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A Comparative Study on the Reactivity of Electrogenerated Bromine with Cyclohexene in Acetonitrile and the Room Temperature Ionic Liquid, 1-Butyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide

Gary D. Allen,[†] Marisa C. Buzzeo,[†] Ieuan G. Davies,[‡] Constanza Villagrán,[§] Christopher Hardacre,[§] and Richard G. Compton*[,†]

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom, Central Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, United Kingdom, and School of Chemistry/QUILL, Queen's University Belfast, Belfast, Northern Ireland, BT9 5AG, United Kingdom

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The reactivity of electrogenerated bromine with cyclohexene has been studied on a platinum microelectrode by linear sweep and cyclic voltammetry in both the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, and the conventional aprotic solvent, acetonitrile. Variation in the voltammetric response was observed in the two solvents, indicating that the bromination reaction proceeded via separate mechanisms. To identify the different products, electrolysis was conducted on the preparative scale and NMR spectroscopy confirmed that while bromination of the organic substrate in the ionic liquid yields *trans*-1,2-dibromocyclohexane, in acetonitrile, *trans*-1-(*N*-acetylamino)-2-bromocyclohexane is instead obtained as the major product. The reaction mechanism for bromination in acetonitrile has been modeled using digital simulation.

1. Introduction

The voltammetry of bromide has been investigated in traditional aprotic solvents over the past fifty years.[1−4] Most investigations have been performed in acetonitrile, where both the tribromide anion, Br_3^-, and molecular bromine, Br_2, are reportedly generated upon oxidation. The bromination of multiple bonds via electrophillic addition and substitution are well-known reactions and the reactivity of electrogenerated bromine species with a number of organic substrates, including xylene, styrene, phenol, and cyclohexene has been reported in conventional solvents.[5−14]

Herein we report the oxidation of bromide in the room-temperature ionic liquid, 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[C_4mim][N(Tf)_2]$) and acetonitrile (MeCN). The subsequent reactivity of the electrogenerated bromine species with cyclohexene is investigated in both solvents and the individual voltammetric responses compared and contrasted. Bulk electrolysis was performed to confirm the products of this reaction, which vary primarily as a result of the differing nucleophilicities of the two solvents.

Room temperature ionic liquids (RTILs) are compounds composed entirely of ions and exist in the liquid state around 298 K and below. They offer numerous advantages as solvents in electrochemistry, including high thermal stability, low volatility, wide potential windows, and finally, good conductivity, which negates the need for added electrolyte, a prerequisite in the traditional solvent matrix.[15−21] Other properties of RTILs must be considered carefully, however, when they are employed as electrochemical solvents. The viscosities of ionic liquids are typically at least an order of magnitude greater than conventional solvents and thus the rate of mass transport is significantly slower in the former. This has a direct effect on the diffusion of species within RTILs and has been shown to result in interesting voltammetric behavior.[22,23]

Although our studies were primarily aimed at investigating the voltammetric response of bromide and cyclohexene, our positive results suggest that such reactions in ionic liquids could potentially be applied to large-scale organic synthesis. Significant consideration would have to be given to reaction conditions and product extraction techniques, but the recyclability of RTILs and the reduced waste as compared to traditional solvent systems where added electrolyte is generally unrecovered merits them attractive alternatives. In the past decade, various examples of electrosynthesis conducted in ionic liquids have appeared in the literature, including the electrocyclic addition of carbon dioxide to epoxides, the activation of molecular oxygen in the presence of a Mn(III) catalyst and the reduction of alkyl and benzyl halides, resulting in the direct formation of a carbon−carbon bond.[24−26] Additionally, a number of polymerization reactions in ionic liquids have also been documented.[27−29] This, however, is the first report of the electrochemical bromination of an alkene in an ionic liquid.

2. Experimental Section

2.1. Chemical Reagents. 1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[C_4mim][N(Tf)_2]$) was synthesized from the corresponding halide salt via a metathesis reaction in aqueous lithium bis[(trifluoromethyl)sulfonyl]imide, as described by Bonhôte et al.[16] 1-Ethyl-3-methylimidazolium bromide ($[C_2mim]Br$) was prepared by the reaction of 1-methylimidazole (Aldrich) and ethyl bromide (Aldrich) in MeCN at

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* To whom correspondence should be addressed. Tel: 01865 275413. Fax: 01865 275410. E-mail: richard.compton@chemistry.ox.ac.uk.

[†] Physical and Theoretical Chemistry Laboratory, University of Oxford.

[‡] Central Chemistry Research Laboratory, University of Oxford.

[§] Queen's University Belfast.

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~80 °C. 1-Methylimidazole and ethyl bromide were purified by distillation under reduced pressure prior to use. [C_2mim]Br was purified by recrystallization from its MeCN solution by addition of ethyl acetate (Riedel-de-Haën) several times under a dry nitrogen atmosphere and then dried under vacuum. Acetonitrile (MeCN, Fisher Scientific), cyclohexane (Fisher), cyclohexene (Fisher), trans-1,2-dibromocyclohexane (Aldrich), ferrocene (Aldrich), lithium bromide (LiBr, Aldrich), lithium perchlorate ($LiClO_4$, Fluka), phenol (Aldrich), styrene (Aldrich), and tetrabutylammonium perchlorate (TBAP, Fluka) were used directly without further purification.

2.2. Electrodes. The 10 μm diameter platinum (Pt) microdisk working electrode (Cypress Systems) was carefully polished before each experiment using a 1.0 μm alumina slurry (Buehler, Lake Bluff, IL), followed by a 0.3 μm alumina suspension (Buehler). The electrode was then polished on a clean, damp cloth (Microcloth, Buehler), immersed in 10% nitric acid solution to remove any adventitious adsorbates, and then rinsed with MeCN. The diameter of the microdisk electrode was calibrated electrochemically using 2 mM ferrocene in 0.1 M TBAP/MeCN, assuming a value for the diffusion coefficient of 2.3×10^{-9} m^2 s^{-1} at 20 °C.[30] The Pt rotating disk electrode (7 mm diameter) was polished in a similar manner using 6 μm diamond spray (Kemet International Ltd., Kent, U.K.).

Most microelectrode voltammetric experiments in [C_4mim][N(Tf)$_2$] were carried out using a glass cell designed for investigating microliter samples of ionic liquids under vacuum conditions, a schematic of which can be found in previous reports.[22,31] A trimmed disposable micropipet tip was fitted to the end of the microdisk electrode to provide a cavity into which a small sample of ionic liquid (~20 μL) was delivered. A conventional two electrode setup was utilized with a Pt microdisk working electrode and a 0.5 mm diameter silver (Ag) wire (99.99%, Advent Research Materials Ltd, Oxford, U.K.) acting as the quasi-reference electrode. The system was purged in vacuo (Edwards High Vacuum Pump, Model ES 50) for 40 min prior to any measurements and for the duration of the experiment thereafter.

For microelectrode experiments requiring a larger volume of ionic liquid and those in which [C_4mim][N(Tf)$_2$] was replaced by MeCN, a traditional five-arm glass cell was employed, in which a Pt wire was added as a counter electrode to complete a conventional three-electrode arrangement. These systems were purged with nitrogen (BOC Gases, Guildford, U.K.) for 40 min prior to any measurements and for the duration of all experiments.

2.3. Instrumentation. A commercial potentiostat, PGSTAT 20 (Eco Chemie Utrecht, Netherlands), was used for the electrochemical experiments in conjunction with a Pentium-based PC.

Proton nuclear magnetic resonance (δ_H) spectra were recorded on a Bruker AC 200 (200 MHz), Bruker AV 400 (400 MHz), or a Bruker DPX 400 (δ_H) spectrometer. Spectra (400 MHz) were assigned using COSY. Carbon nuclear magnetic resonance (δ_C) spectra were recorded on a Bruker AV 400 (100.6 MHz) spectrometer. Spectra were assigned using HMQC; multiplicities were assigned using DEPT sequence. All chemical shifts are quoted on the δ scale in ppm using residual solvent as internal standard.

2.4. Bulk Electrolysis. Bulk electrolysis was performed at a 7 mm Pt rotating disk electrode to ensure thorough mixing of reagents. A coiled Ag wire quasi-reference electrode and a coiled Pt wire counter electrode completed the cell arrangement. Lithium bromide (2×10^{-3} moles) and excess cyclohexene were stirred continuously while the potential was held on the plateau of the second oxidative wave for 10 and 24 h in 0.1 M $LiClO_4$/MeCN (50 mL, $E = 1.8$ V) and [C_4mim][N(Tf)$_2$] (10 mL, $E = 1.8$ V), respectively, or until the desired charge had been passed. A white powder accumulated on the counter electrode during the course of the electrolysis. These experimental conditions were not optimized; current efficiencies are therefore not reported. Acetonitrile was removed on a rotary evaporator and NMR spectra were obtained on the resulting residue. The product was extracted from the ionic liquid with three successive cyclohexane washes (3 × 10 mL), which were combined and washed with a saturated brine solution (30 mL) to remove any residual [C_4mim][N(Tf)$_2$]. The cyclohexane was then removed on a rotary evaporator and the residue analyzed by NMR. The following spectra were obtained. ^1H and ^{13}C NMR: **($C_6H_{10}Br_2$)** δ_H (400 MHz, $CDCl_3$), 1.50 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CHBr}$), 1.78 (2H, m, $\mathrm{C}\mathit{H}'_2\mathrm{CH_2CHBr}$), 1.90 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CHBr}$), 2.49 (2H, m, $\mathrm{C}\mathit{H}'_2\mathrm{CHBr}$), 4.45 (2H, s, $\mathrm{C}\mathit{H}\mathrm{Br}$); **($C_8H_{14}NOBr$)** δ_H (400 MHz, $CDCl_3$), 1.20−2.40 (8H, m, $\mathrm{CHNH(C}\mathit{H}_2\mathrm{)_4CHBr}$), 2.00 (3H, m, $\mathrm{C}\mathit{H}_3$), 3.90−4.10 (2H, m, $\mathrm{C}\mathit{H}\mathrm{Br}$, $\mathrm{C}\mathit{H}\mathrm{NH}$), 5.99 (1H, m, $\mathrm{N}\mathit{H}$); **($C_8H_{14}NOBr$)** δ_C (100 MHz, $CDCl_3$) 23.4 (s, CH_3), 24.3 (t, CH_2), 26.4 (t, $C'H_2$), 33.2 (t, $C''H_2$), 37.1 (t, $C'''H_2$), 55.0 (d, CH), 55.4 (d, CH), 169.7 (s, C=O).

3. Results and Discussion

3.1. Oxidation of Bromide in [C_4mim][N(Tf)$_2$]. The voltammetry of the oxidation of bromide was first investigated in the RTIL 1-butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]imide ([C_4mim][N(Tf)$_2$]). Figure 1 shows the steady-state voltammograms (10 mV s^{-1} scan rate) recorded for the direct oxidation of increasing concentrations of [C_2mim]Br in [C_4mim][N(Tf)$_2$] at a platinum microdisk electrode (10 μm diameter). Two well-defined anodic waves occur at $E_{1/2} = 1.1 \pm 0.1$ V (vs Ag) and 1.5 ± 0.1 V, respectively. Bromide, Br^-, is initially oxidized to bromine, Br_2 (first wave), which reacts with an equivalent of Br^- to form the tribromide species, Br_3^-:

$$2Br^- - 2e^- \rightarrow Br_2 \tag{1}$$

$$Br_2 + Br^- \rightleftharpoons Br_3^- \tag{2}$$

At higher potentials, the tribromide is oxidized further:

$$Br_3^- \rightleftharpoons Br^- + Br_2 \tag{3}$$

$$Br^- - e^- \rightarrow {}^1/_2 Br_2 \tag{4}$$

$$\text{Overall:} \qquad Br_3^- - e^- \rightarrow {}^3/_2 Br_2 \tag{5}$$

The second oxidation might occur as written in eqs 3 and 4 or via the direct oxidation of tribromide, as in eq 5.[1−4] The detailed mechanism is considered elsewhere.[32]

According to this mechanism, the overall number of electrons transferred per bromide for the first limiting current ($i_{lim,1}$) is $^2/_3$; both reactions 1 and 2 are occurring. The second limiting current ($i_{lim,2}$), however, is solely due to reaction 1, and therefore the number of electrons transferred per mole of bromide increases to 1. Thus, the ratio of $i_{lim,1}/i_{lim,2}$ should be 1.5, which is indeed observed under steady-state conditions (scan rate = 0.01 V s^{-1}) at the Pt microdisk electrode over the bromide concentration range under study (2−30 mM). A plot of limiting current against bromide concentration (see inset, Figure 1) is linear and a value of $1.4 \pm 0.2 \times 10^{-11}$ m^2 s^{-1} was calculated for the diffusion coefficient of bromide in the ionic liquid by

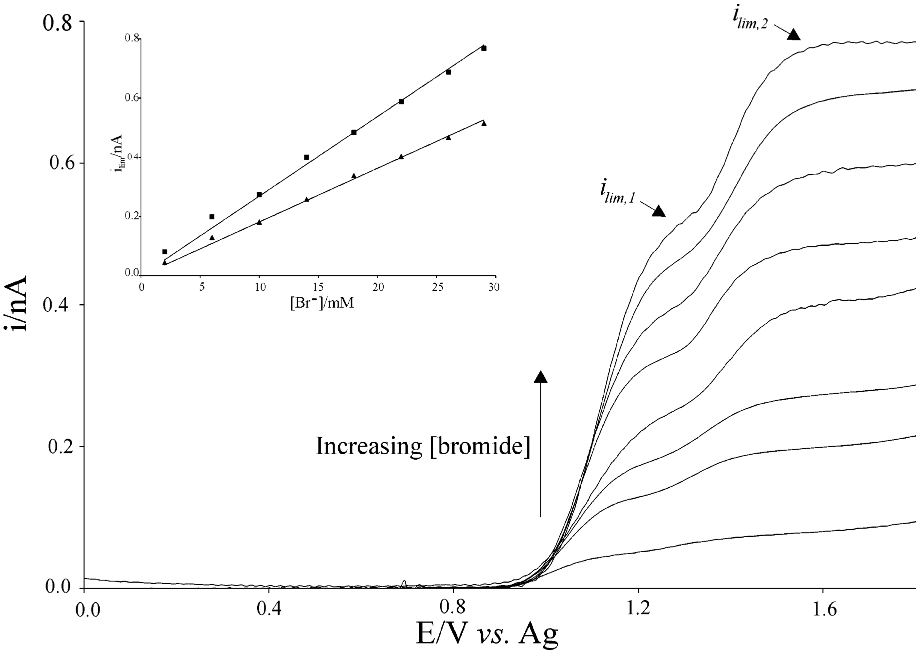


Figure 1. Steady-state linear sweep voltammograms (scan rate 10 mV s^{-1}) for the oxidation of [C_2mim]Br in [C_4mim][N(Tf)$_2$] at a 10 μm Pt microdisk electrode at increasing concentrations of bromide (2−30 mM). The inset shows a plot of limiting current vs bromide concentration, $i_{\mathrm{lim},1}$ = (▲), $i_{\mathrm{lim},2}$ = (■).

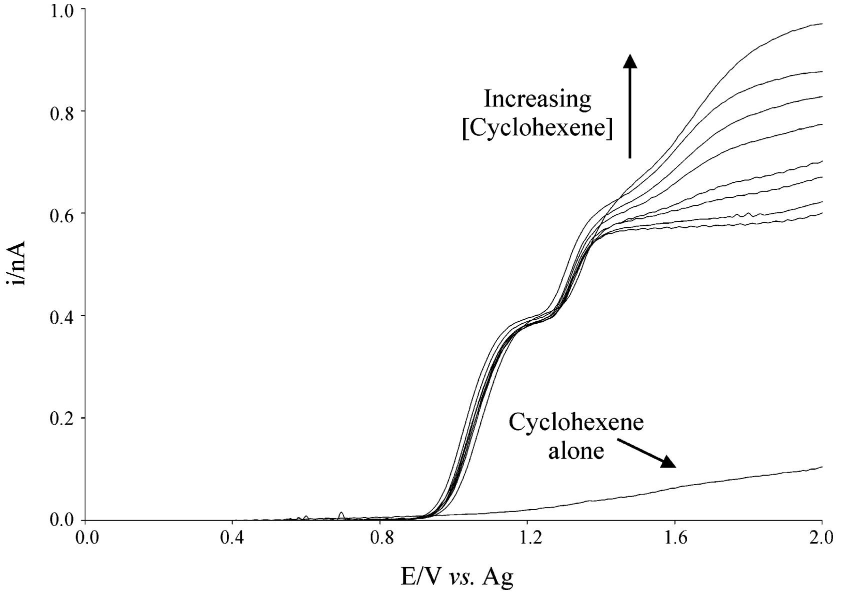


Figure 2. Steady-state cyclic voltammograms (scan rate 10 mV s^{-1}) for the reactivity of [C_2mim]Br in [C_4mim][N(Tf)$_2$] at a 10 μm Pt microdisk electrode at increasing concentrations of cyclohexene (3−50 mM). Also shown is a voltammogram for cyclohexene alone in [C_4mim][N(Tf)$_2$].

rearrangement of the following equation:

$$i_{\mathrm{lim}} = 4n\mathrm{F}rDc \qquad (6)$$

where i_{lim} is the limiting current, n is the number of electrons transferred, F is the Faraday constant (96 485 C mol^{-1}), r is the radius of the microdisk electrode, D is the diffusion coefficient of the electroactive species, and c is its bulk concentration. This value is consistent with a previously reported diffusion coefficient of chloride in [C_4mim][BF$_4$], where D was found to be 1.1×10^{-11} m^2 s^{-1}.[33]

3.2. Reactivity of Electrogenerated Bromine with Cyclohexene in [C_4mim][N(Tf)$_2$]. The reactivity of the electrogenerated bromine with cyclohexene was next investigated in [C_4mim][N(Tf)$_2$]. The voltammetry of cyclohexene alone was first studied on a Pt microdisk electrode in the ionic liquid to ensure that the organic substrate was not electroactive in the potential window of interest. A solution of cyclohexene (~100 mM) in [C_4mim][N(Tf)$_2$] was prepared and the potential was swept in the anodic direction until the onset of solvent breakdown. The resulting scan, as can be seen in Figure 2, confirms that the voltammogram for cyclohexene alone is essentially unchanged from the RTIL itself. To investigate the possible reactivity, micromolar additions of cyclohexene were then added to 20 mM [C_2mim]Br/[C_4mim][N(Tf)$_2$] and their effect studied by linear sweep voltammetry (LSV) at a platinum microdisk electrode. The first two waves shown in Figure 2 are due to the oxidation of bromide (as explained in the previous section), but the new, third wave, emerging at $E_{1/2} = 1.9 \pm 0.1$ V (vs Ag) is believed to be due to the direct oxidation of *trans*-1,2-dibromocyclohexane (DBCH), formed upon reaction of

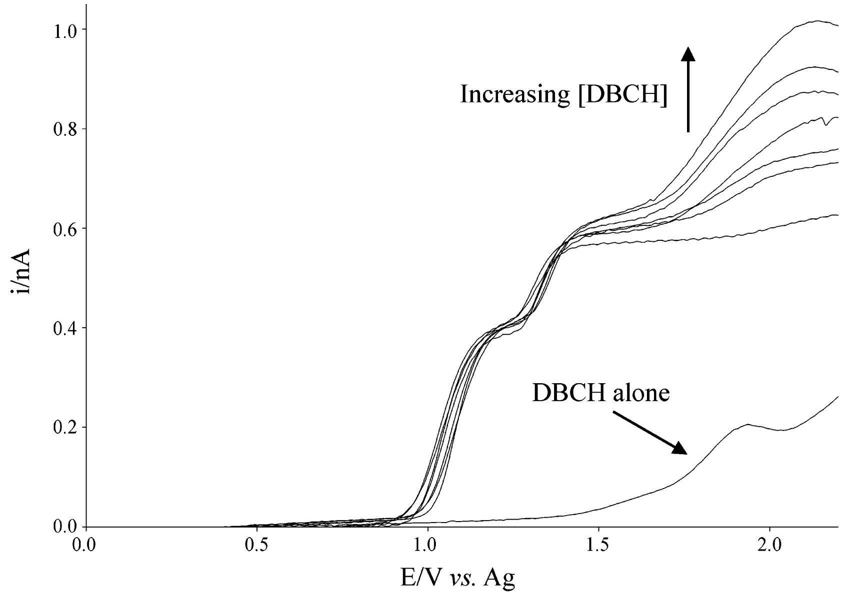
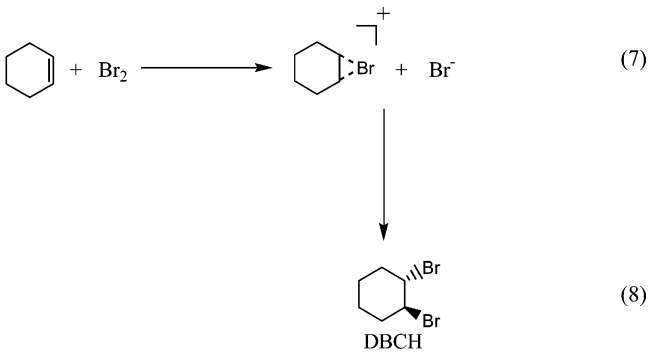


Figure 3. Steady-state linear sweep voltammograms (scan rate 10 mV s^{-1}) for the oxidation of *trans*-1,2-dibromocyclohexane in [C$_4$mim][N(Tf)$_2$] at a 10 μm Pt microdisk electrode at increasing concentrations (40−220 mM) in the presence of 20 mM [C$_2$mim]Br. Also shown is a voltammogram for the oxidation of DBCH (150 mM) alone in [C$_4$mim][N(Tf)$_2$].

SCHEME 1



electrogenerated bromine with cyclohexene. As is outlined in Scheme 1, an electrophillic addition reaction occurs between bromine and cyclohexene, whereby the bromonium intermediate is attacked by bromide to yield the trans product. Accordingly, the size of this third wave increases with additions of cyclohexene (3−50 mM) as more DBCH is generated.

To investigate this proposed product, the oxidation of *trans*-1,2-dibromocyclohexane in [C$_4$mim][N(Tf)$_2$] was then studied by LSV at a Pt microelectrode, and an anodic wave was observed at $E_{1/2} = 1.9 \pm 0.1$ V V (vs Ag). DBCH was then added to the [C$_2$mim]Br/[C$_4$mim][N(Tf)$_2$] system so as to emulate like reaction conditions, and as shown in Figure 3, analogous voltammetry is observed, supporting our hypothesis. Further evidence was then gained from performing bulk electrolysis at a Pt rotating disk electrode on the Br$^-$/[C$_4$mim][N(Tf)$_2$] system, with the potential held on the plateau of the second wave so as to generate the speculated product, DBCH, before occurrence of its own oxidation. NMR spectroscopy gives evidence that the isolated product is the *trans*-1,2-dibromocyclohexane species, with a characteristic peak for the protons on the substituted carbons appearing at 4.45 ppm. For a complete ^{1}H NMR assignment, see section 2.4.

The bromination investigation was also extended to other organic substrates. Solutions of phenol (100 mM) and styrene (100 mM) in [C$_4$mim][N(Tf)$_2$] were studied by LSV; however, there was no evidence of the reactivity of electrogenerated bromine in the ionic liquid with these organic substrates on the voltammetric time scale at the Pt microdisk electrode. In the case of phenol, reactivity is expected to proceed via an aromatic substitution reaction and thus the lack of a proton sink in this medium may explain why none is observed.

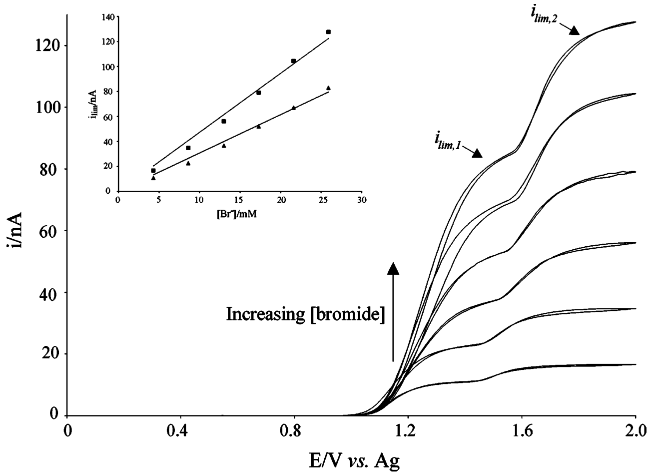


Figure 4. Steady-state cyclic voltammograms for the oxidation of [C$_2$mim]Br in 0.1 M TBAP/MeCN at a 10 μm Pt microdisk electrode at increasing concentrations of bromide (4−26 mM). The inset shows a plot of limiting current vs bromide concentration, $i_{\text{lim},1}$ = (▲), $i_{\text{lim},2}$ = (■).

3.3. Oxidation of Bromide and Reactivity of Electrogenerated Bromine with Cyclohexene in MeCN. For comparative purposes, the voltammetric investigation of [C$_2$mim]Br was repeated in MeCN. Figure 4 shows steady-state voltammograms measured at a platinum microdisk electrode. As can be seen, the response in MeCN is very similar to that observed in the ionic liquid and the oxidation is believed to proceed via the same mechanism. The calculated diffusion coefficient, $D = 1.7 \pm 0.2 \times 10^{-9}$ m^2 s^{-1}, is in good agreement with literature values and appropriately larger than the value determined for the ionic liquid given the significantly different viscosities ($\eta_{\text{MeCN}} = 0.345$ cP, $\eta_{[\text{C}_4\text{mim}][\text{N(Tf)}_2]} = 44$ cP at $T = 25$ °C).[1,15,16,34,35] The reactivity of bromine with cyclohexene was also studied in MeCN by linear sweep and cyclic voltammetry. A third wave is not observed in the voltammograms (see Figure 5), indicating that

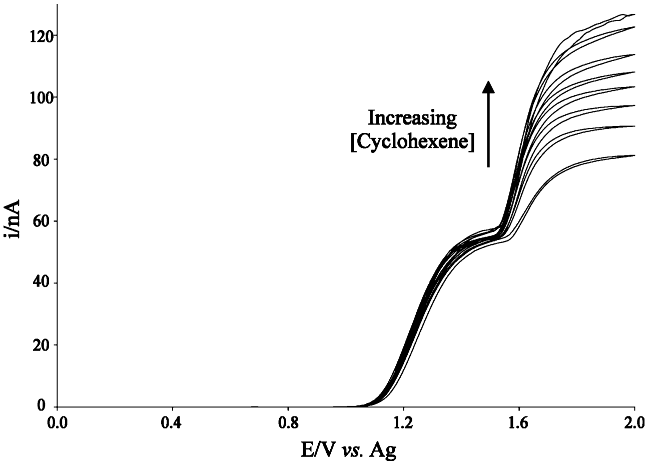
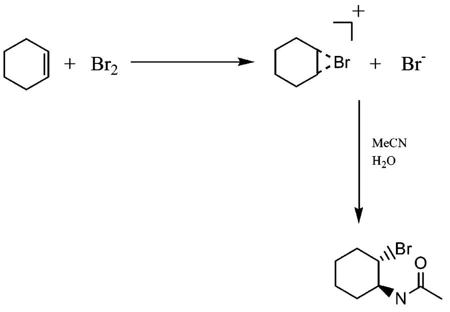


Figure 5. Steady-state cyclic voltammograms (scan rate 10 mV s^{-1}) for the reactivity of $[C_2mim]Br$ in MeCN at a 10 μm Pt microdisk electrode to increasing concentrations of cyclohexene (2−42 mM).

SCHEME 2

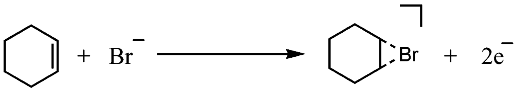


(9)

(10)

DBCH is not generated in this system; however, a catalytic increase *is* seen in the second oxidative wave. Again, bulk electrolysis was performed to determine the identity of the product, and on the basis of the obtained NMR spectra (see section 2.4), the product is believed to be a solvent-incorporated acetamide, as indicated in Scheme 2. The initial reactivity step is analogous to the RTIL; however, the bromonium intermediate is then attacked by MeCN to yield *trans*-1-(*N*-acetylamino)-2-bromocyclohexane. Although bromide is a better nucleophile than MeCN, the vast excess of solvent allows it to effectively compete with the former, preventing formation of the dibromo-substituted product. Moreover, given the expected greater nucleophilicity of MeCN as compared to $N(Tf)_2^-$, the solvent-trapped adduct would not have been expected in the RTIL medium.

This proposed mechanism would explain the increase observed in the second wave, which is believed to be due to oxidation of bromide that is regenerated in the first step of Scheme 2, eq 9. This increase will eventually reach a limit as the number of electrons transferred per bromide switches from one, in the absence of cyclohexene, to two, as is evident in the overall reaction of eqs 1 and 9:



(11)

Therefore, the limiting current of the second wave would be expected to double in the presence of a sufficient excess of cyclohexene.

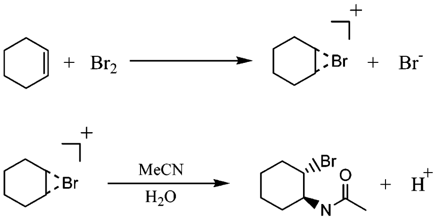
Although a previous report has suggested that DBCH is the product of electrochemical bromination in acetonitrile,[6] two independent studies have shown evidence of solvent incorporation when bromine and cyclohexene are homogeneously mixed in specific molar ratios.[5,11] The NMR evidence of the acetamide product, the absence of a third wave (due to DBCH oxidation) and the catalytic increase seen in the second oxidative wave strongly suggests that DBCH is not produced in this system. We have further supported this proposition by using a computer simulation to model the observed voltammetric response, assuming the reaction mechanism given in Scheme 2, and it is to those simulations which we will next turn our attention.

SCHEME 3

$$Br^- - e^- \longrightarrow Br^{\cdot} \qquad (12)$$

$$2Br^{\bullet} \longrightarrow Br_2 \qquad (13)$$

$$Br_2 + Br^- \longrightarrow Br_3^- \qquad (14)$$



(15)

(16)

3.4. Modeling the Reaction of Electrogenerated Bromine with Cyclohexene in MeCN. The reaction mechanism of the bromination of cyclohexene in MeCN was modeled using a one-dimensional digital simulation program (DigiSim 3.03, BAS Technicol). The initial oxidation of bromide was simulated via a fictitious $Br^{\bullet}$ intermediate due to a inherent limitation of Digisim, which only accepts a mechanism entered in terms of single or multielectron-transfer steps ($A \rightleftharpoons B + ne^-$, $n > 1$) and first- or second-order homogeneous reactions.[32,36] This mechanism for bromide oxidation, involving the $Br^{\bullet}$ species, was then expanded to include the subsequent reactivity of the electrogenerated bromine with cyclohexene (see Scheme 3).

The forward scans of the steady-state voltammograms shown in Figure 5 were simulated in Digisim, using the approximation of a hemispherical diffusion regime for a microelectrode, where $r_e^{\text{hemisphere}} = 2/\pi\ r_e^{\text{disk}}$.[37,38] A diffusion coefficient for cyclohexene ($D = 2.4 \times 10^{-9}$ m^2 s^{-1}) was estimated using the Wilke−Chang expression[39]

$$D = \frac{7.4 \times 10^{-8} T\sqrt{xM}}{\eta V^{0.6}} \qquad (17)$$

where T is the absolute temperature, x is the solvent association constant ($x = 1$ for MeCN), M is the molar mass of the solvent (41 g mol^{-1}), η is the solvent viscosity (0.345 cP), and V is the volume of solute at normal boiling point (estimated from atomic contributions[39]). A value for the pseudo first-order forward rate constant for the solvent-attack step (Scheme 3, eq 16) was taken from the literature ($k_{f,2} = 2 \times 10^9$ M^{-1} s^{-1}).[12] With all other parameters held constant, $k_{f,1}$ and the equilibrium constant ($K_{eq,1}$) for eq 15 were adjusted so as to optimize the fit between experimental and simulated wave shapes for the reaction of bromine with cyclohexene. A value of $4 \pm 1 \times 10^5$ M^{-1} s^{-1} was found to give the best fit for $k_{f,1}$. A lower limit of 1×10^{-3} was determined for $K_{eq,1}$; the model was insensitive to changes above this value. If $K_{eq,1}$ is set any lower than this limit, however, insufficient bromide is generated and the catalytic increase is not observed in the simulated limiting current.

A comparison of experimental and simulated cyclic voltammograms for various cyclohexene additions is shown in Figure

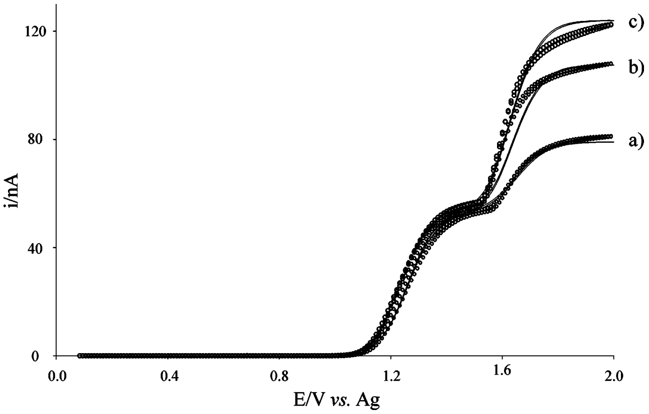


Figure 6. Comparison of experimental (○) and simulated (—) voltammograms for the bromination of cyclohexene in MeCN at various cyclohexene concentrations: (a) 0 mM; (b) 8 mM; (c) 18 mM.

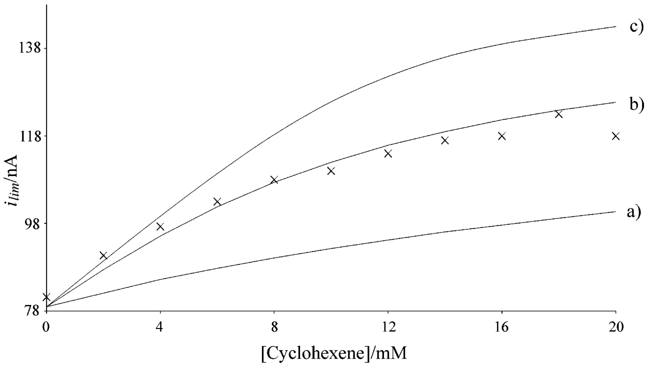


Figure 7. Comparison plot of experimental (x) and simulated (—) limiting currents against cyclohexene concentration in MeCN. Also shown is the deviation in the fit when $k_{f,1}$ is changed by an order of magnitude: $k_{f,1}$ = (a) 4×10^4, (b) 4×10^5, and (c) 4×10^6 M^{-1} s^{-1}.

6, and Figure 7 shows the variation of the limiting current with cyclohexene additions over the entire concentration range. Also shown in Figure 7 is the deviation observed when $k_{f,1}$ is varied by an order of magnitude in either direction, demonstrating the sensitivity of the model toward this parameter. The close agreement between experimental and simulated data is fully consistent with the proposed mechanism for the bromination reaction in acetonitrile.

4. Conclusions

The reactivity of electrogenerated bromine with cyclohexene has been investigated in both the room-temperature ionic liquid, 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]-imide ($[C_4mim][N(Tf)_2]$) and the traditional aprotic solvent, acetonitrile (MeCN). We have shown that, although the direct oxidation of bromide in both $[C_4mim][N(Tf)_2]$ and MeCN results in similar voltammetry, the reaction of electrogenerated bromine with cyclohexene occurs via separate mechanisms and yields different products in the two solvents as a result of their different nucleophilicities. Bulk electrolysis, followed by NMR spectroscopy, confirmed that bromination in the ionic liquid results in the formation of *trans*-1,2-dibromocyclohexane, whereas the solvent-incorporated *trans*-1-(*N*-acetylamino)-2-bromocyclohexane is instead synthesized in acetonitrile. The reaction in acetonitrile has been modeled by a computer simulation program to yield a rate constant of $k_{f,1} = (4 \pm 1) \times 10^5$ M^{-1} s^{-1} for the initial bromination step and further supports the proposed mechanism. This is the first report of a bromination reaction in a room temperature ionic liquid and commends its potential application in larger scale organic electrosynthesis, with the possibility of electrogeneration of bromine from bromide.

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