ELECTROCHEMICAL INVESTIGATIONS OF LEWIS ACID INTERACTIONS WITH KETONES IN A ROOM-TEMPERATURE IONIC LIQUID

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ABSTRACT

The voltammetric behavior of fluorenone in the room-temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4) has been studied. As in acetonitrile, two successive one-electron transfers were observed, although the second process is less reversible in EMIBF4 than in acetonitrile. Addition of BF3 etherate produces an additional reduction peak at more positive potentials, indicative of complexation of fluorenone by BF3. Upon addition of aluminum chloride to the melt, formation of chloride is indicated, probably by interaction with the BF4- anion. Complexation of fluorenone still occurs, however, implying that aluminum chloride is converted to another species, possibly BF3, in this process.

INTRODUCTION

Room-temperature ionic liquids have received much attention as solvent media for organic reactions (1, 2). An important class of reactions is those in which Lewis acids play an important role, such as Friedel-Crafts and isomerization reactions. In this work, the behavior of boron trifluoride and aluminum chloride, with respect to the ketone fluorenone, in the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4) ionic liquid has been studied. In addition, some of the electrochemical characteristics of fluorenone reduction have been compared in EMIBF4 and acetonitrile.

EXPERIMENTAL

1-ethyl-3-methylimidazolium tetrafluoroborate (97%) was obtained from TCI America. A cyclic voltammogram of the melt as received at platinum showed a reduction peak at -0.9V, indicating the presence of protons. Addition of basic alumina removed this peak and presumably the protons responsible for it. It has also been found that vacuum treatment 90°C removes protons as well as volatile impurities.

Potentials are referred to a Ag/AgCl electrode, prepared by immersing a Ag/AgCl wire (Cypress Systems) in 0.1 M EMIC / EMIBF4. EMIC is 1-ethyl-3-methylimidazolium chloride. Voltammetry was carried out using a PARC 283 potentiostat in a Vacuum Atmospheres Corporation drybox.
RESULTS AND DISCUSSION

Initial studies were carried out in acetonitrile (AN) to compare with the results obtained in the EMIBF₄ system. The behavior of ketones in nonprotic media is characterized by successive one-electron redox processes (Figure 1), the first of which is generally reversible (3). The second process generates a dianion, which is much more reactive toward proton donors than is the radical anion formed in the first step. Such behavior is illustrated in Figure 2, which shows a voltammogram of fluorenone (FL) in acetonitrile / 0.1M TEA BF₄. The first reduction process occurs at a potential of -1.25 V. Note that the second redox process is mostly reversible. Addition of BF₃ etherate results in the formation of a new reduction peak at -0.31V, attributed to the reduction of the FL : BF₃ complex. Further additions of BF₃ etherate lead to the disappearance of the peak for the uncomplexed ketone at -1.25 V. An estimate of the K value for the complexation of fluorenone with BF₃ according to the equation

\[
\text{FL} + \text{BF}_3 \text{AN} \rightarrow \text{FLBF}_3 + \text{AN} \quad (1)
\]



was calculated by using the peak heights for the FL:BF₃ complex as a measure of its concentration as BF₃ etherate was added. The peak current for the fully formed complex was assumed to correspond to a concentration equal to the initial FL concentration, and the concentration of uncomplexed FL was obtained by difference. It was also assumed, with justification below, that, upon addition to acetonitrile, ether is displaced from BF₃ etherate by AN. A K value of 159 (+/- 20) was obtained for the complexation process. If BF₃ AN is used in equation (1) instead of BF₃ etherate, constant values of K are not obtained.

In EMIBF₄, the first fluorenone reduction process (Figure 3) occurs at a similar potential (-1.12V) as it does in acetonitrile; however, the difference in peak potentials for the first and second reduction processes is considerably less than it is in acetonitrile. In addition, the second reduction process is not as reversible as in acetonitrile. These observations apparently reflect the fact that the EMI cation possesses appreciable acidity at the C2 ring carbon (4), thereby serving as a proton donor to the fluorenone dianion. Acetonitrile, with a pKa of 25 (5), does not protonate the dianion as much as the EMI cation. Addition of BF₃ etherate to FL in EMIBF₄ produces another reduction process at -0.88V, again ascribed to reduction of the FL:BF₃ complex. This potential is much closer to that for the uncomplexed FL than it is in acetonitrile, apparently indicating that the extent of complexation of FL by BF₃ is somewhat less than in acetonitrile. This observation may involve the much higher concentration of BF₄⁻ in the EMIBF₄ solvent (approx. 4 M) compared to that in acetonitrile (0.1 M). It is possible that interaction between added BF₃ and BF₄⁻ in the EMIBF₄ forms the species B₃F₇, which has been observed in other systems (6). In this work, however, preliminary investigations did not detect Raman bands due to this species, probably due to lack of sensitivity of the instrument. Extensive interaction between BF₃ and BF₄⁻ would be expected to result in a lesser degree of complexation of FL by BF₃ in EMIBF₄, with a correspondingly lower separation between reduction potentials for complexed and free FL.

Turning now to another Lewis acid, the results for the use of AlCl₃ in EMIBF₄ will now be discussed. It has been found that addition of AlCl₃ to EMIBF₄ results in the formation of chloride in the melt, as confirmed by addition of EMIC to the melt and the
resulting oxidation peak at +1.5V (Figure 4). From the amounts of AlCl₃ and EMIC added, an equimolar amount of chloride, with respect to added AlCl₃, is formed in this process. A possible pathway for chloride formation is

\[
\text{AlCl}_3 + BF_4^- \rightarrow BF_3 + \text{AlCl}_3F^- \quad (2)
\]

\[
\text{AlCl}_3F^- + BF_4^- \rightarrow BF_3 + \text{AlCl}_3F_2^- + Cl^- \quad (3)
\]

Some support for this scenario has been found by careful additions of EMIC (0.065 mmol) to a EMIBF₄ melt to which AlCl₃ had been added (also 0.065 mmol). One might expect that simple neutralization would take place (Lewis acid AlCl₃ with Lewis base chloride); however, when 0.045 mmol FL was added, a reduction peak for the complexed FL, similar to that found upon addition of BF₃ etherate to EMIBF₄, was observed. This implies that the solution is not neutral. If the second step in the proposed sequence proceeds to a significant extent, some BF₃ would be available to complex FL in the melt. Although fluoride is expected to interact more strongly with boron than with aluminum, it is possible that the much higher concentration of BF₄⁻ (approx 4M) relative to added AlCl₃ (50 mM) may drive the reactions to the right more than might otherwise be expected.

CONCLUSIONS

The voltammetric behavior of fluorenone in the room-temperature ionic liquid EMIBF₄ is consistent with two one-electron redox systems, similar to those observed in acetonitrile. The EMI cation is sufficiently acidic, however, to lessen the reversibility of the second step by protonating the fluorenone dianion. Addition of BF₃ etherate to EMIBF₄ results in the formation of a BF₃ fluorenone complex, as deduced from the appearance of a reduction process at potentials more positive than that for uncomplexed fluorenone. Upon addition of aluminum chloride to EMIBF₄, chloride is formed, implying that aluminum chloride is converted to another acidic species, possibly by interaction with BF₄⁻ in the melt.

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Figure 1. General reduction pathway for fluorenone in nonaqueous media.

Figure 2. Cyclic voltammograms of 11 mM fluorenone in acetonitrile / 0.10 TEA BF₄, at glassy carbon, 100 mV/s.
Figure 3. Cyclic voltammograms of fluorenone in EMIBF$_4$ ionic liquid, at glassy carbon, 100 mV/s.

Figure 4. Cyclic voltammograms showing formation of chloride (+1.5V oxidation peak) upon addition of aluminum chloride to EMIBF$_4$.