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# Removal of Protons from Ambient-Temperature Chloroaluminate Ionic Liquids

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The application of high vacuum effectively removes protons from ambient-temperature chloroaluminate ionic liquids, or molten salts, consisting of mixtures of 1-ethyl-3-methylimidazolium chloride and aluminum chloride. Electroanalytical and NMR techniques are used to show the efficacy of the proton removal process. In addition, a combination of electroanalytical and NMR measurements suggests that protons, when present in these ionic liquids as Al-O-H entities, are not electrochemically active.

## INTRODUCTION

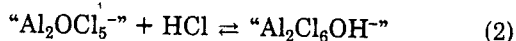
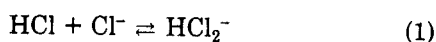
Ambient-temperature ionic liquids, molten salts, composed of mixtures of aluminum chloride ( $\text{AlCl}_3$ ) with 1-ethyl-3-methylimidazolium chloride (ImCl) have been employed in numerous chemical and electrochemical studies (1-3). These ionic liquids are referred to as acidic, basic, or neutral depending on whether the mole ratio of  $\text{AlCl}_3$  to ImCl is greater than, less than, or equal to unity, respectively.

The purity of these ionic liquids is highly dependent on the quality of the ImCl and  $\text{AlCl}_3$  (4, 5). The extreme care normally taken in the preparation and handling of ImCl inevitably fails to exclude contamination by trace amounts of water. When weighed amounts of ImCl and  $\text{AlCl}_3$  are mixed in a drybox this trace contamination is carried through into the resulting molten salt. While water, as  $\text{H}_2\text{O}$ , does not appear to exist in these molten salts (6-10), it does react with the melt components giving rise to a variety of oxide- and proton-containing impurities. The level of protonic impurities typical of these molten salts is on the order of 10 mM; this represents a purity of 99.97% by weight in a neutral melt.

In this work we focus on simplified methods to remove protonic impurities from ambient temperature ionic liquids. The electrochemical behavior of both organic and inorganic solutes in these ionic liquids may be drastically affected by protonic impurities and, to a lesser extent, by oxide impurities; this is particularly true in acidic melts where a proton behaves as a Brønsted superacid (11-13). Thus, the removal of both protons and oxides has been an important consideration when working in these solvents (14-16).

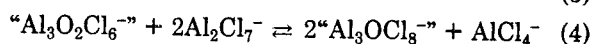
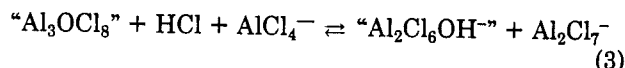
There are several methods that can be employed to remove protons from the ambient-temperature molten salts. These include reaction with alkylaluminum chlorides (14) and passage of the melt through an ion-exchange column (17). The major problem with both these methods is the possibility of unwanted species being introduced, left over, or generated by reaction with the analytes of interest.

In basic melts, protons have been shown to participate in two equilibria, one without (eq 1) (8) and the other with (eq 2) (9), oxide. In eq 2 the quotation marks represent species



which were proposed from the modeling of  $^{17}\text{O}$  NMR measurements of the oxide equilibria in these molten salts (9).

In acidic melts there are three major oxide-containing species, one of which contains protons. HCl appears to be the only other proton-containing species in acidic melts. The proposed equilibria between the three oxide species and HCl are (9)



where again the quotation marks represent species proposed from the NMR modeling. In addition to the above equilibria, the equilibrium between HCl in the gas phase and in solution must also be considered:



The presence of this final equilibrium suggests removal of HCl from the melt may be accomplished through evacuation at a pressure significantly less than the HCl equilibrium vapor pressure; this, in turn, would displace the melt proton/oxide equilibria (eqs 1-3) toward formation of HCl and eventually result in the complete removal of proton from the melt.

We report here a procedure for the removal of proton from both basic and acidic molten salts which involves the evacuation of the melts to pressures less than  $5 \times 10^{-6}$  Torr for several hours. This procedure is effective in both the absence and presence of oxides. When coupled with the use of phosgene to remove oxides from the melt by chloride displacement (15, 16), both oxide and proton impurities can be removed in a simple, clean process. In addition, the use of aluminum to remove proton from acidic melts is discussed.

## EXPERIMENTAL SECTION

All the melt preparation and the electrochemical experiments were performed in a Vacuum Atmospheres drybox under a nitrogen atmosphere. The synthesis and purification of ImCl,  $\text{AlCl}_3$ , and ImCl( $^2\text{HCl}$ )<sub>2</sub> were performed as previously described (4, 5, 18). Since ImHCl<sub>2</sub> is not stoichiometric, its stoichiometry was determined by dissolution of a weighed amount in water with titration of the  $^2\text{H}^+$  by NaOH. The value of  $x$  was found to be  $0.824 \pm 0.001$ . This solution, hereafter, will be referred to as Im $^2\text{HCl}_2$ .  $^2\text{H}_2\text{O}$  (99.98%) and  $\text{H}_2^{17}\text{O}$  (20% isotopic enrichment) were obtained from Cambridge Isotope Laboratories. Aluminum (foil, Reynolds) and phosgene (liquid phase 99.0%, Matheson) were used as received.  $\text{Li}_2\text{CO}_3$  was dried at 400 °C under vacuum prior to use.

Electrochemical experiments were performed on a computer-controlled system as described previously (19). Normal pulse voltammograms (NPV) were recorded at 25 °C with pulse and waiting times of 0.1 and 7 s, respectively (the waiting time included 3 s of stirring). The working electrode was a platinum disk (area 0.0201 cm<sup>2</sup>) obtained from Bioanalytical Systems. The counter electrode was a platinum flag, and the reference electrode was an aluminum wire (5N Alfa Inorganics) immersed in a 1.5:1 acidic melt and equilibrated for 24 h. The initial and final potentials of the working electrode in the basic melts were 0 and -1 V and in the acidic melts were 1.5 and 0.5 V versus the 1.5:1 Al/Al(III) reference.

All NMR samples were prepared in a drybox, pipetted into 10-mm tubes (Wilma Glass Co.), and then capped and sealed with Parafilm.  $^2\text{H}$  and  $^{17}\text{O}$  NMR experiments were performed using a Varian VXR-400 S spectrometer operating at 61.395 and

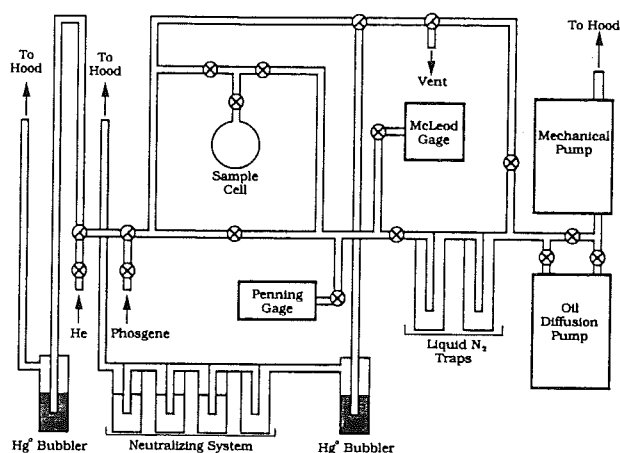


Figure 1. Apparatus used for oxide and proton removal.

54.219 MHz, respectively. The  $^2\text{H}$  and  $^{17}\text{O}$  NMR experiments were performed at 90 °C with the spectrometer unlocked. Natural-abundance  $\text{D}_2\text{O}$  in water was used as the reference for the  $^2\text{H}$  NMR analyses, and natural-abundance  $\text{H}_2^{17}\text{O}$  in water was used as the reference for the  $^{17}\text{O}$  NMR analysis. Both references were assigned a value of 0 ppm, with referencing performed by substitution.

The schematic of the apparatus used for oxide and proton removal is shown in Figure 1. Phosgene slowly penetrates most types of commercial elastomeric tubing (i.e., Tygon, neoprene, latex), and it is soluble in both silicon and petroleum-based greases and oils (20, 21). Consequently, the apparatus in Figure 1 was constructed primarily of glass and Teflon. The apparatus employs an oil diffusion pump coupled with a mechanical pump to achieve pressures down to  $10^{-7}$  torr. A neutralizing system consisting of an overflow trap coupled to three gas washing bottles filled with aqueous 5% w/w NaOH as neutralizing solutions effectively eliminates excess phosgene. After oxide and proton removal have been accomplished, the apparatus provides a bypass so phosgene in the liquid nitrogen traps can be purged and subsequently neutralized.

**CAUTION:** Phosgene is an extremely toxic chemical. At room temperature it is a colorless gas with an odor resembling that of moldy hay (22). The odor detection limit for phosgene in air is considered to be 0.5 ppm while the recommended time-weighted average threshold limit value (TLV) is 0.1 ppm (20, 23).

Normally, 25–50 mL of melt was loaded into a sample cell in the drybox. The sample cell was then transferred outside the drybox and attached to the apparatus (Figure 1). During preparation the melt was maintained at 25–30 °C, and throughout the procedure the melt was mixed with stirring from a magnetic stirrer. The cell was evacuated to  $10^{-3}$  Torr with the mechanical pump and then refilled with helium; this was repeated three to five times to completely replace the atmosphere in the cell with helium. The sample cell was then evacuated a final time to  $10^{-3}$  Torr; only this time it was refilled with phosgene. Under a slight positive pressure the phosgene was allowed to react with the melt for 5–10 min. To ensure exhaustive oxide removal the evacuation, refill, and reaction with phosgene were repeated two more times. After the third refill with phosgene the cell was again evacuated to  $10^{-3}$  Torr. The melt was then heated to 70–75 °C and the oil diffusion pump engaged. This final evacuation removed remaining traces of phosgene as well as the protons from the melt. The final evacuation was complete when the equilibrium pressure was  $<5 \times 10^{-6}$  Torr; this was normally achieved in an overnight evacuation.

The procedure for proton removal without oxide removal was identical to the procedure described above with the exception that after the atmosphere in the cell had been replaced with helium the cell was then evacuated to  $<5 \times 10^{-6}$  Torr. A complete step-by-step operating procedure and detailed diagram of the system are available on request.

## RESULTS AND DISCUSSION

**Basic Molten Salts.** A series of experiments were performed in order to investigate the various aspects of proton

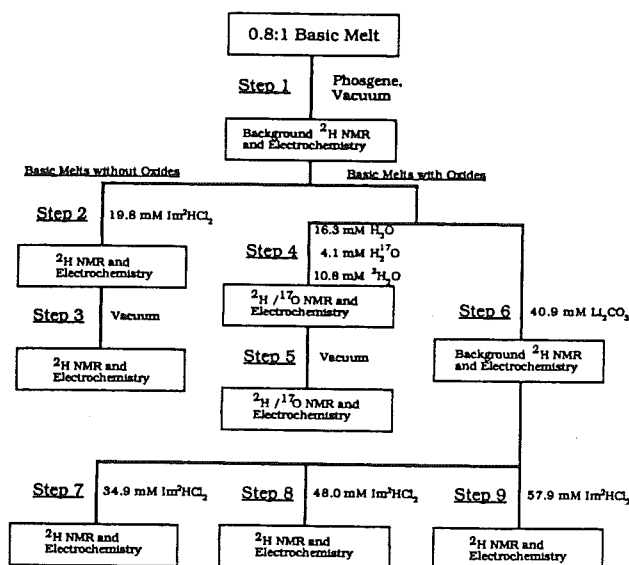


Figure 2. Flow chart diagram of basic melt experiments.

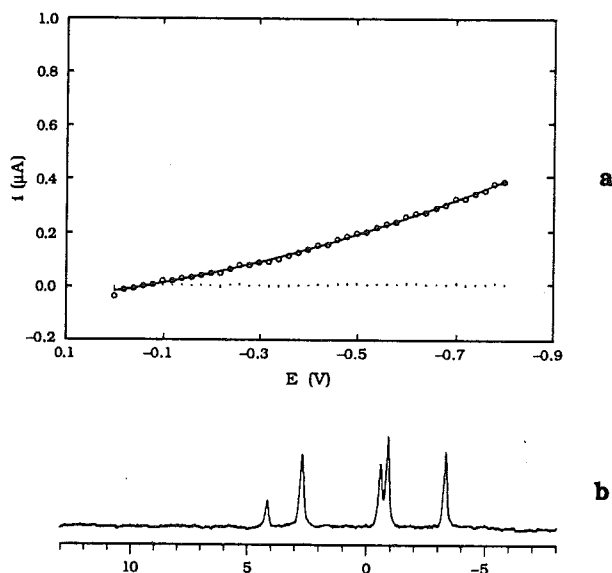


Figure 3. (a) Normal pulse voltammogram of a proton/oxide-free 0.8:1 melt (+), empirical second-order polynomial (continuous line), and their difference (vertical lines). (b)  $^2\text{H}$  NMR spectrum of a proton/oxide-free 0.8:1 melt.

removal from the 0.8:1 basic melts. The experimental scheme is diagrammed in Figure 2. A large quantity of 0.8:1 melt was initially treated with phosgene and vacuum to remove oxide- and proton-containing impurities (step 1, Figure 2). This melt was then used for all the work on the basic melts. It must be noted that in this manuscript both  $^2\text{H}^+$  (deuteron) and  $\text{H}^+$  (proton) will generically be referred to as proton. Figure 3a shows the NPV of this proton- and oxide-free melt. The proton reduction wave is absent, and the background current is featureless and is mainly capacitive.

The limiting current,  $i_l$  (A) on NPV is given by the Cottrell equation (24):

$$i_l = \frac{nFA\sqrt{DC}}{\sqrt{\pi t_p}} \quad (6)$$

where  $n$  is the number of electrons,  $F$  is the Faraday constant,  $D$  ( $\text{cm}^2/\text{s}$ ) is the diffusion coefficient,  $C$  ( $\text{mol}/\text{cm}^3$ ) is the concentration, and  $t_p$  (s) is the pulse time.

In order to evaluate the smallest concentration of protons that could be detected, the following procedure was used. The

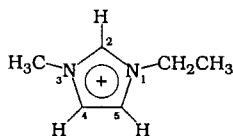
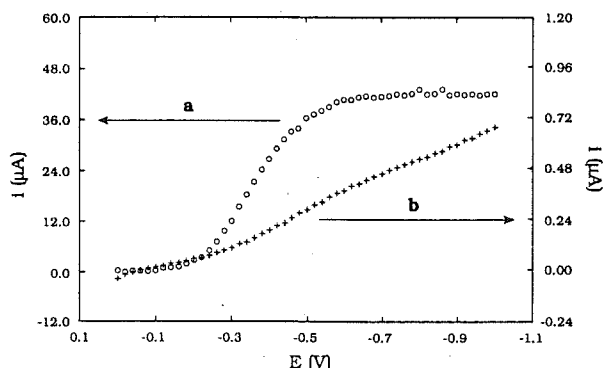
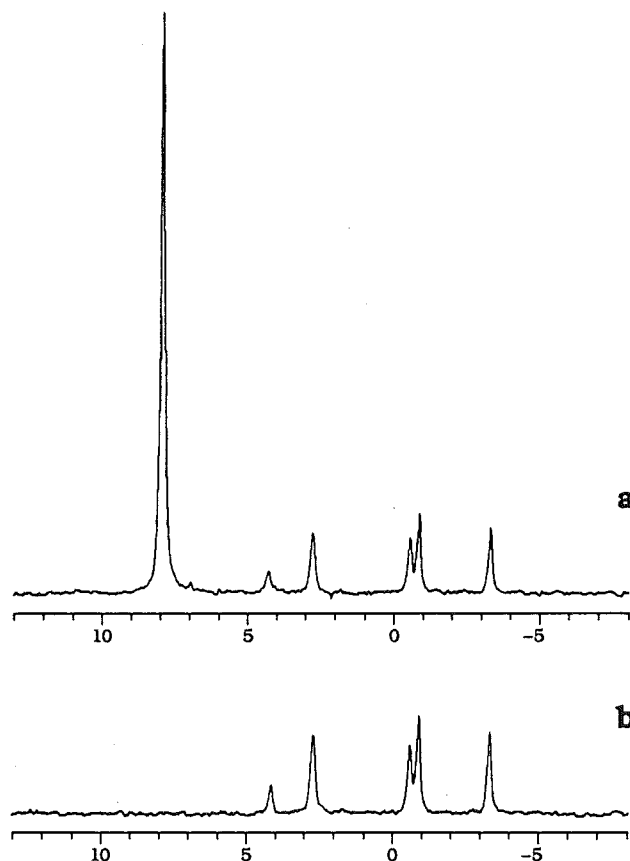
Figure 4. Im<sup>+</sup> cation ring numbering.

Figure 5. Normal pulse voltammograms of a oxide-free 0.8:1 melt (a) containing 19.8 mM protons (O). (b) The same melt after 5 h of evacuation (+).

residual background current versus potential trace was fitted to a second-order polynomial and the standard deviation of the experimental points computed. A faradaic current, resulting from proton reduction, with magnitude 3 times the standard deviation, was taken to correspond to the smallest detectable proton concentration. An amount 3 times the standard deviation, 11 nA, corresponds to a solution containing ca. 5.5  $\mu$ M protons under the experimental conditions used in this study.

A similar analysis can be performed on the  $^2\text{H}$  NMR data using the peak intensity for a specific  $^2\text{H}$  resonance versus the baseline noise. Figure 3b shows the  $^2\text{H}$  NMR spectrum of the proton/oxide-free melt (step 1, Figure 2) where the natural-abundance  $^2\text{H}$  on the imidazolium cation (Im<sup>+</sup>) are observed. The assignments of  $^2\text{H}$  resonances ( $\pm 0.1$  ppm) are as follows: (Figure 4) 4.1 ppm,  $^2\text{H}$ -2; 2.7 ppm,  $^2\text{H}$ -4 and  $^2\text{H}$ -5; -0.7 ppm, N-C $^2\text{H}_2$ ; -1.0 ppm N-C $^2\text{H}_3$ ; -3.4 ppm, C $^2\text{H}_3$ . At 90 °C the Im<sup>+</sup> concentration of a 0.8:1 melt is 4.83 M. The percent of natural-abundance deuterium is 0.015 (25). Therefore, one methyl group resonance corresponds to 2.17 mM  $^2\text{H}$  (4.83 mol of Im<sup>+</sup>/L  $\times$  1 methyl/Im<sup>+</sup>  $\times$  3 H methyl  $\times$  1.5  $\times$  10<sup>-4</sup> mol of  $^2\text{H}$ /mol of H = 2.17  $\times$  10<sup>-3</sup> mol of  $^2\text{H}$ /L). The signal to noise ratio for the methyl  $^2\text{H}$  resonance was 34. Here the signal is the peak intensity, and the noise is defined as 1 standard deviation of the experimental noise. Using the same criterion of detectability as the electrochemical data (i.e. 3 times the standard deviation), the smallest detectable  $^2\text{H}$  concentration by  $^2\text{H}$  NMR spectrometry is 192  $\mu$ M under the experimental conditions used in this study ( $[2.17 \times 10^{-3} \times 3]/34 = 1.92 \times 10^{-4}$ ).

**Melts without Oxide Ions.** After the initial background electrochemistry and  $^2\text{H}$  NMR analysis, Im $^2\text{HCl}_2$  was added to the oxide- and proton-free 0.8:1 melt to result in a proton concentration of 19.8 mM (step 2, Figure 2). The NPV and  $^2\text{H}$  NMR spectrum for the resulting solution are shown in Figures 5a and 6a, respectively. The large  $^2\text{H}$  peak in Figure 6a at  $7.9 \pm 0.1$  ppm corresponds to the population weighted average of the  $^2\text{HCl}$  and  $^2\text{HCl}_2^-$  resonances under fast exchange conditions (eq 1) (9). This melt was then evacuated for 5 h (step 3, Figure 2), and the above measurements were repeated. Figures 5b and 6b, respectively, show the resulting NPV and  $^2\text{H}$  NMR spectrum. In Figure 6b the  $^2\text{H}$  resonance for  $^2\text{HCl}/^2\text{HCl}_2^-$  is clearly absent. In Figure 5b a very small wave due to proton reduction,  $i_1 = 150$  nA, is observed. By com-

Figure 6.  $^2\text{H}$  NMR spectra of an oxide-free 0.8:1 melt (a) containing 19.8 mM protons. (b) The same melt after 5 h of evacuation.

parison of this wave with the limiting current observed for the reduction in 19.8 mM solution,  $i_1 = 40$   $\mu$ A, the proton concentration after 5 h of evacuation was estimated to be 74  $\mu$ M. After a longer evacuation of this solution, ca. 16 h, the small proton reduction wave was no longer observed.

**Melts Containing Oxides.** The addition of 20%  $\text{H}_2$   $^{17}\text{O}$ -enriched water and  $^2\text{H}_2\text{O}$  to the proton/oxide-free 0.8:1 melt (step 4, Figure 2) resulted in a solution containing, formally, 16.3 mM  $\text{H}_2\text{O}$ , 4.1 mM  $\text{H}_2$   $^{17}\text{O}$ , and 10.8 mM  $^2\text{H}_2\text{O}$ . The  $^2\text{H}$  NMR spectrum of this solution exhibited a resonance at  $4.3 \pm 0.1$  ppm, which falls on top of the natural-abundance  $^2\text{H}$  resonance for the  $^2\text{H}$ -2 on the Im<sup>+</sup> ring. The  $^{17}\text{O}$  NMR spectrum of this solution shows a broad peak at  $52.2 \pm 0.5$  ppm. The single deuterium and oxygen resonances at 4.3 and 52.2 ppm, respectively, result from the fast exchange between oxide- and proton-containing species in the basic melts (eqs 1 and 2), and the observed chemical shifts represent the population weighted average resonance of these species.

Using the sum of the integrated intensities of the natural abundance  $^2\text{H}$  for the imidazolium N-CH $_2$  and N-CH $_3$  as an internal standard, the integrated intensity of the peak at 4.3 ppm, when corrected for the contribution of  $^2\text{H}$ -2, corresponds to a  $^2\text{H}$  concentration of 19.4 mM; this is in reasonable agreement with the total amount added, 21.5 mM. However, the NPV of this melt shows a limiting current of 85.4  $\mu$ A, which is well below what was expected for a melt containing 62.1 mM protons. Indeed, in an oxide-free melt, where 40  $\mu$ A corresponds to 19.8 mM, the limiting current should be ca. 125.5  $\mu$ A.

Following 6 h of evacuation (step 5, Figure 2), the NPV showed a small wave with  $i_1 = 130$  nA, while in the  $^2\text{H}$  NMR spectrum the only observable peaks were those due to the natural-abundance deuterium resonances of the Im<sup>+</sup>. The total integrated intensity of the  $^{17}\text{O}$  NMR spectrum of the evacuated melt remains constant; however, the peak is shifted

Table I. NPV and  $^2\text{H}$  NMR Data for Melts Containing Various Amounts of Protons and Oxides

step no. (Figure 2)	[oxide], <sup>a</sup> mM	[proton], <sup>a</sup> mM	$i_l$ , $\mu\text{A}$	[proton] <sup>b</sup> from NPV, mM	[proton] from $^2\text{H}$ NMR, mM	[proton] <sup>a</sup> [oxide] <sup>a</sup>	[proton] <sup>b</sup> NPV [proton] <sup>a</sup>
2	0	19.8	40.0	19.8	17.7	$\infty$	1
4	31.1	62.2	85.4	42.3	56.2 <sup>c</sup>	2.00	0.680
9	40.9	57.9	42.7	21.1	51.4	1.42	0.364
8	40.9	48.0	25.8	12.8	46.3	1.17	0.267
7	40.9	34.9	12.9	6.4	35.0	0.85	0.183

<sup>a</sup> Nominal values. <sup>b</sup> Using 40  $\mu\text{A}$  in oxide-free melt per 19.8 mM as a standard. <sup>c</sup> Taking into account that  $^2\text{H}$  represents only 34.55% of all the protons present in solution.

15.1 ppm downfield to  $67.3 \pm 0.5$  ppm. Zawodzinski and Osteryoung (9) observed an almost identical shift of 15.2 ppm in the  $^{17}\text{O}$  resonance of oxide in a 0.8:1 melt when going from a melt containing two protons per oxide ion to a melt without protons (26). Thus the effect of evacuation was to shift the  $^{17}\text{O}$  NMR resonance to the proton free limiting value.

While extended evacuation of normal molecular solvents is not possible because of the high solvent vapor pressure, it is not a problem in the case of room-temperature ionic liquids. Because of their ionic nature, the vapor pressure of these molten salts and their components are well below the pressures employed in this study (27). The only volatile components in these ionic liquids are dissolved drybox gases and, of course, HCl. The above NPV and NMR data establish that evacuation effectively removes protons from basic melts in the presence and absence of oxides. The effect of the evacuation is to remove HCl via eq 5; this in turn drives the two basic melt proton equilibria (eqs 1 and 2) toward formation of HCl, which is then removed.

The observation of a less than expected normal pulse limiting current for the proton reduction in the presence of oxides (step 4, Figure 2) was investigated further. Oxide, in the form of  $\text{Li}_2\text{O}_3$ , was added to the proton/oxide-free 0.8:1 melt (step 6, Figure 2) to a concentration of 40.9 mM (1 mol of oxide/mol of  $\text{Li}_2\text{CO}_3$  is produced) (6). From this solution three different melts were then prepared containing 34.9, 48.0, and 57.9 mM  $^2\text{H}$  added as  $\text{Im}^2\text{HCl}_2$  (steps 7–9, respectively, Figure 2). The NPV and  $^2\text{H}$  NMR data for these three melts along with the melt from steps 2 and 4 (Figure 2) are summarized in Table I. The proton concentrations computed from the  $^2\text{H}$  NMR integrated intensities by the method described above agree relatively well with the amount of proton added. However, in the melts containing oxides the proton concentrations calculated from the NPV limiting currents differ significantly from that expected on the basis of the added amount of proton. As the proton/oxide ratio increases, the proton concentration calculated from NPV data approaches the added concentration. This clearly indicates that the presence of oxides, regardless of their origin, reduces the limiting current observed for proton reduction. It is possible that the reduction of proton on the aluminum hydroxy chloride ion (eq 2) occurs at a potential outside the negative limit of the melt window.

**Acidic Molten Salts.** The removal of oxides from acidic melts with phosgene has been reported (15, 28). However, we have had difficulty achieving similar results. We suspect the problem arises from the fact that phosgene probably forms a 1:1 adduct with  $\text{AlCl}_3$  in the acidic melts (29). This, in turn, may necessitate the addition of sufficient phosgene to the melt to complex most if not all the  $\text{AlCl}_3$  before oxides could be removed. Therefore it may be that the vacuum fill method used in this work fails to add adequate phosgene to the acidic melts to achieve removal of oxides. Consequently, only the removal of proton from acidic melts containing oxides was studied.

The chemistry of protons in acidic melts appears simpler than in basic melts since protons are partitioned between only

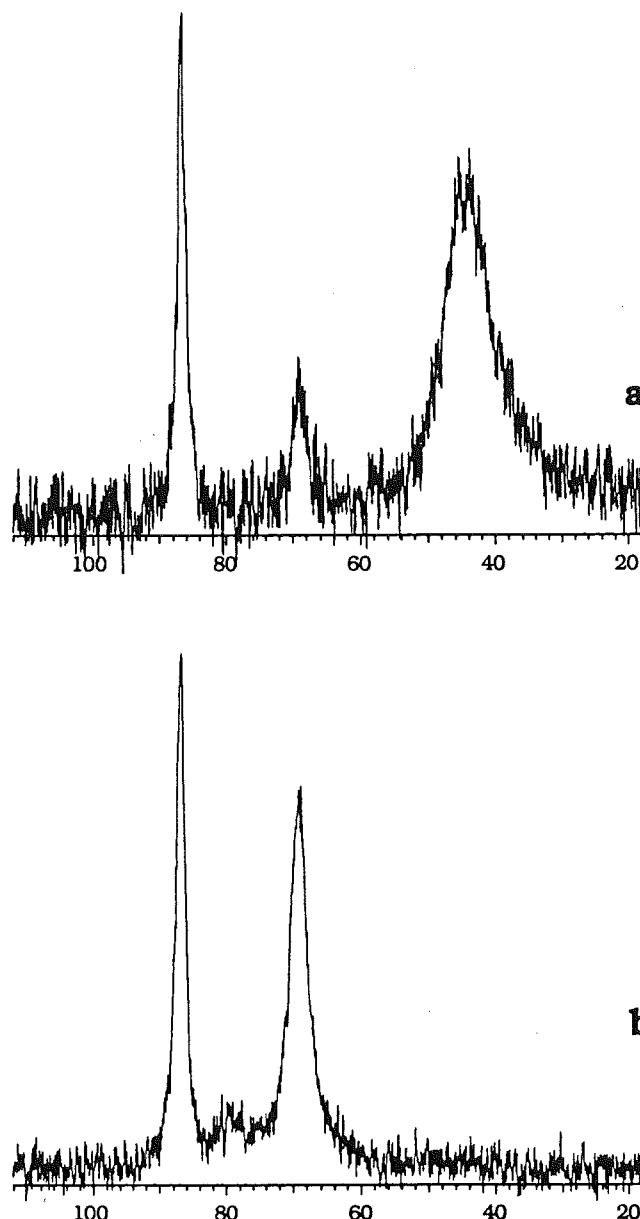


Figure 7.  $^{17}\text{O}$  NMR spectra of a 1.2:1 melt (a) containing 13.1 mM of 20%  $^{17}\text{O}$ -enriched water. (b) The same melt after evacuation.

two species, HCl and  $\text{Al}_2\text{Cl}_6\text{OH}^-$  (eqs 3 and 4). However, studying this chemistry has been difficult. For example, the voltammetry of proton in acidic melts is not reproducible (7). The proton reduction wave is ill defined and decreases with time. Thus, NPV does not provide a reliable measure of the proton concentration in acidic melts. Furthermore, we have recently determined that in acidic melts  $^2\text{H}$ , in the form of  $^2\text{HCl}$ , exchanges with H at the C-4 and C-5 positions on the  $\text{Im}^+$  ring (10). Consequently,  $^2\text{H}$  NMR spectrometry also

cannot be used quantitatively to investigate proton removal from acidic melts.

Since  $^{17}\text{O}$  NMR spectrometry was the remaining quantitative method at our disposal for studying proton removal, the following experiment was performed. A 1.2:1 acidic melt was made 13.1 mM in 20%  $^{17}\text{O}$ -enriched water. The  $^{17}\text{O}$  NMR spectrum of this solution shows three resonances at 87, 69, and 44 ppm (Figure 7a). The peaks at 87 and 69 ppm have been assigned to the aluminum oxy chloro species,  $\text{Al}_3\text{O}_2\text{Cl}_6^-$  and  $\text{Al}_3\text{OCl}_3$ , respectively, and the peak at 44 ppm has been assigned to the aluminum hydroxy chloride species,  $\text{Al}_2\text{Cl}_5\text{OH}^-$  (9). This melt was then evacuated overnight and the  $^{17}\text{O}$  NMR analysis repeated (Figure 7b). While the total integrated intensity remained the same, the NMR spectrum exhibited only the two peaks due to the aluminum oxy chlorides (Figure 7b). From the signal to noise ratio, the aluminum hydroxy chloride concentration was estimated to be less than 0.1 mM. Under the assumption that the acidic melt proton/oxide equilibrium, eq 3, is valid, the absence of detectable  $\text{Al}_2\text{Cl}_5\text{OH}^-$  indicates that HCl has also been removed. Thus, it appears that evacuation also removes proton from acidic melts.

An alternative to proton removal by evacuation has been investigated in the acidic melt. When aluminum metal was added to the solid  $\text{ImCl}$  and solid  $\text{AlCl}_3$  as the acidic melt was prepared, bubbles were observed at the aluminum surface. The NPV of this melt showed no faradaic wave in the potential region of the proton reduction. In acidic melts the reduction of  $\text{Al(III)}$  occurs at  $-0.4$  V while the reduction of protons occurs at ca.  $+0.5$  V (1, 7). Therefore, Al metal should reduce protons (30).

### CONCLUSIONS

The NMR and NPV results indicate that protons can effectively be removed from basic melts by evacuation. This method is unaffected by the presence of oxides. However, oxides do affect the proton reduction limiting current observed in NPV. This probably results from the electrochemical inactivity of proton, as aluminum hydroxy chloride ion, within the melt window.  $^{17}\text{O}$  NMR results indicate that evacuation also removes proton from acidic melts.

### ACKNOWLEDGMENT

Helpful discussions with Dr. Michael Carter are appreciated.

**Registry No.**  $\text{ImCl}$ , 65039-09-0;  $\text{AlCl}_3$ , 7446-70-0;  $\text{H}^+$ , 12408-02-5;  $\text{H}_2^{17}\text{O}$ , 13768-40-6; Pt, 7440-06-4;  $\text{D}_2$ , 7782-39-0;  $^{17}\text{O}$ , 13968-48-4;  $^2\text{H}^+$ , 14464-47-2;  $^2\text{H}_2\text{O}$ , 7789-20-0; phosgene, 75-44-5.

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