Evidence has been obtained that the ring protons of 1-ethyl-3-methylimidazolium chloride (EMIC) can act as proton donors towards electrochemically generated bases in the aluminum chloride: EMIC molten salt. Reduction of benzophenone in the deuterated (2 position of EMIC) basic melt yields benzhydrol deuterated at the carbinol carbon, showing that the intermediate carbanion is basic enough to be protonated by the EMI cation. Anthracene undergoes a two-electron reduction in the basic melt, giving dideuteroanthracene. Considering that both benzophenone and anthracene can be reversibly reduced in one-electron processes in acetonitrile, these results indicate that the AlCl₃ : EMIC melt environment is considerably more acidic than are conventional solvents such as acetonitrile.

INTRODUCTION

The aluminum chloride : 1-ethyl-3-methylimidazolium chloride (EMIC) molten salt system has proved to be a useful medium in which to carry out electrochemical reductions of organic compounds (1,2,3). In the basic melt, which is composed of a molar excess of EMIC, the melt species are the EMI cation and chloride and tetrachloroaluminate anions. The attractive feature of this melt regime is that the negative potential limit, determined by EMI cation reduction (−2.3 V vs 2:1 AlCl₃ : EMIC reference electrode), is sufficiently negative to allow the reduction of aromatic ketones (1,2). Upon studying the reduction of several ketones in this melt, it has become evident that the reduction products are often protonated as they are generated in the melt. The chemistry of protons resulting from trace amounts of water in the melt components has been thoroughly explored, and methods are available for virtually complete removal of these protons (4). The protonation of the reduction products must, then, be
due to the EMI cation. Considering that the imidazolium ring system is known to possess ring protons of considerable acidity (5), it was decided to investigate the proton-donating ability of the melt system towards several representative electrogenerated bases.

EXPERIMENTAL

Molten salt components were prepared according to standard procedures (4), all operations being carried out in a Vacuum Atmospheres glovebox. Protonic impurities in the basic melts, in which most of the present work was carried out, were removed by placing the melt under high vacuum at 65-70°C. The proton level was assessed by voltammetry at a platinum electrode and was found to be in the 0.3 - 0.5 mM range. Deuterated EMIC (2 position; 2-d-EMIC) was prepared by dissolving EMIC in D2O for three days (5). Melts prepared from 2-d-EMIC were purified by the same vacuum treatment as used for EMIC-based melts.

Voltammetric experiments were carried out using a PAR 174A Voltammetric Analyzer, with a Bioanalytical Systems CV-27 unit for potential scan waveforms. Voltammograms were taken at vitreous carbon electrodes (Tokai GC-30, 3 mm diameter, sealed in Pyrex). Preparative scale electrolyses were carried out in vitreous carbon crucibles (Atomergic Chemetals Corp.) with a PARC 273 Electrochemical Analyzer.

Following preparative electrolysis, the melt was generally extracted with hexane (previously distilled over sodium) to obtain neutral products, after which the melt was hydrolyzed over ice and extracted with benzene to remove other products. Product determination was carried out primarily by GC/MS (HP 5988A and HP 5890/5971A) and HPLC (C18 column, methanol/water eluent) methods.

RESULTS AND DISCUSSION

Benzophenone

Benzophenone was chosen as a system for investigation because of the variety of possible anionic products formed during its reduction. Acid/base interactions between these anions and the EMI ring were expected to be manifested by the formation of protonated products. In the basic melt, benzophenone is reduced in a single process (Figure 1), giving tetraphenyloxirane (10-15%, isolated in the hexane extract) and benzhydrol (85-90%, from hydrolysis/benzene extract). The
The coulometric value of 1.7 - 1.8 agrees with the product yields, considering that these products are formed in one and two-electron processes, respectively. The nature of these products suggests the initial formation of the ketyl (anion radical) which, as in the acidic melt, very quickly undergoes complexation of the oxygen by chloroaluminate (Figure 2). Further reactions of this species are very rapid, the anodic process for ketyl oxidation back to benzophenone being observed only at scan rates above 10 V/s. Coupling of two ketyl species leads to oxirane formation, whereas further reduction produces the alcohol (benzhydrol) which exists in the melt as the complexed anion (Figure 2) and must be isolated after melt hydrolysis.

The isolation of benzhydrol from the basic melt poses the question of whether the protonation (uptake of 2 protons) occurs in the melt during reduction or during the workup procedure. The O-H bond is evidently formed during workup because the product exists as the complexed anion in the melt and is therefore not extracted into hexane, gaining the proton during addition of water to the melt. The carbanion, however, is much more basic than the oxygen anion, suggesting the possibility that the proton is donated in the melt by the EMI cation. This is entirely reasonable given the rather great acidity of the proton on the 2 position of the EMI ring (5). When the reduction of benzophenone is carried out in a basic melt composed of 2-d-EMIC, the mass spectrum (Figure 3) contains a peak one mass unit higher (185) than that seen for benzhydrol (184), showing conclusively that the carbanion in this system abstracts hydrogen from the EMI cation. A close look at the spectra reveals that there appears to be a considerable amount of benzhydrol in the product from the deuterated melt, judging from the sizeable signal at 184. This peak could arise from a M-1 process from the deuterated product; however, the corresponding process for benzhydrol (upper spectrum) seems to be a rather minor one. Assuming that the fragmentation pathways of the protio and deuterio analogs of benzhydrol are the same, this finding indicates that the EMI cation also supplies protons from the 4 and 5 positions. These positions, although not as acidic as that in the 2 position, are still acidic enough to exchange with D2O at elevated temperatures (5) and probably play a minor role in protonating the benzhydrol carbanion.

**Anthracene**

The reduction of anthracene has also been extensively studied in nonaqueous systems, providing another system (aromatic anions) for comparison of proton-accepting ability.
In acetonitrile/0.1 M TEAP, anthracene undergoes a reversible one-electron reduction; however, the two-electron reduction (dianion) is irreversible due to protonation of the dianion formed in the second step. In the EMIC-based melt, anthracene reduction occurs in a single step, two-electron process (Figure 4). This behavior implies that the anion radical undergoes protonation by the melt, leading to ECEC behavior in which the chemical steps are protonations. The product isolated from a preparative electrolysis of 20 mM anthracene (hexane extraction) is dihydroanthracene in good yield. This level of product formation, in the absence of protonic impurities, is by itself good evidence for protonation of reduction products by the EMI cation. In addition, the reduction product isolated from the deuterated melt (2-d-EMIC) gives dideuterioanthracene as seen by mass spectrometry.

**Triphenylmethyl chloride**

Reduction of triphenylmethyl chloride (trityl chloride) in the basic melt produces triphenylmethane in a two-electron process. The process involves the cleavage of the C-Cl bond to form the trityl radical, which is then reduced to the trityl anion. Once again, carrying out the reduction in the deuterated melt gave the deuterated analog (m/z 245). As in the case of benzophenone, there was an appreciable response for the protio analog at m/z 244, again suggesting that protons in the 4 and 5 EMI ring positions are capable of some proton donation under these conditions.

**CONCLUSIONS**

Generation of carbanionic species in the AlCl₃ : EMIC molten salt has demonstrated that the EMIC ring system is capable of donating protons to these species. An estimate for the pKₐ of the proton on the 2 position of the EMIC ring can be made considering its facile exchange with D₂O. It appears that the pKₐ for the EMIC proton is similar to the value of 15.7 for the H₂O/OH⁻ system (6). Complete exchange occurs in an environment containing somewhat more than a ten-fold molar excess of D₂O, producing an estimate (upper limit) of 17 for the pKₐ of the 2 proton of EMIC. This value is given some support by the fact that protonation of the anthracene anion radical occurs in the melt, whereas this species is not protonated in anthracene, which has a pKₐ of 25 [aqueous scale, (6)]. The trityl anion is much more basic [pKₐ 32, (6)] and is expected to be protonated in the melt.
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Figure 1. Cyclic voltammogram of benzophenone in basic melt (0.8 : 1.0)
Conditions: 31 mM, 100 mV/s, temperature = 40°C

Figure 2. Mechanistic pathway for benzophenone reduction in basic melt
Figure 3. Mass spectra in the molecular ion region for
(a) benzophenone reduction product in 2-d-EMIC-based melt
(b) benzhydrol

Figure 4. Cyclic voltammogram of anthracene in basic melt (0.8 : 1.0)
Conditions: 20 mM, 100 mV/s, temperature = 40°C