(at 90 K). Further experiments are being undertaken to clarify the photochemistry.

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Lewis and Brønsted Acid Adducts in Ambient Temperature Chloroaluminate Molten Salts: NMR Observations

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In this report we show that when an organic base, *N,N*-dimethylaniline (DMA), is added to an acidic ambient temperature molten salt, an aluminum chloride adduct is formed; on addition of proton, which behaves as a superacid, the $AlCl_3$ is displaced in an equilibrium process.

It has recently been shown that the value of the Hammett acidity function for protons in acidic ambient temperature chloroaluminate molten salts indicates they are Brønsted superacids.[1,2] The molten salt, composed of a mixture of 1-ethyl-3-methylimidazolium chloride (ImCl) and $AlCl_3$, is acidic, basic, or neutral when the mole ratio of $AlCl_3$:ImCl is greater than, less than, or equal to unity, respectively.[3] The basic melts contain chloride ion, a Lewis base, while the acidic melts contain heptachlorodialuminate ion, $Al_2Cl_7^-$, a strong Lewis acid. The underlying Lewis acidity of the molten salt changes with melt composition; thus a variation of the Brønsted acidity with melt composition also results. Our interest is in the chemical and electrochemical behavior of solutes in these unusual Lewis/Brønsted acid solvents, and here we report NMR studies of the interaction of an organic base, DMA, with the Lewis and Brønsted components of this superacid medium.

The effect of melt composition on the ${}^{13}C$ NMR resonance of the DMA methyl groups is shown in Figure 1.[4] The chemical shift remains essentially unchanged from neat DMA to DMA in a basic melt, where no $AlCl_3$ adduct forms. However, the methyl resonance shifts 6.5 ppm downfield when DMA is added to an acidic melt. Identical trends are observed in the ${}^1H$ NMR of DMA. The electrochemistry of DMA also shows marked dependence on melt composition. The oxidation potential for DMA shifts 1.75 V positive going from a basic to an acidic, proton free, melt.[5] These results indicate removal of electron density from the DMA molecule and are consistent with the formation of an $AlCl_3$ adduct in the acidic melt. This behavior is chemically reversible; changes observed are reversed moving from acidic to basic melts. DMA is a stronger base than $AlCl_4^-$ and is capable of displacing $AlCl_4^-$ from $Al_2Cl_7^-$ to form the adduct

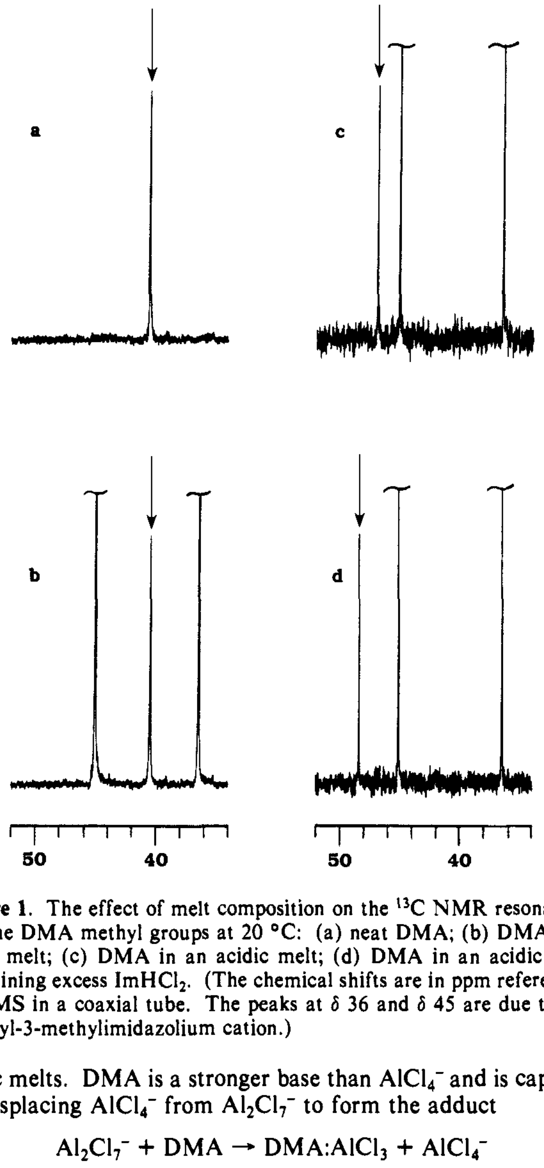

Figure 1. The effect of melt composition on the ${}^{13}C$ NMR resonances for the DMA methyl groups at 20 °C: (a) neat DMA; (b) DMA in a basic melt; (c) DMA in an acidic melt; (d) DMA in an acidic melt containing excess $ImHCl_2$. (The chemical shifts are in ppm referenced to TMS in a coaxial tube. The peaks at δ 36 and δ 45 are due to the 1-ethyl-3-methylimidazolium cation.)

$$Al_2Cl_7^- + DMA \rightarrow DMA{:}AlCl_3 + AlCl_4^- \qquad (1)$$

These conclusions are in agreement with suggestions in our previous electrochemical studies on DMA in a similar chloroaluminate molten salt system (a mixture of *n*-butylpyridinium chloride and $AlCl_3$).[6] Reaction 1 appears to be complete in a melt where $Al_2Cl_7^-$ is in excess over DMA. When the concentration of $Al_2Cl_7^-$ is less than that of the DMA, a mixture of DMA and DMA:$AlCl_3$ results. The ${}^{13}C$ and ${}^1H$ NMR of the mixture of the two species at 20 °C show a single spectrum that is the population weighted average of the spectra for the DMA and DMA:$AlCl_3$, indicating that the exchange between DMA and DMA:$AlCl_3$ is fast on the NMR time scale ($k > 10^5$ s^{-1}).

The quantitative addition of protons to these molten salts can be achieved by use of 1-ethyl-3-methylimidazolium hydrogen dichloride ($ImHCl_2$).[4a] The addition of $ImHCl_2$ in excess of the DMA to acidic melts shifts the ${}^{13}C$ resonance for the DMA methyl groups 1.5 ppm further down field (Figure 1d) and causes the ${}^1H$ resonance for the DMA methyl protons to be split into a doublet (${}^3J_{H-H}$ = 5.3 Hz, Figure 2b). In addition, the ${}^1H$ spectrum shows a new broad peak at δ 7.8 (Figure 2a). Irradiation of this peak in a double-resonance experiment collapses the DMA methyl proton doublet, clearly showing coupling of the two peaks. Thus, we have assigned the peak at δ 7.8 ppm to the dimethylanilinium N-H proton. The addition of $ImHCl_2$ to an acidic melt containing DMA:$AlCl_3$ also results in a decrease in the DMA oxidation wave.[5] These observations support the displacement of $AlCl_3$ from

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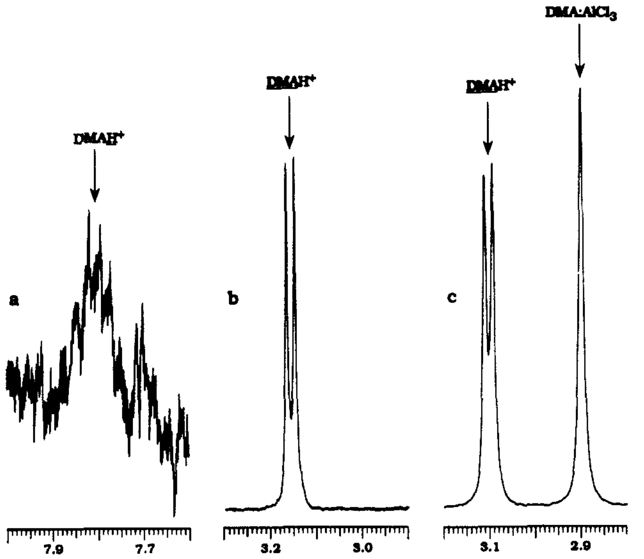

Figure 2. The ^{1}H NMR spectra of DMA in acidic melts at 20 °C: (a and b) the ^{1}H resonance of the dimethylanilinium N–H proton and $N(CH_3)_2$ protons, respectively, in the presence of excess $ImHCl_2$; (c) the ^{1}H resonance of the $N(CH_3)_2$ protons for a mixture of $DMAH^+$ and $DMA:AlCl_3$. (The chemical shifts are in ppm referenced to TMS in a coaxial tube.)

DMA to produce a protonated species, $DMAH^+$.

It has been proposed that the proton in acidic chloroaluminate molten salts exists as HCl.[4a] Recent results indicate, however, that while small amounts of "free" HCl are present in acidic melts, the proton appears to exist primarily in an as yet unidentified "acidic" form.[7] Thus, for the sake of the following discussion we choose to write the "acidic" form of the proton as $HCl–AlCl_3$. (Mixtures of HCl and $AlCl_3$ appear to have acidities in the range of what is considered a Brønsted superacid.[8,9]) Consequently, the reaction of the proton with $DMA:AlCl_3$ is

$$DMA:AlCl_3 + HCl–AlCl_3 \rightleftarrows DMAH^+ + Al_2Cl_7^- \quad (2)$$

When the added proton concentration is less than the DMA concentration, the observed NMR spectrum is simply the superposition of the spectra of $DMAH^+$ and $DMA:AlCl_3$ (Figure 2c), indicating the exchange between $DMAH^+$ and $DMA:AlCl_3$ is slow on the NMR time scale. Our preliminary results indicate that while $HCl–AlCl_3$ is a much stronger acid than $Al_2Cl_7^-$, acidic melts contain an equilibrium mixture of $DMAH^+$ and $DMA:AlCl_3$ (reaction 2).

Previous studies of proton transfer to DMA have shown that, even in strong aqueous acids, the process is diffusion controlled.[10] However, in acidic chloroaluminate molten salts, when excess proton is added, the dimethylanilinium $N(CH_3)_2$ protons (figure 2b) exhibit a doublet, demonstrating proton transfer on $DMAH^+$ is slow. The apparent slow proton transfer could result from the highly acidic, and as yet unknown, nature of protons in this solvent, the presence of a complexing Lewis acid, or a combination of both. We are currently studying proton transfer reactions of DMA and other bases in this new superacid medium in an attempt to gain further understanding of the problem.

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High Turnover Rates in pH-Dependent Alkene Epoxidation Using NaOCl and Square-Planar Nickel(II) Catalysts

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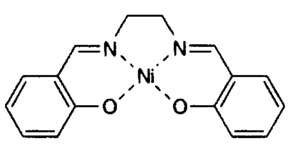
Transition-metal-catalyzed transfer of oxygen atoms to organic substrates is of interest in the study of bioinorganic mechanisms and the development of efficient catalysts for laboratory and industrial organic synthesis.[1] Certain nickel(II) catalysts have recently joined the plethora of metalloporphyrin complexes capable of facilitating this reaction using OCl^-, PhIO, or $KHSO_5$ as terminal oxidant.[2,3] These studies were undertaken because of the intriguing possibility that a heretofore unprecedented high-valent nickel–oxo species may be responsible for substrate oxidation.[4] The only known high-valent oxide of nickel is the poorly characterized nickel(III) peroxide formed from Ni^{2+} salts and basic hypochlorite.[5] Here, we report an unusual pH dependence of the OCl^--based reactions which leads to dramatic rate accelerations in olefin epoxidation at reduced pH.



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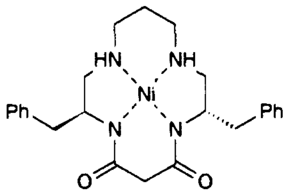

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We previously described the use of NaOCl under phase-transfer conditions in the presence of Ni^{II}(salen) (**1**)[2c] or Ni^{II}(dibenzyldioxocyclam) (**2**)[2d,e] as an alkene epoxidation system. At pH 12.5, epoxidation is slow, requiring 4–5 h for 20–40 turnovers of catalyst. As indicated in Figure 1, the epoxidation of styrene is dramatically accelerated by lowering the pH of the aqueous phase to 9.3 (curve C). Using 2.5 mol % catalyst, >20 turnovers to give epoxide occur in 15 min. A pH–rate profile of the reaction showed an inverted bell-shaped curve with a maximum at 9.3. Similarly, addition of certain CH_2Cl_2-soluble weak acids also increased the reaction rate. For example, the use of a 2:1 ratio of salen:Ni(salen) provided nearly the same rate enhancement as lowering the pH (curve B). In addition to salen, both *o*- and *p*-salicylaldehydes (pK_a 6.8 and 7.7, respectively) were effective as additives, while catalytic amounts of simple phenols, electron-rich phenols (2,6-di-*tert*-butyl-*p*-cresol), and water-soluble phenols (*p*-nitrophenolate) were ineffective. A combination of both lowering the pH and addition of salen led to the highest reaction rate (curve D).

Reaction conditions were optimized for one of the more reactive substrates, *trans*-β-methylstyrene (see Table I).[6] Under the best

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