INTRODUCTION OF PROTONS WITH SOLUTES IN AMBIENT TEMPERATURE CHLOROALUMINATE MOLTEN SALTS: ELECTROCHEMISTRY AND NMR SPECTROSCOPY OF PROTONATED AND UNPROTONATED ANTHRACENE

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ABSTRACT

The Brønsted acidity of protons in an ambient temperature molten salt, AlCl₃:1-ethyl-3-methylimidazolium chloride (ImCl), can be varied by changing the underlying acidity of the molten salt. In a basic melt, where the mole ratio of AlCl₃:ImCl is less than 1, the proton is a relatively weak acid, whereas in an acidic melt, where the mole ratio of AlCl₃:ImCl is greater than 1, its acidity increases enormously. Electrochemistry has been employed to study the interactions of protons with anthracene in the acidic melt. It was found that anthracene is protonated to give the anthracenium ion, which cannot be oxidized within the melt electrochemical window; however, it can be reduced to yield H₂ and free anthracene. NMR spectra show anthracene to be unprotonated in the basic melt, whereas in the acidic melt it forms a proton adduct.

INTRODUCTION

Ambient temperature organic chloroaluminate molten salts, AlCl₃:MC₁, where MC₁ is either 1-ethyl-3-methylimidazolium chloride (ImCl) or n-butylpyridinium chloride (BuPyCl), are excellent solvents for studying the electrochemistry of organic compounds. These molten salts are liquids at room temperature over a wide range of AlCl₃:MC₁ ratios. Melts are acidic, neutral, or basic when the

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AlCl₃:ImCl molar ratio is greater than, less than, or equal to unity, respectively (1). The acidic melts contain heptachlorodialuminate ion, Al₂Cl₇⁻, which is a strong Lewis acid, while the basic melts contain chloride ion, a Lewis base.

Recent work by Smith and co-workers (2,3) has shown that the value of the Hammett acidity function for protons in acidic AlCl₃:ImCl melts is in the range of a Bronsted superacid. Furthermore, their work demonstrated that the relative superacidity of protons in acid melts can be varied by changing the underlying melt Lewis acidity.

Anthracene has been shown to be protonated to the anthracenium ion in acidic AlCl₃:ImCl melts containing proton (3). We had demonstrated much earlier that the electrochemically generated cation radical of anthracene is somewhat stable in an acidic AlCl₃:BuPyCl melt, but did not study this quantitatively (4).

Here we report on the investigation of the electrochemistry and NMR spectroscopy of anthracene in this mixed Lewis–Brønsted acid system.

**EXPERIMENTAL**

The preparation and purification of the AlCl₃:ImCl melts was performed as previously described (5). The source of protons for all experiments, 1-ethyl-3-methylimidazolium hydrogen dichloride (ImHCl₂), was prepared by reaction of ImCl with HCl(g) (6). 1-ethyl-3-methylimidazolium deuterium dichloride (ImDCl₂) was obtained by substituting DCl(g) for HCl(g). Anthracene–h₁₀ (99.9%, Aldrich), anthracene–d₁₀ (98% D, Cambridge Isotope), and 9,10-dihydro-anthracene (97%, Aldrich) were used as received. Methylaluminum sesquichloride (MAC), Me₃Al₂Cl₃ (Aldrich), was used as appropriate to remove protonic impurities from the melts.

All electrochemical experiments were performed under a purified helium atmosphere in a Vacuum Atmospheres dry-box. Electrochemical experiments were performed using an EG&G PARC Model 273 Potentiostat/Galvanostat controlled by a DEC PDP-8/e computer (7). Working electrodes, obtained from Bioanalytical Systems, were either Pt disc (area = 0.02 cm²) or glassy carbon, GC, (area = 0.071 cm²). The reference electrode consisted of an Al wire (5N Alfa Inorganics) immersed in a 1.5:1 AlCl₃:ImCl melt in a separate fritted tube. The counter electrode was a coiled Al wire.
2H NMR experiments were performed on a Varian VXR-400 S spectrometer operating at 61.395 MHz with broad-band proton decoupling. Samples were prepared in the dry-box and pipetted into 10–mm tubes (Wilmad Glass Co.). The tubes were then capped and sealed with Parafilm prior to removal from the dry-box. The 2H NMR experiments were performed with the spectrometer unlocked. Natural abundance D2O in water was used as the reference and assigned a value of 0 ppm. Referencing was performed by substitution.

**RESULTS AND DISCUSSION**

I. **Anthracene in proton free acidic AlCl3:ImCl melts.**

Anthracene in acidic AlCl3:ImCl melts is oxidized in two one-electron oxidation steps as shown by the cyclic staircase voltammogram (CSV) in Figure 1a for a scan positive from 1 V at GC. A CSV for a negative scan from 1 V (Figure 1b) reveals a small wave at ca 0.3 V corresponding to the reduction of anthracenium ion produced from the protonation of anthracene by adventitious protonic impurities (*vide infra*). The first one-electron oxidation produces a cation radical which is sufficiently stable for the corresponding reduction wave to be observed, even at relatively slow scan rates. The second oxidation wave is due to the formation of a dication for which there is no associated reduction wave.

Normal pulse voltammograms were obtained as a function of pulse width for anthracene oxidation in a 1.2:1.0 melt with a small excess of MAC. Table I summarizes the normal pulse parameters pulse width (tₚ), half-wave potential (E₁/₂), diffusion–limited current (iᵢ), and the slope of E vs. log[i/(iᵢ – i)] which has a theoretical value of 59 mV for a one-electron process at 25 °C. The values for the slope in Table I for the first oxidation vary; however, they are consistent with a one-electron process. The E₁/₂ values for the first oxidation are essentially constant and independent of tₚ. The second anthracene oxidation wave appears much more complex than the first. The E₁/₂ values for the second wave remain relatively constant at shorter pulse widths but shift to less positive potentials at longer pulse widths. The limiting currents for the second oxidation are approximately the same as those for the first oxidation indicating that the second oxidation wave is also a one-electron process. This is in contrast to previous work on anthracene oxidation in more conventional solvents, such as acetonitrile, where the first wave, ex-
cept at very high scan rates at microelectrodes, is a two–electron process (8,9).

The diffusion coefficient for anthracene was calculated from the normal pulse limiting currents using the Cottrell equation

\[ i_1 = nFAC(D/\pi t_p)^{1/2} \] (1)

where \( n \) is the number of electrons, \( F \) is the Faraday constant, \( A \) is the area of the electrode, \( C \) is the concentration of the diffusing species, and \( t_p \) is the pulse width. A plot of \( i_1 \) vs \( t_p^{-1/2} \) for the first oxidation is linear (\( R = 0.999 \)) with a slope of 39.2 \( \mu A \) s\(^{-1/2} \). From this slope a diffusion coefficient of 1.1 \( \times 10^{-6} \) cm\(^2\) s\(^{-1} \) was calculated for anthracene in a 1.2:1.0 melt at 27 °C.

The \(^2\)H NMR spectra of anthracene–\( d_{10} \) in benzene and in a 1.2:1.0 melt are shown in Figure 2. The observed spectra in both solvents are essentially identical to that previously reported for fully deuterated anthracene (10). The spectrum for the 1.2:1.0 melt indicates that anthracene does not form an AlCl\(_3\) adduct in acidic melts. This contradicts conclusions made in previous work in the acidic AlCl\(_3\):BuPyCl melts (4), but it is in agreement with more recent work in the acidic AlCl\(_3\):ImCl melts (3). To obtain the spectrum in Figure 2b great care was taken to remove all protonic impurities.

Kinetics of Anthracene Radical Cation Decomposition. The first oxidation wave was examined in more detail using cyclic staircase voltammetry. Theoretical curves were fit to voltammograms assuming an initial reversible one–electron transfer followed by an irreversible homogeneous reaction, i.e. a classic \( E_C^{1/2} \) case (10,12). The \( E_{1/2} \) value for the electron transfer and the first order rate constant, \( k \), were obtained using a non–linear least squares program developed in this laboratory (13). The fitted voltammograms were collected for several melt compositions. These melts were made by starting with 20 mM anthracene in a 2.0:1.0 melt and adding ImCl to produce the less acidic melt compositions; consequently, the anthracene concentration decreased to ca. 15 mM for the least acidic melt.

Representative values for \( E_{1/2} \) and \( k \) for various melt compositions and scan rates are shown in Table II. Characteristic voltammograms at various scan rates and two different melt acidities are shown in Figure 3. The dots are the experimental data, and the
solid line is the fit of the data. In general the \( E_0C_1 \) model fits the data quite well. Apparent in Table II, however, is the decrease in the homogeneous rate constant with increasing melt acidity. This would seem to indicate the stability of the cation radical is enhanced in melts of greater Lewis acidity. Also apparent in Table II is an increase in the rate constant and a slight shift of \( E_{1/2} \) towards positive potentials with increasing scan rate. Ideally, the same \( k \) and \( E_{1/2} \) values should be obtained for all scan rates for a particular melt. There is no obvious reason for these shifts with scan rate, and we can offer no explanation for this trend at this time.

When rate constants for anthracene concentrations of 7, 20, and 35 mM in a 1.5:1.0 melt were determined for a scan rate of 100 mV s\(^{-1}\) values of 0.17, 0.22, and 0.27 s\(^{-1}\), respectively, were obtained. The increase in pseudo first-order rate constant with increasing anthracene concentration may indicate a higher-order process such as coupling of radical cations to form bianthracenes (14). The relatively small change in the rate constant with concentration does not alter the discussion of the rate constant as a function of melt composition since the concentration of anthracene varied only from 20 to 15 mM for the experiments summarized in Table II.

In the acidic melts the anthracene radical cation is much more stable than in conventional organic solvents (8,15). In rigorously dried acetonitrile, for example, a value for the first-order rate constant of 125 s\(^{-1}\) has been determined (8). Although no rate constant was determined, the radical cation in dichloromethane over alumina was found to be quite stable, judging from the fact that a reverse peak for the reduction of the radical cation was seen at a scan rate of ca. 100 mV s\(^{-1}\) (16).

II. Anthracene in acidic AlCl\(_3\):ImCl melts containing proton.

It has been shown recently that proton in acidic AlCl\(_3\):ImCl is a Brønsted–superacid which readily protonates anthracene forming the anthracenium cation (3). Figure 4 shows both anodic and cathodic scans at GC starting from 1 V in a 1.5:1.0 melt containing 18 mM anthracene and 28 mM of the proton source, ImHCl\(_2\). The anthracenium ion is not oxidized in the melt window. On the other hand, the anthracenium ion reduction at ca. 0.3 V is the major electrochemical process in this solution. The oxidation waves for unprotonated anthracene are also seen, albeit at much lower currents, indicating that anthracene is not quantitatively protonated even in the presence of an excess of protons. No proton reduction is observed because protons are not electroactive at GC within the melt.

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window (17). However, when a cathodic scan from 1 V is performed on Pt, reduction waves for both proton and anthracenium ion are seen. Normal pulse voltammograms for anthracenium ion reduction in this solution were performed at various pulse widths. Table III summarizes the relevant parameters. Although anthracene is not quantitatively protonated at 28 mM ImHCl2, it is more than 90% protonated. Thus, the anthracenium ion concentration can be approximated as 18 mM. From the slope of a plot of $i_1$ vs. $t_p^{-1/2}$ ($R = 0.997$) an estimate for the anthracenium ion diffusion coefficient of $4 \times 10^{-7}$ cm$^2$ s$^{-1}$ was obtained assuming an $n$ value of 1. Unfortunately, at high proton concentrations the mechanism of anthracenium ion reduction changes (vide infra), and $n$ approaches two. Consequently, it was not possible to add a large excess of protons to quantitatively protonate the anthracene without changing the reduction process.

The $^2$H NMR spectrum of 15 mM anthracene-$d_{10}$ with 30 mM ImDCl$_2$ in a 1.2:1.0 melt is shown in Figure 5a. The observed spectrum is consistent with a fully deuterated anthracenium ion (18), confirming the conclusions made from the electrochemical experiments. Unfortunately, due to the inherent broad nature of $^2$H peaks it was not possible to determine the completeness of deuteration. Interestingly, the $^2$H spectrum of 15 mM anthracene-$h_{10}$ with 30 mM ImDCl$_2$ in a 1.2:1.0 AlCl$_3$:ImCl melt (Figure 5b) is essentially identical, except for peak intensities, to that for the fully deuterated anthracenium ion (Figure 5a). The presence of a deuterium spectrum indicates that H–D exchange occurs at all positions on the anthracene ring. This is not entirely surprising when considering the highly acidic nature of proton in acidic melts and the fact that Lewis acids have been shown to catalyze H–D exchange on anthracene (10).

A cyclic staircase voltammogram of anthracene oxidation at Pt in the presence of excess ImHCl$_2$ is shown in Figure 6a. A significant increase in the anthracene oxidation wave was observed when the potential was held at 0.7 V before scanning through the wave (Figure 6b). At 0.7 V "free" protons are reduced but anthracenium ion is not. These results strongly suggest that, at the electrode surface, the equilibrium

$$
\begin{align*}
\text{H} \quad \text{H} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\end{align*}
\rightleftharpoons
\begin{align*}
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\end{align*} 
+ \text{H}^+$

\text{(2)}$

is followed by

\[ H^+ + e^- \rightarrow \frac{1}{2} H_2 \]  (3)

As the proton concentration at the electrode surface is reduced by the reduction of "free" proton, the anthracenium ion dissociates (Eq. 2) producing anthracene.

An attempt was made to determine the equilibrium constant for Eq. 2. Aliquots of ImHCl\textsubscript{2} were added to an acidic melt containing anthracene and the decrease in the first anthracene oxidation wave and the concomitant increase in the anthracenium ion reduction wave were monitored at GC by normal pulse voltammetry. Unfortunately, evaluation of the equilibrium constant proved difficult due to the slow decomposition of the anthracene/anthracenium solution. Consequently, an equilibrium constant was obtained for only one melt composition. For a 1.2:1.0 melt with 31 mM anthracene a value of 0.02 mol L\textsuperscript{-1} was obtained for the equilibrium constant. The observed trend for other melt acidities was toward greater protonation with increasing melt acidity.

The reduction of the anthracenium cation was examined at GC and Pt electrodes. Figures 7b and 8b show cyclic staircase voltammograms at GC and Pt, respectively, for anodic scans recorded in a 1.5:1.0 melt containing 18 mM anthracene and 28 mM ImHCl\textsubscript{2} after holding the potential at 0.1 V (reducing the anthracenium ion) for 5 s. These are compared to anodic scans starting at 1 V where small amounts of unprotonated anthracene are observed (Figures 7a and 8a respectively). At GC, where the H\textsuperscript{+}/H\textsubscript{2} couple is inactive, reduction of anthracenium takes place and produces unprotonated anthracene as indicated by the large increase in the anthracene oxidation wave at 1.3 V. At Pt, reduction of anthracenium ion and free proton takes place and produces both H\textsubscript{2} (oxidation wave at ca. 0.9 V) and unprotonated anthracene.

Cyclic staircase voltammograms of anthracenium ion reduction showed a shift of the reduction wave to more negative potentials and an increase in the peak current with increasing proton concentrations. With a large excess of protons the peak current reached a relatively constant value approximately twice that of the anthracenium cathodic current at lower proton levels. At high proton concentrations the anthracene oxidation wave at 1.3 V disappears, and on the reverse anodic scan, a new oxidation wave at 1.9 V is observed. Figure 9 compares the oxidation wave following an anodic scan from a potential hold at 0.1 V with the oxidation wave
observed upon addition of 9,10-dihydroanthracene to a 1.5:1 melt. It appears that at high concentrations of proton, the anthracenium ion is reduced to form 9,10-dihydroanthracene.

The reduction scheme we see in the molten salt for the anthracenium ion is shown in Scheme I. We do not understand the details of the process; however, in view of the fact that we see the anthracenium reduction at both GC and Pt, and at about the same potentials, whereas on GC we do not see reduction of "free" proton (nor H₂ oxidation), it is reasonable to conclude that the electron interacts initially with the ring system and ultimately ends up reducing the proton.

III. Anthracene in basic AlCl₃:ImCl.

Anthracene oxidation is not observed in the basic AlCl₃:ImCl melts because the anodic window is limited to ca. 1 V by chloride oxidation. Furthermore, in basic melts containing anthracene and a large excess of ImHCl₂, there was no evidence of a reduction wave for anthracenium ion. Figure 10a shows a ²H NMR spectrum of 15 mM anthracene–d₁₀ in a 0.7:1.0 melt. The spectrum is essentially identical to that found in benzene and in a 1.2:1.0 melt (Figure 2). When 30 mM of ImDCl₂ was added to this melt the spectrum in Figure 10b was obtained. The only observable change is the appearance of a new peak at δ 6.1, which is due to the DCl₂⁻ ion. This indicates that anthracene does not protonate in basic melts. Finally, unlike the acidic melt, the ²H NMR spectrum for 15 mM anthracene–h₁₀ and 30 mM ImDCl₂ in a 0.7:1.0 melt (Figure 10c) shows no evidence of H–D exchange.

SUMMARY

In acidic, proton free, melts anthracene is oxidized in two one-electron steps. The first oxidation forms a cation radical that is relatively stable, and the second oxidation produces a dication which is unstable. In acidic melts containing proton, anthracene is protonated in an equilibrium process to form the anthracenium cation. The reduction of the anthracenium ion produces anthracene and H₂. In basic melts anthracene exhibits no electrochemistry. However, NMR experiments show that anthracene does not form a proton adduct in basic melts.
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**Scheme I:**

**Small Excess of Proton**

\[
\text{Small Excess of Proton}
\]

\[
\begin{align*}
\text{+ e} & \quad \rightarrow \\
\text{+ } \frac{1}{2} \text{H}_2
\end{align*}
\]

**Large Excess of Proton**

\[
\text{Large Excess of Proton}
\]

\[
\begin{align*}
\text{+ H}^+ + 2 \text{e} & \quad \rightarrow \\
\text{? e} & \quad \rightarrow \text{??}
\end{align*}
\]
Table I. Normal Pulse Parameters for Oxidation of 9.6 mM Anthracene in 1.2:1.0 AlCl$_3$:ImCl; GC Electrode at 24 °C.

| $t_p$, ms | $E_{1/2}$, V | $i_1$, $\mu$A | Slope,$^b$ mV |
|-----------|--------------|----------------|--------------|
| 25        | 1.304        | -233           | 55.7         |
| 50        | 1.306        | -168           | 62.5         |
| 100       | 1.303        | -144           | 68.8         |
| 250       | 1.306        | -68.9          | 51.8         |
| 500       | 1.296        | -39.4          | 46.8         |

Second Oxidation Wave

| $t_p$, ms | $E_{1/2}$, V | $i_1$, $\mu$A$^a$ | Slope,$^b$ mV |
|-----------|--------------|-------------------|--------------|
| 25        | 1.934        | -210              | 86.5         |
| 50        | 1.942        | -136              | 73.9         |
| 100       | 1.937        | -89.8             | 52.6         |
| 250       | 1.921        | -56.9             | 60.0         |
| 500       | 1.898        | -27.4             | 34.8         |

$^a$Measured from plateau of first oxidation.  $^b$Reciprocal slope of $E$ vs. log(|$i_d$ - $i$|/$i$).
Table II. Kinetic Parameters from Staircase Cyclic Voltammetry for Anthracene Oxidation in various melt compositions: GC electrode at 26 °C.

| Scan Rate, mV/s | $E_{1/2}, \text{V}$ | $k, \text{s}^{-1}$ |
|-----------------|-----------------|-----------------|
|                 | 2.0:1.0 Melt (0.8 → 1.7 V)$^a$ |                 |
| 50              | 1.310 (0.002)   | 0.10 (0.01)     |
| 100             | 1.313 (0.002)   | 0.12 (0.01)     |
| 250             | 1.317 (0.002)   | 0.14 (0.03)     |
|                 | 1.78:1.0 Melt (0.8 → 1.7 V)$^a$ |                 |
| 50              | 1.306 (0.002)   | 0.12 (0.01)     |
| 100             | 1.309 (0.002)   | 0.17 (0.02)     |
| 250             | 1.312 (0.002)   | 0.23 (0.03)     |
|                 | 1.46:1.0 Melt (0.8 → 1.6 V)$^a$ |                 |
| 50              | 1.304 (0.002)   | 0.18 (0.02)     |
| 100             | 1.305 (0.002)   | 0.25 (0.03)     |
| 250             | 1.308 (0.002)   | 0.35 (0.04)     |
|                 | 1.21:1.0 Melt (0.8 → 1.6 V)$^a$ |                 |
| 50              | 1.300 (0.003)   | 0.19 (0.03)     |
| 100             | 1.302 (0.003)   | 0.29 (0.04)     |
| 250             | 1.304 (0.002)   | 0.41 (0.06)     |
|                 | 1.0:1.0 Melt (0.8 → 1.5 V)$^a$ |                 |
| 50              | 1.318 (0.004)   | 0.16 (0.04)     |
| 100             | 1.316 (0.003)   | 0.52 (0.10)     |
| 250             | 1.316 (0.005)   | 0.74 (0.14)     |

$^a$Potential range scanned.
Table III. Normal Pulse Parameters for Reduction of ca. 18 mM Anthracenium in 1.5:1.0 AlCl$_3$:ImCl at GC.

| t$_p$, ms | E$_{1/2}$, V | i$_{1}$, µA | i$_{1}$t$_p^{1/2}$, µA ms$^{1/2}$ |
|----------|--------------|-------------|-------------------------------|
| 25       | 0.353        | 269         | 1345                          |
| 50       | 0.379        | 177         | 1251                          |
| 100      | 0.385        | 124         | 1240                          |
| 250      | 0.400        | 78.5        | 1241                          |
| 500      | 0.423        | 51.6        | 1153                          |
Figure 1. Cyclic staircase voltammograms for 18 mM anthracene in 1.5:1.0 AlCl$_3$:ImCl at GC electrode. a) cathodic scan from 1 V, 500 mV s$^{-1}$; b) anodic scan from 1 V, 500 mV s$^{-1}$. On addition of MAC wave at 0.4 V was eliminated.

Figure 2. $^2$H NMR spectra of 15 mM anthracene–d$_{10}$ in a) benzene; b) 1.2:1.0 AlCl$_3$:ImCl.
Figure 3. Cyclic staircase voltammograms, GC electrode, for a–c) 8.5 mM anthracene in 1.2:1.0 melt at a) 2,000 b) 500 c) 50 mV s⁻¹ and d) 15 mM anthracene in 2.0:1.0 melt at 50 mV s⁻¹.
Figure 4. Cyclic staircase voltammogram for 18 mM anthracene and 28 mM ImHCl$_2$ in 1.5:1.0 AlCl$_3$:ImCl at GC electrode. a) cathodic scan from 1 V; b) anodic scan from 1 V. Scan rate 500 mV s$^{-1}$. No MAC was added so actual proton concentration is greater due to protonic impurities.

Figure 5. $^2$H NMR of 1.2:1.0 AlCl$_3$:ImCl 30 mM ImDCI$_2$. a) 15 mM anthracene--$d_{10}$ b) 15 mM anthracene--$h_{10}$. Peak at δ 2.5 is the acidic form of proton.
Figure 6. Cyclic staircase voltammograms for 18 mM anthracene and 28 mM ImHCl$_2$ in 1.5:1.0 AlCl$_3$:ImCl melt at a Pt electrode. a) anodic scan from 1 V; b) anodic scan after a 5 s hold at 0.7 V. Scan rate 500 mV s$^{-1}$.

Figure 7. Cyclic staircase voltammogram for 18 mM anthracene and 28 mM ImHCl$_2$ in 1.5:1.0 AlCl$_3$:ImCl melt at a GC electrode. a) anodic scan from 1 V; b) anodic scan after a 5 s hold at 0.1 V. Scan rate 500 mV s$^{-1}$.
Figure 8. Cyclic staircase voltammogram for 18 mM anthracene and 28 mM ImHCl₂ in 1.5:1.0 AlCl₃:ImCl melt at a Pt electrode. a) anodic scan from 1 V; b) anodic scan after a 5 s hold at 0.1 V. Scan rate 500 mV s⁻¹.

Figure 9. a) Cyclic staircase voltammogram for 18 mM anthracene and 177 mM ImHCl₂ in a 1.5:1.0 AlCl₃:ImCl melt at a GC electrode. Anodic scan from a 5 s hold at 0.1 V, 500 mV s⁻¹. Eₚₐ = 1.95 V. b) cyclic staircase voltammogram for 11 mM 9,10-dihydroanthracene in same melt. Eₚₐ = 1.96 V.
Figure 10. $^2$H NMR spectra of 0.7:1.0 AlCl$_3$:ImCl melt a) 15 mM anthracene-$d_{10}$ b) solution in a) with 30 mM ImDCl$_2$, and c) 15 mM anthracene-$h_{10}$ and 30 mM ImDCl$_2$. 