PROTONS IN AMBIENT TEMPERATURE CHLOROALUMINATE MOLTEN SALTS:
ELECTROCHEMICAL AND NMR STUDIES OF THEIR INTERACTION WITH
DIMETHYLANILINE

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ABSTRACT

The Brønsted acidity of protons in the ambient
temperature molten salt, AlCl₃:1-ethyl-3-methylimidazolium
chloride (ImCl), can be varied by changing the underlying
acidity of the molten salt. We have examined the
electrochemistry and NMR spectroscopy of dimethylaniline,
DMA, in a basic melt, where the mole ratio of AlCl₃:ImCl is
less than 1, and in an acidic melt, where the mole ratio of
AlCl₃:ImCl is greater than 1, with and without the addition
of protons. The oxidation of DMA in the acidic melt is ca
1.5 V more positive than in the basic melt, indicating AlCl₃
adduct formation. On addition of proton to either melt, the
DMA oxidation wave is shifted outside of the melt
electrochemical window, indicating formation of protonated
adducts in both acidic and basic melts. ¹³C and ¹H NMR
spectra show the presence of both the protonated and
unprotonated species and, in the acidic melt, the presence of
both an AlCl₃ adduct and a protonated adduct.

INTRODUCTION

In prior work in ambient temperature molten salts, consisting of
aluminum chloride mixed with an organic chloride, either N-
butylpyridinium chloride or 1-ethyl-3-methylimidazolium chloride, ImCl,
we noted that very large shifts in the potential for proton reduction,
of the order of +1.5 V, were observed as the melt composition was varied
from acidic (excess AlCl₃), to basic (excess organic chloride) (1). These shifts in potential could be correlated by donor-acceptor
to imply large changes in the donicity of the underlying solvent (2,3).
Recent work by Smith and co-workers determined the value of the Hammett
acidity function, H⁺, for protons, added as HCl(g), in the ImCl-AlCl₃
melt. In slightly acidic ImCl-AlCl₃ melts, an H⁺ value of -12.6 was
found, while in a melt saturated with AlCl₃, -67 mol % AlCl₃, the H⁺
value was -18 (4,5). Thus, protons in these melts are more acidic than
100% H₂SO₄, where H⁺ = -12, which is arbitrarily assigned as the lower
limit for superacidity. Therefore, protons in the ambient temperature
melts may be considered Brønsted superacids.
Prior work in our laboratory on the electrochemistry of a variety of amines in these molten salts had indicated the possible formation of AlCl₃ adducts, particularly in acidic melts (6). We concluded, at that time, that dimethylaniline formed an aluminum chloride adduct in the acidic melt. A similar conclusion regarding the formation of AlCl₃ adducts was arrived at from studies of quinones in the molten salts (7,8).

Here we report on the effect of quantitative proton addition on the chemistry and electrochemistry of dimethylaniline.

EXPERIMENTAL

All experiments were carried out in a Vacuum Atmosphere dry-box under a Helium atmosphere. 1-ethyl-3-methylimidazolium chloride was synthesized following reported procedures (9); aluminum chloride (Fluka, iron free) was purified by sublimation.

The molten salt ImHCl₂ was prepared from direct reaction of ImCl and HCl(g) (10). Methylaluminum sesquichloride (MAC), Me₂AlCl₃, was obtained from Aldrich and used without further purification.

Cyclic voltammetric studies were performed with an EG&G PARC Model 175 Universal Programmer with a Model 173 Potentiostat/Galvanostat. Voltammograms were plotted on a Houston Instruments Model 2000 X-Y recorder. All other electrochemical studies were carried out using an EG&G Model 273 Potentiostat/Galvanostat controlled by a DEC PDP-8/e computer (11). An LNO3 Plus laser printer was used to obtain plots from the computer experiments.

For cyclic and pulse voltammetric studies, Pt disc (radius 0.08 cm) or glassy carbon, GC, electrodes, (radius 0.15 cm) were used. The electrodes were obtained from Bioanalytical Systems. For all melt electrochemical measurements the reference electrode was an Al wire (5N Alfa Inorganics) immersed in a 1.5:1 AlCl₃:ImCl melt in a separate fritted glass compartment. The counter electrode was a coiled wire of Al.

Rotating disc voltammetric experiments were carried out with a three electrode system consisting of a Pine Instruments Pt-Pt ring-disk electrode (r₁ = 0.09 in, r₂ = 0.097 in, r₃ = 0.101 in), a Pine Instrument's RDE-4 potentiostat, and an Al wire counter and reference electrode.

¹H NMR experiments were performed using either a Varian Gemini-300 or a Varian VXR-400 S spectrometer operating at 300.075 or 399.952 MHz, respectively. ¹³C NMR experiments were performed using broad-band proton decoupling on the instruments indicated above operating at 75.462 and 100.57 MHz, respectively. ¹H and ¹³C samples were prepared in the dry-box and pipetted into 5-mm tubes fitted with precision coaxial inserts (Wilmad Glass Co.). All NMR samples were capped and sealed with
Parafilm prior to removal from the dry-box. $^1$H and $^{13}$C chemical shifts are reported relative to 0.1% TMS in CDCl$_3$ in the coaxial insert.

RESULTS AND DISCUSSION

I. Electrochemistry and NMR of DMA and protonated DMA in 0.8:1.0 AlCl$_3$:ImCl.

Staircase cyclic voltammetry was performed to obtain an overview of the DMA electrochemical behavior in the presence and absence of deliberately added protons. Figure 1 shows a staircase cyclic voltammogram of DMA at a Pt electrode in a basic melt. An oxidation wave at 0.75 V is observed which is near the melt's anodic limit. No reduction waves associated with products of DMA oxidation are observed upon scan reversal. Based on previous work, we assume that the DMA oxidation is a 2-electron process (6).

Normal pulse, NP, voltammograms were obtained as a function of pulse width and DMA concentration. In these NP experiments the initial surface boundary conditions were reestablished after each pulse by holding the electrode at the open-circuit potential and stirring the solution for 2 s, followed by a waiting period of 5.9 s, prior to each new pulse application. The relevant parameters obtained from these experiments for a solution 53 mM in DMA are summarized in Table I for Pt and GC electrodes. As $t$ is decreased, $E$ is observed to shift anodically. Plots of $i_p$ vs [DMA], for 50 and 100 ms pulse widths, are linear but have a non-zero intercept; this is the result of the presence of an initial protonic impurity, most likely arising from water, which protonates DMA, forming DMAH$^+$ (1). This species (see below) cannot be oxidized in the melt window. The level of protonic impurities in the basic melt can be estimated from the intercepts of such plots, and experiments to be described below, and is of the order of 4 mM.

A diffusion coefficient for DMA can be calculated from the limiting current (Cottrell equation) for the NP voltammograms,

$$i_{\text{lim}} = nFAC(D/\pi t_p)^{1/2}$$

[1]

where $n$ is the number of electrons involved in the process, $F$ is the Faraday constant, $A$ the area of the electrode, $C$ the concentration of the diffusing species, and $t_p$ is the pulse width. A plot of log $i_{\text{lim}}$ vs log $t$ is linear with slopes of 0.49 and 0.52 for the Pt and GC electrodes, respectively, indicating a diffusion controlled reaction. Because the exact concentration of DMA undergoing oxidation in these experiments is somewhat less than that added, as discussed above, plots of $i_{\text{lim}}$ vs C, which have slopes independent of C, should provide more accurate values for the determination of the diffusion coefficient of DMA than plots of $i_{\text{lim}}$ vs $t_p$. Diffusion coefficients, using the plot of $i_{\text{lim}}$ vs $t_p$, at Pt were found to be 1.92 x 10$^{-7}$ and 1.60 x 10$^{-7}$ cm$^2$ s$^{-1}$ for pulse widths of 100 and 50 ms, respectively, assuming an $n$ value of 2.
A $^{13}$C NMR spectrum for the methyl carbons is shown in Figure 2 for neat DMA, 2-a, and DMA in the basic melt, 2-b; the chemical shifts are identical and show that DMA does not form an AlCl$_3$ adduct in the basic melt.

Staircase cyclic voltammograms at a Pt electrode for a melt containing no DMA, added DMA, then proton, added as ImHCl$_2$, are shown in Figure 3. ImHCl$_2$ is a quantitative source of protons (10). Figure 3-a shows voltammograms of the melt with no added DMA; a cathodic wave at ca -0.4V is seen, and is due to the presence of protonic impurities (1). Upon addition of DMA, Figure 3-b, the wave at -0.4V disappears, a new cathodic wave, at -0.7V, appears, and the anodic DMA oxidation wave can be seen. The wave at -0.7V appears to be due to the reduction of proton from the protonated DMA (see below). On addition of ImHCl$_2$ in excess of the amount of DMA present, Figure 3-c, the DMA oxidation wave disappears, and, on a cathodic going scan, reduction waves for "free" proton and an increase in the protonated DMA wave is seen. In a basic melt, "free" protons exist largely as HCl$_2^-$ (10).

Although DMA oxidation is found at a GC electrode, no cathodic waves are seen. Protons cannot be reduced in the melt at the GC surface, and apparently the DMA$^+$ is also not reducible on this surface (1).

To further investigate the reaction between DMA and proton, an amperometric titration was carried out. The change of the NP limiting current for the DMA oxidation wave was examined as a function of added ImHCl$_2$. ImHCl$_2$ was added to a solution initially 53 mM in DMA. The results are shown in Figure 4. The DMA oxidation limiting current is seen to decrease linearly with added HCl$_2^-$, indicating a quantitative reaction with the DMA. The current goes to zero after the solution is ca 55 mM in HCl$_2^-$. Staircase cyclic voltammetric reduction waves following the addition of trimethylaluminum sesquichloride, MAC, to the DMA solution containing excess proton, result in marked changes. MAC, like ethylaluminum chloride, is an effective reagent for proton removal (12). The staircase voltammograms initially show only one reduction wave at a potential characteristic of the free proton; as more MAC is added, two reduction waves, corresponding to the free proton reduction and the proton on the DMA$^+$, appear. As still more MAC is added, the free proton reduction wave disappears, leaving only the DMA$^+$ reduction wave. The DMA$^+$ wave decreases slowly with time, indicating a sluggish reaction of the DMA$^+$ with MAC.

To further examine the DMA$^+$ reduction, reverse pulse, RP, voltammetry was carried out at a Pt electrode (13). In this experiment, the potential of the Pt electrode was stepped from an initial value, $E_i$, of +0.2, to -1.1 V for a generation time, t$. It was then stepped in 20 mV increments to increasingly positive potentials for a time, t, the analysis pulse, to examine the oxidation of products generated during the DMA$^+$ reduction. After each generation and analysis pulse, the
solution was stirred for 2.1 s, and then maintained in a quiet state for 5.9 s to renew the surface concentrations to their initial state. An NP oxidation wave for a DMA containing solution, and an RP wave for the same solution, as shown in Figure 5. As should be the case if t values for the NP and RP experiments are the same, the two oxidation waves coincide. Also shown is the RP voltammogram resulting when the mole ratio of DMA to ImHCl₂ was 1:1. At the -1.1V generating potential, the DMAH⁺ is reduced, as discussed above. A slight "do" cathodic current is seen on the reverse pulse voltammogram. We assign the first oxidation wave at ca 0.2 V to the oxidation of H₂ generated during the reduction, while the second oxidation wave is at the same potential as that for the DMA oxidation. Since no excess HCl₂ is present, the H₂ arises from the DMAH⁺ reduction; the DMA is liberated from the proton-adduct at the same time, and its oxidation is seen as well. The reaction taking place during the DMAH⁺ reduction, therefore, may be written as:

\[
\text{DMAH}^+ + e^- \rightarrow \text{DMA} + \frac{1}{2} \text{H}_2 \quad [2]
\]

It was not possible to quantitative the reverse pulse voltammetry due to the absence of theory and the lack of quantitatively reproducible voltammograms. Qualitatively, however, similar behavior was always observed.

Some rotating ring-disc voltammetry was carried out to confirm the above observations. A series of ring disc voltammograms at a Pt-Pt electrode are shown in Figure 6 for an experiment in the basic 0.8:1.0 melt. Comparison is made between a ring scan, with the disc being open-circuited, and with the disc held at various cathodic potentials to reduce the protonated DMAH⁺. The melt contains an excess of DMA over proton added as ImHCl₂. Two features are noted. First, as the potential of the disc is made increasingly negative, an increase in the DMA oxidation current is clearly noted. The increase in current also becomes approximately constant for disc potentials more negative than -0.9 V. Secondly, a slight anodic current is noted in the vicinity of zero volts, which we attribute to the oxidation of H₂ formed during the DMAH⁺ reduction. These results are in reasonable agreement with the results of the RP experiment, indicating the regeneration of the DMA and the presence of hydrogen.

The \(^{13}\text{C}\) spectrum for the methyl carbons on addition of proton to DMA in a basic melt is shown in Figure 7. Under conditions where an excess of proton is in solution, i.e., only DMAH⁺ is in solution, the line is at 46 ppm (vs TMS), compared to 41 ppm for DMA in the basic melt. The \(^1\text{H}\) spectrum shows a line for HCl₂, at 13.55 ppm, and a line at 13.4 ppm which we attribute to proton on the amine nitrogen; this indicates exchange between the two species is slow on the NMR time scale. However, only a single line, at 3.01 ppm, is observed for the methyl protons, although a doublet is expected, and is seen in the acidic melt (see below); this single line indicates some exchange and an approach to the slow exchange limit. In basic melts containing both DMA and the protonated DMAH⁺, a single \(^{13}\text{C}\) line is found, the position of which is proportional to the population weighed average of the species.
present. This indicates that the exchange between the protonated and unprotonated DMA is fast on the NMR time scale.

II. Electrochemistry and NMR of DMA and protonated DMA in acidic AlCl$_3$:ImCl.

A staircase cyclic voltammogram for the oxidation of DMA at GC is shown in Figure 8-a. The peak current occurs at 2.5 V, near the acidic melt anodic limit at a GC electrode. The overpotential for the oxidation of Cl$^-$ from AlCl$_4^-$, the limiting reaction in an acidic melt, is much larger on GC than on Pt, by ca 0.5 V, thus forcing these studies, at least in the examination of the DMA oxidation, to be carried out at GC electrodes.

The oxidation potential of DMA in the 1.2:1.0 AlCl$_3$:ImCl melt is ca 1.75 V more positive than in the basic melt. This effect was attributed, in our previous study on this system, to the formation of a DMA:AlCl$_3$ adduct in the acidic melt, and this has also been verified by NMR spectroscopy, which show marked changes in the $^{13}$C NMR chemical shift in going from basic to acidic melts (see below). Thus, in the acidic melt, the reaction:

$$\text{AlCl}_3^- + \text{DMA} \rightleftharpoons \text{DMA:AlCl}_3^- + \text{AlCl}_4^- \quad [3]$$

takes place. No such complexation is observed in the basic melt. The Lewis acid, AlCl$_3$, removes electron density from the DMA molecule, making it more difficult to oxidize.

Addition of ImHCl$_2$ to the acidic melt containing DMA results in a marked decrease in the DMA oxidation wave at +2.5 V; we assume this is due to the replacement of the AlCl$_3$ by a proton on the DMA. Cyclic staircase voltammograms for this are shown in Figure 8-b through 8-e. However, in the acidic melt the DMA oxidation wave does not disappear upon addition of an amount of ImHCl$_2$ equivalent to the DMA.

The DMA limiting current was monitored as a function of DMA concentration, and, as in the basic melts, plots of $i_{\text{lim}}$ vs [DMA] had non-zero intercepts. From the x-intercept, the concentration of an impurity, proton, was estimated as ca 7.4 mM. The higher impurity level in the acidic melt may result from a difference in the quality of the reagents or from the greater scavenging ability of the acid melt for adventitious water in the dry box. From the slope of $i_{\text{lim}}$ vs [DMA] the diffusion coefficient of DMA in the acidic melt is calculated to be 8.4 and 9.1 x $10^{-7}$ cm$^2$ s$^{-1}$ for 50 and 100 ms pulse widths, respectively. From the slope of $i_{\text{lim}}$ vs $t^{-1/2}$ plots, the diffusion coefficient is calculated to be 5.1 and 6.9 x $10^{-7}$ cm$^2$ s$^{-1}$ for 30.3 and 50.5 mM DMA, respectively. If these were corrected for the 7.4 mM DMA initially tied up with proton, the values of 9.7 and 9.5 x $10^{-7}$ cm$^2$ s$^{-1}$ for the 30 and 50 mM solutions, respectively, were obtained. The values are about five times greater than those in the basic melt. Based solely on viscosity effects, we would anticipate that the diffusion coefficient of the DMA would be two to three times larger in the acidic melt than in the basic.
melt (14). However, in view of the formation of the AlCl$_3$ adduct, we also might anticipate a larger diffusing entity in the acidic melts.

Normal pulse parameters in the 1.2:1 melt for a 30 and 51 mM DMA are summarized in Table II. Values of $I_{1/2}/C_{DMA}$ are tabulated for the [DMA] corrected for the protonic impurity and are quite constant. The value of the ratio of the limiting currents for the two concentrations of DMA are also in good agreement with the ratio of the concentrations of DMA if these concentrations are corrected for the ca 7 mM protonic impurity which effectively removes the DMA from the melt as discussed above.

A plot of the $i_{1/2}$ for a normal pulse voltammogram of DMA oxidation vs [ImHCl$_2$] added is shown in Figure 9. The DMA oxidation current initially shows a linear decrease, but then shows marked curvature, and an extrapolation to the [ImHCl$_2$] axis yields an intersection well in excess of the amount (51 mM) of DMA present in solution. This indicates the presence of an equilibrium between a DMA:AlCl$_3$ adduct and a protonated DMA adduct, DMAH$^+$. In more acidic melts the extent of the curvature seen during such a titration increases.

The $^{13}$C spectrum of the methyl carbons in the acidic melt are shown in Figure 2-c. A shift to 47 ppm is seen, compared to 41 ppm in the basic melt. We take this to show the presence of an AlCl$_3$ adduct. Melts containing mixtures of free DMA and the AlCl$_3$ adduct a single peak for the methyl carbons is found. The position of this line is proportional to the population weighted average of the species present. This indicates that the exchange between the free DMA and the AlCl$_3$ adduct is fast on the NMR time scale.

If excess proton is added to an acidic melt containing DMA, i.e., to the DMA:AlCl$_3$ species, the methyl $^{13}$C peak shifts down-field by 1.5 ppm, to 48.5 ppm, and a new H line at 7.8 ppm, vs TMS, is seen. A split in the methyl protons, indicative of coupling, is also seen. (Irradiation of the 7.8 ppm line results in a collapse of the doublet, clearly indicating coupling of the two peaks.) These results are shown in Figure 10. A comparison of the chemical shift for the H peak for DMAH$^+$ in the basic and acidic melt indicates it is at 13 ppm (vs TMS) and 7.8 ppm, respectively. We believe the large difference is the result of the interaction of the proton on the DMA with chloride ion in the basic melt.

NMR spectra for a melt containing both DMAH$^+$ and the DMA:AlCl$_3$ adduct are shown in Figure 11. Lines for both the protonated and AlCl$_3$ species are clearly evident. This indicates that the exchange between the protonated DMA and the DMA-AlCl$_3$ adduct is slow on the NMR time scale. To our knowledge this is the first NMR observation of a mixture of both a Brønsted and Lewis acid adduct of an organic base.

Of concern in this work is the relative acidity of protons and Al$_2$Cl$_7^-$ in the melts. To compare relative acidities, it is necessary to
remember that the concentration of the $\text{AlCl}_3^-$ is ca 0.86 M in the 1.2:1 melt. Since DMA is complexed by $\text{AlCl}_3^-$ in the acidic melt, the proton versus $\text{AlCl}_3^-$ competition reaction is represented by:

$$\text{DMA} : \text{AlCl}_3 + \text{HCl} \rightarrow \text{DMAH}^+ + \text{AlCl}_3^-$$  [4]

Since only small additions of $\text{ImHCl}_2$ are required to produce significant decreases in the DMA concentration, the proton competes very effectively for DMA despite the high concentration of $\text{AlCl}_3^-$. While the DMA-proton reaction may not be quantitative, it appears that the equilibrium constant for Equation 4 is large.

**SUMMARY**

The results presented indicate that DMA is not complexed in the basic melt, but forms an $\text{AlCl}_3$ adduct in the acidic melt. The formation of protonated DMA takes place in both basic and acidic melts; the reaction of DMA with proton in the basic melt appears quantitative, while in the acidic melt, where a DMA:$\text{AlCl}_3$ adduct is formed, an equilibrium between the protonated species and $\text{AlCl}_3$ adduct exists. Both electrochemistry and NMR support these conclusions.

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Table 1

$E_{1/2}$ and Limiting Current Variation with Pulse Width for 52.8 mM DMA in 0.8:1.0 AlCl$_3$:ImCl melt at Pt and GC Electrodes

| $t_p$ (ms) | $-i_{\text{lim}}^1$ (uA) | $E_{1/2}^1$ (V) | $-i_{\text{lim}}^2$ (uA) | $E_{1/2}^2$ (V) |
|-----------|----------------|----------------|----------------|----------------|
| 1000      | 45.1           | 0.74           | 140            | 0.76           |
| 750       | 51.3           | 0.77           | 162            | 0.76           |
| 500       | 65.7           | 0.78           | 209            | 0.77           |
| 250       | 91.5           | 0.79           | 297            | 0.79           |
| 100       | 140            | 0.81           | 472            | 0.81           |
| 75        | 164            | 0.83           | 527            | 0.82           |
| 50        | 233            | 0.84           | --             | --             |

1. $i_{t_p}^{1/2} = 46.1 \pm 2.7$
2. $i_{t_p}^{1/2} = 145 \pm 4$

Table 2

$E_{1/2}$ and Limiting Current Variation with Pulse Width for 30.3 and 50.5 mM DMA in 1.2:1.0 AlCl$_3$:ImCl melt at GC Electrode

| $t_p$ (ms) | $-i_{\text{lim}}^1$ (uA) | $E_{1/2}^1$ (V) | $-i_{\text{lim}}^2$ (uA) | $E_{1/2}^2$ (V) | $i_{\text{lim}}^{(50.5)}/i_{\text{lim}}^{(30.3)}^*$ |
|-----------|----------------|----------------|----------------|----------------|----------------|
| 1000      | 162            | 2.27           | 309            | 2.29           | 1.90           |
| 750       | 187            | 2.28           | 361            | 2.30           | 1.93           |
| 500       | 224            | 2.29           | 449            | 2.31           | 2.00           |
| 250       | 346            | 2.31           | 664            | 2.34           | 1.92           |
| 100       | 520            | 2.34           | 993            | 2.37           | 1.91           |
| 75        | 621            | 2.36           | --             | --             | --             |
| 50        | 751            | 2.37           | --             | --             | --             |
| 25        | 993            | 2.40           | --             | --             | --             |

* Ratio of concentrations added (50.5/30.3) = 1.66; ratio of concentrations corrected for loss of initial DMA due to ca 7.4 mM proton impurity (see text) ((50.5 - 7.4)/30.4 - 7.4)) = 1.88.

1. $i_{t_p}^{1/2}/C_{\text{corr}} = 7.18 \pm 0.24$
2. $i_{t_p}^{1/2}/C_{\text{corr}} = 7.35 \pm 0.20$
Figure 1. Staircase cyclic voltammogram for DMA in 0.8:1 melt at a Pt electrode, A = 0.02 cm$^2$. Scan rate 250 mV s$^{-1}$ (step height 10 mV, step width 40 ms). [DMA], mM: a) 10.4; b) 29.7; c) 52.8.

Figure 2. $^{13}$C spectrum of methyl carbons in a) neat DMA; b) basic melt and c) acidic melt.
Figure 3. Staircase cyclic voltammograms for DMA in 0.8:1 melt conditions as in Figure 1. Pt electrode. Sweep rate 100 mV s$^{-1}$: (step height 10 mV, step width 100 ms). a) Melt background; b) 17 mM DMA added; c) as b, but 30 mM ImHCl$_2$ added.

Figure 4. Normal pulse voltammetric limiting current for oxidation of DMA vs [ImHCl$_2$] added to a 0.8:1 melt. $t_p$, 100 ms. [DMA]$_{\text{initial}}$ = 53 mM. Pt electrode.
Figure 5. Normal and reverse pulse voltammograms for 0.8:1 melt containing DMA and DMA + ImHCl₂. Pt electrode. Pulse width 50 ms; delay time between pulses 8s (2.1 s stirred, 5.9 s quiescent); a) NP - 37 mM DMA; b) RP on same solution from -1.1 V, t = 5s; c) RP from -1.1V on same solution but after 37 mM ImHCl₂ added; t = 5s.

Figure 6. Rotating disc ring voltammograms for DMA, in basic melt; [DMA] = 54 mM; [ImHCl₂] = 31 mM. Ring scan rate 10 mV s⁻¹. a, b, etc are ring voltammograms with disc at open circuit. Ring voltammograms with disc at: a') -0.5V; b') -0.7V; c') -0.9V; d') -1.1V; e') -1.3V; f') -1.5V; g') -1.7V.
Figure 7. $^{13}$C and $^1$H NMR of DMA in basic melt following addition of ImHCl$_2$ to basic melt.

Figure 8. Staircase cyclic voltammogram for DMA in acidic, 1.2:1, melt. GC electrode, $A = 7.07 \times 10^{-2}$ cm$^2$. Scan rate 250 mV s$^{-1}$, (step height 10 mV, step width 40 ms). With and without addition of ImHCl$_2$. [DMA] = 51 mM. [ImHCl$_2$], mM: a) 0; b) 8; c) 29; d) 52; e) 81.
Figure 9. Normal pulse limiting currents for DMA oxidation versus [ImHCl₂] added. GC electrode. Initial [DMA], 51 mM. tₚ, ms: a) 50; b) 100.

Figure 10. ¹H NMR(a,b) and ¹³C(c) spectra for DMA in acidic melt containing proton well in excess of DMA present.
Figure 11. $^{13}\text{C}(a)$ and $^1\text{H}(b)$ NMR spectra for DMA in acidic melt containing DMA in excess of proton.