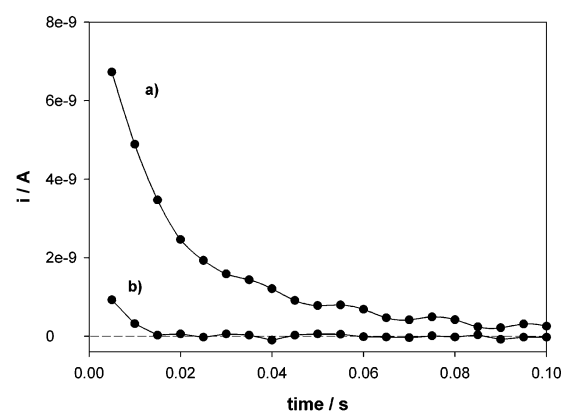

Figure 3. Chronoamperometric responses at a 11 μm carbon fiber microelectrode in (a) [Bmim][NTF$_2$] and (b) [Bmpyrd][NTF$_2$] media to a 0.9 V potential step (−0.400 to 0.500 V vs Fc/Fc$^+$.)

metric responses of a 11 μm diameter carbon fiber microelectrode in [Bmim][NTF$_2$] and [Bmpyr][NTF$_2$] RTILs to a 0.9 V potential step. It can be seen that the decay time of the capacitive charging current is much longer in the [Bmim] media than that in the [Bmpyr] RTIL. Considering this, it seems likely that that the apparently slow heterogeneous kinetics in [Bmim] RTIL observed here are due, partially at least, to the slow relaxation of the electrochemical double layer.

It is also immediately clear, from comparison of the voltammograms obtained in [Bmim] RTIL with those recorded in [Bmpyr] RTIL, that the half-wave potentials for the primary and secondary redox processes are significantly shifted anodically in [Bmim]. The shift for the primary process is 0.975 V while that for the secondary process is 0.525 V. Such anodic shifts are not uncommon in electrochemical systems.[14,31] For example, supramolecular interactions such as hydrogen bonding, $\pi-\pi$ interaction, and electrostatic interaction between flavin and apoenzymes have been implicated in $E_{1/2}$ modulations of the flavin/flavin radical anion redox couple of over +0.5 V.[14] Such shifts are due to the thermodynamic stabilization of the radical anion by the aforementioned interaction processes. Stabilization can be quantified from the half-wave potential shift (ΔE) as a free energy change (ΔG) using the expression

$$\Delta G = -nF\Delta E \qquad (1)$$

where n is the number ($n = 1$). Through the use of this approach, the radical anion stabilization in [Bmim] RTIL relative to that

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of the [Bmpyr] RTIL is 94 kJ mol^{-1} while the stabilization of the dianion species is 51 kJ mol^{-1}. It is well-known that significant $\pi-\pi$ interaction (between imidazolium and aromatic substrate) occurs in imidazolium-based ionic liquids[32] and that the [Bmim] cation is highly electropositive[33] and, also, that the benzaldehyde radical anion is highly electronegative;[9] it is therefore not surprising that significant stabilization of the radial anion and dianion species occurs in this medium as opposed to the nonaromatic [Bmpyr] liquid.

To obtain the rate constants for the dimerization and alcoholate stabilization reactions in the [Bmim]-based medium, simulations of the voltammograms were performed. This simulation is less straightforward that that in [Bmpyr] (vide supra) because the apparent stabilization interaction of the radical anion (and dianion) with the RTIL medium will suppress its diffusion coefficient relative to that of the parent benzaldehyde. For example, it is known that for benzophenone-type radical anions in water/ethanol solvents, suppression of diffusion of up to a factor of 3 occurs,[34] which is attributed to intermolecular charge polarization.

With this in mind, simulations were performed where the best fit required a radical anion diffusion coefficient of 8.0×10^{-8} cm^2 s^{-1} instead of 3.0×10^{-7} cm^2 s^{-1} (the bulk benzaldehyde diffusion coefficient). Figures 2a and 2b (filled dots, open circles) show the best fit simulation for the 1000 and 500 V s^{-1} voltammograms where reasonably good fits are obtained. It should noted that the secondary reduction process appears very asymmetrical; it was found that a transfer coefficient of 0.55 was necessary to obtain an acceptable fit. From these simulations, the second-order rate constant for the dimerization process ($k_{2,\text{Bmim}}$) was found to be 1.0×10^4 mol^{-1} dm^3 s^{-1}, while the first-order rate constant ($k_{1,\text{Bmim}}$) for the alcoholate reaction was 1600 s^{-1}. The value for the dimerization reaction is comparable with that obtained for the [Bmpyr]-based ionic liquid, which is 1.4×10^4 mol^{-1} dm^{-3} s^{-1}, whereas the value for the first-order reaction is slightly faster (i.e., 1600 s^{-1} vs 1000 s^{-1}). These data are comparable with molecular-solvent systems such as alkaline methanol.[18,19]

Conclusions

The electrochemical reduction of benzaldehyde in [Bmpyr]-[NTF$_2$] occurs via two sequential one-electron processes leading to the radical anion and dianion species. The heterogeneous electrochemistry and follow-up chemical reactivity are essentially equivalent to that found in noninteracting molecular-solvent-based electrolytes containing quaternary ammonium electrolytes. Reduction in [Bmim][NTF$_2$] also occurs via the same two sequential reduction processes, again leading to the radical anion and dianion species. However, in other respects, reduction in this medium is very different to that observed in the [Bmpyr]-based ionic liquid. First, the apparent heterogeneous rate constants for the two reduction processes are ca. an order of magnitude smaller than those expected for the reversible couple and observed in [Bmpyr] RTIL. Considering that the viscosities of both liquids are similar, this observation cannot solely be attributed to a bulk viscosity effect.[9] Also, very slow double-layer relaxation is observed for [Bmim]. Since the bulk viscosity of the liquids are similar, it appears that interfacial ordering in [Bmim] media[29] leads to local viscosities that control both solvent-reorganization dynamics and double-layer relaxation, which lead to apparent slow heterogeneous kinetics.

Second, the reduction potentials for the primary and secondary reduction processes are shifted anodically in [Bmim] relative to that in [Bmpyr] RTIL. Since there is a common anion between both RTILs, this effect can be attributed to the physiochemical properties of the two different cations. In particular, the known $\pi-\pi$ interaction that occurs between [Bmim] and aromatic solutes[32] is likely to contribute strongly to the stabilization of the radical anion and dianion species. Such interaction is not possible in the nonaromatic [Bmpyr]. Notwithstanding the more complex electrochemistry in [Bmim], the kinetics of follow-up chemical reactions are similar to [Bmpyr] and molecular-solvent systems.

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