HYDRIDE ION BEHAVIOR IN ACIDIC
CHLOROALUMINATES AT AMBIENT-TEMPERATURE

David F. Wassell, Keith E. Johnson and Lynn M. Mihichuk

Department of Chemistry
University of Regina
Regina, Saskatchewan,
Canada, S4S 0A2

ABSTRACT

1-ethyl-3-methyl-1H-imidazolium (Im) chloroaluminate melts have been treated with CaH2 at ambient temperatures. In basic melts (nAlCl3 < 0.5) the Im+ cation is reduced, in neutral melts there is no reaction while in acidic melts (nAlCl3 > 0.5) aluminum hydride species are formed. The infrared spectra of hydridic melts of different starting AlCl3 mole fractions indicate that AlCl3H+ is formed at modest acidities (nAlCl3 > 0.5) and bridged alanes at higher acidities (nAlCl3 > 0.65). The infrared spectrum of the generated AlCl3H+ correlates with literature Raman data.

AlCl3H+ was shown to react on a 1:1 basis with 2,3-dichloro-1,4-naphthoquinone, presumably to form a phenoxide monoanion; this reaction was conveniently followed spectrophotometrically through the decolorizing of the quinone-AlCl3 adduct (λmax=360 nm, 462 nm).

Cyclic and square wave voltammetry identified the oxidation of AlCl3H+ and confirmed the removal of trace protic species in initial melts with the formation of H2.

INTRODUCTION

Ambient temperature molten salts prepared from an organic salt, e.g. 1-ethyl-3-methyl-1H-imidazolium chloride (ImCl), trimethylsulfonium bromide or pyridinium chloride, and a Lewis acid, e.g. aluminum chloride or bromide, offer systems with a range of Lewis acidity and, through the further addition of a hydrogen halide, also of Bronsted acidity (1). These systems have received considerable study over the past 2 decades because of their potential applications for batteries, metal-winning and organic synthesis. The chemistry of the Lewis basic melts (AlX3 mole fraction < 0.5) shows considerable similarity to systems such as LiCl-KCl, particularly regarding the behavior of many transition metal salts (2), while indications are that the Lewis acidic melts (AlX3 mole fraction > 0.5) are much less complexing in nature (3) and are akin to the systems employed for Friedel-Crafts synthesis (4).

We have studied the proton's behavior in these melts in some detail (1) and established that (a) in Lewis basic melts HX2, H2X3 and even H3X4 (X = halogen) can...
be formed together with AlX₄-HX⁻ and these entities have Hammett acidities comparable to concentrated aqueous halogen acids while (b) in Lewis acidic melts AlX₄-HX⁻ and Al₂X₇-HX⁻ are formed with the latter behaving as a superacid of Hammett acidity comparable or exceeding that of liquid HF. The key to these findings was the control and measurement of the HCl partial pressure over the ImCl-AlCl₃ systems. The results are conveniently expressed as the equilibrium constant for HClY⁻ formation, the Hammett acidity of HClY⁻ or the reduction potential of HClY⁻:

\[
\text{HCl}(g) + Y^{2-}(l) \rightleftharpoons \text{HClY}^{-}(l)
\]

Some random studies of organometallic compounds in these systems have taken place and, with a view to explaining some preliminary observations of the behavior of Cp₂WH₂, we have investigated the chemistry of the simple hydride ion in the ImCl–AlCl₃ melts. Although H⁻ reduces the Im⁺ cation in the basic melts, it is stabilized in the acidic melts and we report here on some characteristics of these solutions.

**EXPERIMENTAL**

Aluminum chloride (Fluka puriss, >99%) was purified by sublimation under reduced pressure as described previously (5). 1-ethyl-3-methyl-1H-imidazolium chloride (ImCl), prepared as previously described, was recrystallized from acetonitrile, vacuum dried above 50°C and stored under nitrogen as large colorless crystals (5). Calcium hydride (Anachemia, 90-95%) was obtained packed under argon. 2,3-dichloronaphthoquinone (Aldrich) was sublimed under vacuum at 220°C to a constant m.p. (197-198°C). HCl gas was from Matheson, Semiconductor Grade, 99.95%.

All syntheses and most manipulations of the melts were carried out in an inert atmosphere glovebox (MBraun Labmaster 100); the working gas was dry nitrogen. Centrifugation was performed with an International Equipment Company clinical centrifuge: the melts were placed in threaded centrifuge tubes, sealed with Teflon® tape, capped, sealed with Parafilm® and then transferred from the glovebox to the centrifuge for a minimum of 2 h centrifugation.

AlCl₃-ImCl melts were prepared as previously described (5) except that in some of the later experiments phosgene was not used to remove hydrolytic impurities but protons were removed with small additions of hydridic melt.

Hydridic melts were prepared by adding calcium hydride to AlCl₃-ImCl melts in an amount just in excess of one hydride ion per chloride ion. This caused the evolution of some gas and complete decoloration of the neutral and acidic melts. The melts were stirred for 12 h and filtered either through a fritted glass funnel or by centrifugation in a sealed tube. The acidic melts appeared cloudy and were thixotropic.
An ImCl-HCl melt was prepared from solid ImCl and high purity HCl as described elsewhere and its HCl content determined from the intensity and location of the anionic $^1H$ NMR signal (5).

Infrared spectra were obtained with a Perkin Elmer 1600 series FTIR instrument, with samples being placed as thin films between NaCl plates in the glovebox before rapid removal and scanning to limit exposure to air. It was necessary to polish the plates with an ethanol-soaked paper towel between uses.

UV-Visible spectra were obtained with a Hewlett Packard 8452A Diode Array Spectrophotometer controlled by standard HP operating software on an HP Vectra 486/20 computer. To obtain the spectra of solutions of 2,3-dichloro-1,4-naphthoquinone (DCNQ) in the melts, known volumes of a $5.89 \times 10^{-4}$ M solution of DCNQ in HPLC grade chloroform were evaporated to dryness in a stream of argon and the solid transferred to the glovebox for addition to a known weight of 55% AlCl$_3$:ImCl melt; samples of the red solution were transferred by pasteur pipet to a 1mm quartz cuvet which was sealed with parafilm and removed to the spectrophotometer.

NMR spectra were obtained with a Bruker AC 200 QNP NMR spectrometer and recorded relative to internal TMS but using a sealed capillary of DMSO-d$_6$ as internal standard.

Cyclic and square wave voltammetry were performed with a Bioanalytical Systems Inc. BAS 100A electrochemical analyser utilising the BAS 100W software package and Gateway 2000 computer. Experiments were carried out in the glovebox with a 10 mL cell; the working electrode was a 0.21 mm$^2$ platinum disc, the auxiliary electrode a coiled aluminum wire and the reference electrode an aluminum wire in a saturated (66 mol %) AlCl$_3$:ImCl melt separated from the bulk by a glass frit.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Figure 1a shows the infrared spectrum of the 55 mol % AlCl$_3$:ImCl melt and Figure 1b the spectrum obtained after the addition of calcium hydride. The addition of gaseous HCl to the hydridic melt produced gas evolution and restored the simple melt spectrum (1a). The hydridic melt is characterized by a broad, strong peak at 1870 cm$^{-1}$, a very broad peak centered at 1700 cm$^{-1}$ and a small peak in the 700 to 600 cm$^{-1}$ region. The addition of lithium hydride generated similar though weaker peaks at 1890 and 1700 cm$^{-1}$. Solid calcium hydride shows a sharp band at 3650 cm$^{-1}$ and a weaker broad band below 1500 cm$^{-1}$ in its infrared spectrum (6) but lithium aluminum hydride shows a very broad strong absorption between 1300 and 2100 cm$^{-1}$. This suggests that the addition of the metal hydrides to the chloroaluminate melt leads to the formation of an aluminum hydride species. In the spectra of inorganic and organometallic neutral species containing Al-H bonds, absorptions in the 1700-1900 cm$^{-1}$ region have been assigned to the Al-H stretching mode and those in the 700-850 cm$^{-1}$ region have been assigned to the Al-H bending mode (7). Some researchers assigned very broad absorptions in the 1200-1400 cm$^{-1}$ region.
cm$^{-1}$ and 1700 cm$^{-1}$ regions to Al-H-Al bridging vibrations (8). Table I presents an assignment of the bands in Figure 1b.

To ascertain whether AlCl$_3^-$, Al$_2$Cl$_7^-$ or both chloroaluminate ions react with the calcium hydride, a series of melts containing 45-65 mol % AlCl$_3$ were reacted with CaH$_2$ and the infrared spectra recorded. Compared to the simple chloroaluminates, hydride in the 45% melt produces a strong absorption in the 3000 cm$^{-1}$ region and a broad band from 1500 cm$^{-1}$ tailing to 1850 cm$^{-1}$; this melt is also darkened by the addition. The spectra in the 1500 to 2500 cm$^{-1}$ region are shown in Figure 2. While the infrared spectrum of the 50% melt is unchanged by hydride, the peak at 1870 cm$^{-1}$ in the 55% melt has shifted to 1900 cm$^{-1}$ in the 65% melt where it is merely a shoulder on the large 1700 cm$^{-1}$ band which spreads from 1000 to 2000 cm$^{-1}$.

The changes in the 45% melt noticeably in the C-H stretching region, suggest that hydride reduces the imidazolium cation (10), presumably at the C2 position (11). The fact that the neutral melt is unaffected but the interaction increases with acidity, indicates that only Al$_2$Cl$_7^-$ is reacting with hydride. This is a simple Lewis acid-base reaction to form AlHCl$_3^-$.

\[
\text{Al}_2\text{Cl}_7^- + \text{H}^+ \rightarrow \text{AlCl}_4^- + \text{AlHCl}_3^-
\]

The Raman spectrum of AlHCl$_3^-$ has been reported (12) to consist of the Al-H stretching vibration at 1844 cm$^{-1}$ which corresponds favorably to the Al-H stretching band assigned to the melts. The development of the broad band at 1700 cm$^{-1}$ as acidity increases then corresponds to the formation of Al-H-Al bridged entities.

**UV-Visible Spectrophotometry**

Some preliminary observations on the chemistry of the hydridic melts suggested that the hydride species adds to a carbonyl group to form an alkoxide:

\[
\text{R}_1\text{R}_2\text{C=O} + \text{AlHCl}_3^- + \text{AlCl}_4^- \rightarrow \text{R}_1\text{R}_2\text{CHO}^- + \text{Al}_2\text{Cl}_7^-
\]

We reasoned that since a number of quinones (13) (anthraquinone, chloranil) form highly colored but stable adducts in acidic chloroaluminates, a quinone might function as a spectrophotometric titrant for AlHCl$_3^-$. 2,3-dichloro-1,4-naphthoquinone forms a deep-red solution in the 55% chloroaluminate melt with absorption maxima at 360 nm ($\varepsilon = 11200$ L cm$^{-1}$ mol$^{-1}$) and 462 nm ($\varepsilon = 3990$ L cm$^{-1}$ mol$^{-1}$) (Figure 3a). The addition of hydridic melt to one containing DCNQ systematically decolorised the latter as shown in Figure 3b–3e. Using both absorption peaks and correcting for the samples removed at each measurement, the DCNQ:AlHCl$_3^-$ ratio is calculated to be:

1.23 ($\lambda = 462$ nm) or 0.96 ($\lambda = 360$ nm)

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with a starting hydride concentration of $7.07 \times 10^{-4} \text{ mol g}^{-1}$.

Thus we may write the reaction as the 1,4-addition of hydride followed by a 1,3-sigmatropic shift to the naphthol monoanion.

**Electrochemistry**

Cyclic voltammograms of the 55% melt with and without added hydridic melt are shown for a modest sweep rate (100 mVs$^{-1}$) and a fast sweep rate (1000 mVs$^{-1}$) in Figure 4. Three features are noteworthy: a redox wave with $E_{\text{ox}}$ of +1.2 V and $E_{\text{red}}$ of +1.0V for the hydridic melt, an oxidation wave at $-0.95$ V apparent in both melts at high sweep rate and an oxidation current AFTER reversal of sweep direction for the hydridic melt. The 0.95 V peak is less clear at sweep rates of 500 and 200 mVs$^{-1}$ but otherwise these rates show no other features. Sweeping in the cathodic direction first, showed no reduction peak at 0.95 V.

Square wave voltammograms from +2.00 to 0 V of the 55% melt with and without added hydridic melt are depicted in Figure 5. The addition of the first hydride produced gas bubbles (H$_2$) and lowered the 0.97 V peak of the parent melt while further hydride led to the replacement of the 0.9 V peak by one at +1.07 V and the development of an inverted peak at +1.60 V.

The cyclic and square wave voltammetry indicate the oxidation of the AlHC$_3^-$ species. The electrode reaction is not reversible ($\Delta E = 200$ mV) and some of the reactant undergoes oxidation that is purely potential-dependent, as evidenced by the square wave inverted peak at 1.60 V and the current being independent of sweep direction in the 1.70 to 2.20 V region of the cyclic voltammograms. These current voltage features are
characteristic of an adsorption process and have been observed for the reduction of Al$_2$Cl$_7$-HCl (1).

For the parent melt cyclic voltammograms, the origin of the high sweep rate peak has not been pursued. The square wave peak at +0.97 V for the parent melt can be ascribed to Al$_2$Cl$_7$-HCl, which is detectable at lower concentrations by square wave voltammetry than by cyclic voltammetry (1).

The primary electrode reaction for the hydridic species may then be written

$$\text{AlHCl}_3^- \xrightarrow{1.2 \text{V}} \text{AlCl}_3^+ + 2e^-$$

possibly followed by

$$\text{AlHCl}_3^+ + \text{AlCl}_4^- \xrightarrow{1.2 \text{V}} \text{Al}_2\text{Cl}_7$$

while the secondary reaction may be represented as

$$\text{AlHCl}_3^- + \text{AlCl}_4^- - e^- \xrightarrow{1.7 \text{ to } 2.2 \text{ V}} \text{H (ads)} + \text{Al}_2\text{Cl}_7^-$$

$$2\text{H (ads)} \rightarrow \text{H}_2$$

These are distinct processes from the reduction of Al$_2$Cl$_7$-HCl, the suggested form of protic impurity existing in acidic melts:

$$\text{Al}_2\text{Cl}_7^-\text{HCl}^- + e^- \rightarrow 2\text{AlCl}_4^- + \frac{1}{2}\text{H}_2$$

While the electrochemical behavior of the hydridic species is characteristic, further elucidation of the details of the processes is called for.

**Theoretical calculations**

Calculations at the MP2/6-311+ G(d,p) level (14), along the lines of recent publications (15), suggest that (in the gas phase) hydride ion should replace chloride in AlCl$_4^-$ and Al$_2$Cl$_7^-$ with the formation, in the first instance, of HAICl$_3^-$. Table II presents the appropriate data. In addition, the vibrational frequencies of HAICl$_3^-$ were calculated and include the values of 666 and 1937 cm$^{-1}$; HAICl$_3^-$ is a symmetric top with an Al-H bond. Previous work showed that HAICl$_3^-$ should be an asymmetric ion with the hydrogen bonded not to aluminum but to two chlorine atoms. While the formation of HAICl$_3^-$ from AlCl$_2^-$ is energetically favored, the generation of AlCl$_2^-$ from AlCl$_3$ is decidedly not. However, the supposed AlCl$_4^-$ ion-pair or salt of HAICl$_3^-$ could be
considered as a product of HAICl$_3^-$ oxidation; this amounts to the stoichiometry HAICl$_2$Cl$_7$. Initial calculations on HAICl$_2$Cl$_7$ suggest that it is a more stable species than the ubiquitous HAICl$_4$.

CONCLUSIONS

1. The species HAICl$_3^-$ is formed from H' and Al$_2$Cl$_7^-$ in Lewis acidic chloroaluminates.
2. HAICl$_3^-$ and bridged alanes formed at higher acidities are characterized by infrared spectra.
3. HAICl$_3^-$ reduces 2,3-dichloro-1,4-naphthoquinone in a 1:1 molar reaction; this reaction can be followed spectrophotometrically at 360 and/or 462 nm.
4. HAICl$_3^-$ reacts with trace protic species in the system and shows characteristic voltammetric behavior.

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Table I. Infrared absorption frequencies and assignments (cm⁻¹) for a 55% aluminum chloride:Im melt before and after addition of calcium hydride based on reference (9).

| Frequency cm⁻¹ | Intensity | Frequency cm⁻¹ | Intensity | Assignment |
|----------------|-----------|----------------|-----------|------------|
|                |           | Imidazolium Cation |         |            |
| 3165 s         |           | 3160 s         |           | aromatic C-H str |
| 3152 s         |           | 3151 s         |           | aromatic C-H str |
| 3119 s         |           | 3119 s         |           | aromatic C-H str |
| 3105 s, sh     |           | 3107 s, sh     |           | aromatic C-H str |
| 2988 m         |           | 2988 m         |           | aliphatic C-H str |
| 2960 m         |           | 2959 m         |           | aliphatic C-H str |
| 2943 m         |           | 2941 m         |           | aliphatic C-H str |
| 1664 vw, b     |           |                |           | comb         |
| 1595 s         |           | 1595 s         |           | C-C=N+      |
| 1571 s         |           | 1570 s         |           | ring str sym |
| 1467 m         |           | 1467 m         |           | ring str sym |
| 1457 m         |           | 1458 m         |           | ring str sym |
| 1427 m         |           | 1427 m         |           | Me C-H b asym |
| 1390 w         |           | 1389 w         |           | Me C-H b asym |
| 1356 w         |           | 1356 w         |           | ring str sym |
| 1341 sh        |           | 1340 sh        |           | Me C-H b sym |
| 1336 w         |           | 1335 w         |           | ring str sym |
| 1291 vw        |           | 1292 vw        |           | ring C-H b sym |
| 1244 vw, b     |           | 1260 vw, vb    |           | N-H i/p b   |
| 1165 vs        |           | 1167 vs        |           | ring str sym |
| 1108 w         |           | 1108 w         |           | ring C-H i/p b |
| 1088 w         |           | 1088 w         |           | ring C-H i/p b |
| 958 vw         |           | 959 vw         |           | N-H i/p b/C-H i/p b |
| 833 s          |           | 833 s          |           | C-H i/p b   |
| 743 s          |           | 743 s          |           | ring o/p b asym |
| 700 m          |           | 700 m          |           | Al-O str    |
| 646 s          |           | obscured       |           | ring b asym |
| 621 s          |           | 620 s          |           | ring b asym |
|                |           |                |           |            |
| Hydride Species |         |                |           |            |
|                |           | 1870 m, b      |           | Al-H str    |
|                |           | 1700 m, vb     |           | Al-H str    |
|                |           | 630-680 s, b   |           | Al-H bend?  |

*a* Intensity abbreviations are: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; vb, very broad. *b* Abbreviations for the assignment are: str, stretching; b, bending; i/p, in plane; o/p, out of plane; sym, symmetrical; asym, asymmetrical.
Table II. Thermodynamic calculations for hydric species using MP2/6-311+G(d,p) basis set.

| Reaction                        | ΔH  | ΔS  | ΔG  |
|--------------------------------|-----|-----|-----|
| H⁺ + AlCl₄⁻ → Cl⁻ + HAICl₃⁻     | -178.5 | 26.9 | -186.5 |
| H⁺ + Al₂Cl₇⁻ → HAICl₃⁻ + AlCl₄⁻ | -366.9 | 23.2 | -373.8 |
| 2H⁺ + Al₂Cl₇⁻ → Cl⁻ + 2HAICl₃⁻  | -545.4 | 50.1 | -560.3 |

Figure 1 Infrared spectrum of the 55% AlCl₃:ImCl melt (a) before and (b) after CaH₂ addition.
Figure 2 Infrared spectra of the (a) 45%, (b) 50%, (c) 55%, (d) 60% and (e) 65% AlCl₃-ImCl melts treated with CaH₂.

Figure 3 UV-visible spectra of 2.28 M CNQ in 55% AlCl₃:ImCl melt alone (a) and after successive additions of hydridic melt (b to e).
Figure 4  Cyclic voltammograms of 55% AlCl₃:ImCl melt containing added hydride with sweep rates of (a) 1000 mVs⁻¹ and (b) 100 mVs⁻¹.

Figure 5  Square wave voltammetry of 55% AlCl₃:ImCl melt (a) before and (b) after addition of hydridic melt.