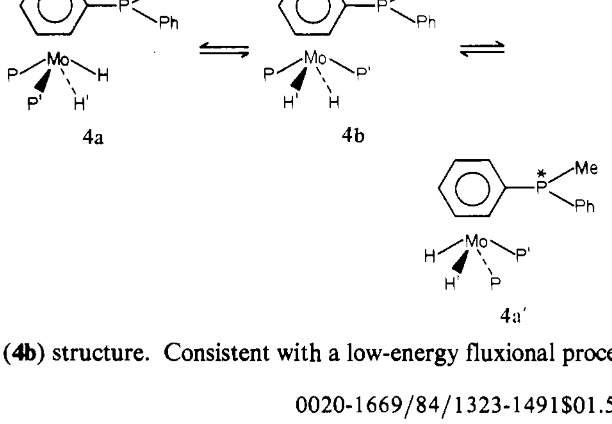
NMR resonance of the reaction solution at −24.8 ppm is characteristic of a "dangling" phosphorus moiety,[9] and it falls downfield of the corresponding resonance for complex **1** (at −31.0 ppm) in keeping with the greater π acidity of the dinitrogen ligand relative to the phosphine ligand.[9b,c] The nuclei (^1H, ^{31}P) in the σ-bonded ligands are diastereotopic because of the chiral, dangling phosphorus center; the ^{31}P NMR spectrum shows an AB pattern characteristic of such monosubstituted complexes.[9b,c] Inequivalent σ-bonded-phosphine methyl and η^6-arene protons are observed in the ^1H NMR spectrum.

Small amounts of 90% pure complex **2** can be obtained by triturating complex **1** with large volumes of hexanes under nitrogen to wash away dissociating phosphine. A more effective preparation involves the use of $[9\text{-BBN}]_2$ as a phosphine sponge reagent (Scheme I). The dinitrogen complex **3** containing the borane attached to the "dangling" phosphorus is isolated in 90% yield simply by stirring a suspension of complex **1** in a solution of excess $[9\text{-BBN}]_2$ in dry hexanes for 20 h under nitrogen and then filtering off the oxygen-sensitive yellow solid. The adduct $MePh_2P\cdot BH(C_8H_{14})$ (**5**) is hexane soluble and can be washed away from the product. Complex **3** ($\nu(N_2)$ = 1995 cm^{-1}) is stable in benzene solution in the presence of excess $[9\text{-BBN}]_2$ and can be recrystallized to analytical purity in this solution. Its ^{31}P NMR spectrum shows a broad singlet due to the "dangling" phosphorus bonded and coupled to boron isotopes and the expected AB system for the σ-bonded ligands. The IR spectra of compounds **3** and **5** have terminal boron–hydride absorptions at ca. 2250 cm^{-1} that signal the presence of boron adducts; these compounds do not contain free $[9\text{-BBN}]_2$, which gives an absorption at 1560 cm^{-1} due to bridging hydrides. There is no evidence for an interaction between the hydride and the dinitrogen ligand. The borane can be quantitatively removed from complex **3** in benzene solution (^{31}P NMR experiment) by adding 1 equiv of diethylamine that has been dried over $LiAlH_4$, but the extremely air-sensitive dinitrogen complex produced has not been isolated in a pure form. All the borane adducts react readily with traces of water to generate hydrogen. Thus, if anhydrous conditions are not maintained, the dihydride complex **4** forms at the expense of complex **2**. The use of other nonoxidizing Lewis acids such as $BF_3\cdot THF$, $AlCl_3$, and BEt_3 to abstract a ligand from complex **1** gave products other than a dinitrogen complex.

Complex **1** also reversibly reacts with hydrogen at 31 °C to give a dihydride complex, **4**, in equilibrium with **1** and free $PMePh_2$, $K_2 = 0.71 \pm 0.03$ (eq 2). Addition of excess phosphine or purging with argon at 35 °C for 20 min regenerates **1**. The dihydride has not been isolated in a pure form but can be characterized in solution. It must undergo a dynamic process that is fast on the NMR time scale that renders the σ-bonded phosphine ligands equivalent since these nuclei give a singlet in the $^{31}P\{^1H\}$ spectrum instead of the AB pattern expected for a static *cis*-dihydride (**4a**, **4a′**) or *trans*-dihydride (**4b**) structure. Consistent with a low-energy fluxional process, the hydride resonance remains a triplet and the methyls of the σ-bonded phosphines remain equivalent when toluene-d_8 solutions of the equilibrium mixture are cooled to −80 °C or heated to +50 °C. A trans structure was found for $Mo(\eta^6\text{-}C_6H_6)(Me)_2(PMe_3)_2$ in the solid state[16] and was proposed as a possible explanation for the magnetic equivalence of ligands in the other known complexes of this type, $Mo(\eta^6\text{-arene})(H)_2(PPh_3)_2$, which are also likely to be fluxional.[11b] A site-exchange mechanism involving structure **4b** as an intermediate is likely (eq 3) although species involving coordinated molecular hydrogen as observed for $W(P(i\text{-}Pr)_3)_2(CO)_3(H_2)$[17] cannot be ruled out.



4a

4b

4a′

(3)

The rates of reaction of **1** with nitrogen and hydrogen are approximately five times slower than that with carbon monoxide under similar conditions. The reaction with carbon monoxide is known to proceed via the rate-determining dissociation of phosphine from **1**.[9c] The former reactions likely also involve dissociation of phosphine from **1** prior to a rate-determining addition of the gas molecules. Ligand lability in **1** likely results from steric crowding of the three bulky *fac* ligands (cone angle 136°).

The reactions of Scheme I represent the first example of the preparation of a dinitrogen complex by phosphine abstraction using a Lewis acid. The 9-BBN dimer is a convenient Lewis acid to use because it is an easily handled, crystalline solid and it forms highly soluble phosphine adducts. On the other hand, it is a strong reducing agent that reacts readily with water. We have found that although it aids in converting $FeH_2(PMePh_2)_4$[4] into $FeH_2(N_2)(PMePh_2)_3$ ($\nu(N_2)$ = 2039 cm^{-1}), it also causes decomposition of the complexes to iron metal. This borane may play an additional role in the formation of complex **3** by providing a nitrogen binding site that is more sterically protected than that of **2** toward attack of larger Lewis bases in solution. Other applications of this "phosphine sponge" reagent are being investigated.

Acknowledgment. This work was supported by a Natural Sciences and Engineering Research Council of Canada operating grant to R.H.M. We thank Peter Jhauj and Edward Lin for the gas-uptake measurements.

Registry No. **1**, 84430-77-3; **2**, 87902-59-8; **3**, 89486-69-1; **4**, 89486-70-4; **5**, 89486-71-5; $[9\text{-BBN}]_2$, 21205-91-4.

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Determination of Equilibrium Constants for the Tetrachloroaluminate Ion Dissociation in Ambient-Temperature Ionic Liquids

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Received July 19, 1983

The major equilibrium describing acid–base properties of tetrachloroaluminate ionic liquids is the dissociation of the tetrachloroaluminate anion.[1-7]

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$$2AlCl_4^- = Al_2Cl_7^- + Cl^- \qquad (1)$$

An equilibrium constant of reaction 1 can be calculated from potentiometric measurements of chloride ion activities on both sides of an equivalent point at the neutral (1:1 $AlCl_3$:RCl, where R^+ is an alkali metal or organic cation) melt composition. In $AlCl_3$–NaCl molten salts an aluminum electrode was successfully used for a determination of chloride ion activities.[1-3] The potential of this electrode is given by eq 2. The

$$E = E^\circ_{Al(III)/Al} + \frac{RT}{3F}\ln a_{AlCl_4^-} - \frac{4RT}{3F}\ln a_{Cl^-} \qquad (2)$$

same procedure was subsequently applied for determinations of the equilibrium constant of reaction 1 in aluminum chloride based molten salts containing chlorides of the organic cations[4-7] *N*-*n*-butylpyridinium chloride (BuPyCl), *N*-*n*-butyl-4-(dimethylamino)pyridinium chloride, and 1-methyl-3-ethylimidazolium chloride (ImCl). However, in basic ($AlCl_3$:RCl < 1) $AlCl_3$–BuPyCl melts, potentiometric measurements were affected by the spontaneous reduction of butylpyridinium cation by elemental aluminum.[4] Considering an unknown positive shift of the measured mixed potential with respect to the equilibrium potential of the Al(III)/Al couple, the calculated values of the equilibrium constant were regarded as maximum values.[4]

In other ambient-temperature chloroaluminate molten salts, aluminum deposition potentials could not be attained in basic melts,[6,7] in spite of more negative reduction potentials of the organic cations than in the $AlCl_3$–BuPyCl melt. Differences between the equilibrium constants obtained for reaction 1 were surprisingly large,[4-7] and we have decided to reconsider problems involved in the potentiometric determination of the tetrachloroaluminate anion dissociation constant.

Experimental Section

The methods used for synthesis of *n*-butylpyridinium chloride and 1-methyl-3-ethylimidazolium chloride were similar to those described previously.[6,8]

A tungsten electrode sealed in glass ($A = 0.0784$ cm^2) served as a working electrode. Aluminum wires dipped in acidic $AlCl_3$–BuPyCl and $AlCl_3$–ImCl melts were used as reference and auxiliary electrodes, and all potentials are referred to the potentials of an Al electrode in 2:1 melts.

Results

Background cyclic voltammetric scans of the basic (0.9:1 $AlCl_3$:RCl mole ratio) and acidic (1.5:1) $AlCl_3$–BuPyCl and $AlCl_3$–ImCl molten salts at a tungsten electrode are shown in Figures 1 and 2. Compared to similar curves recorded at a glassy-carbon electrode,[6,8] they reveal several additional features. The most important difference is a significant increase in the rate of chlorine evolution and chlorine reduction in both basic and acidic melts. Thus, the electrode reaction for the Cl_2/Cl^- system in basic melts, irreversible at a glassy-carbon electrode,[6] becomes almost reversible at a tungsten electrode (Figure 1). Also, chlorine reduction in acidic melts, which has not heretofore been observed in room-temperature chloroaluminate melts, is evident at a tungsten electrode (Figure 2). This shows that the chlorine evolution reaction defines the positive potential (anodic) limits for both acidic and basic $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids.

Table I. Chlorine Electrode Potentials and Values of the Tetrachloroaluminate Ion Dissociation Constants

melt compn	E^a,[a] V	E_p^c,[b] V	E',[c] V	log *K*	ref
1.5:1 $AlCl_3$–BuPyCl	2.31	1.23	1.77		
0.9:1 $AlCl_3$–BuPyCl	0.77	0.745	0.76	−16.9 ± 2	this work
				<−12.4	4
				−12.9	5
1.5:1 $AlCl_3$–ImCl	2.30	1.24	1.77		
0.9:1 $AlCl_3$–ImCl	0.79	0.77	0.78	−16.6 ± 2	this work
				−18.7	6

[a] E^a = potential at which chlorine evolution current equals 25 μA. [b] E_p^c = peak potential for chlorine reduction. [c] E' = estimated chlorine electrode equilibrium potential.

As the negative potential (cathodic) limit in both acidic melts an aluminum deposition current is observed, which at a tungsten electrode is preceded by a small peak reflecting a formation of a monolayer deposit (Figure 2). Aluminum stripping peaks appear after reversing the direction of potential scan. However, in the basic room-temperature chloroaluminates the cathodic limiting currents are due to organic cation reduction; aluminum deposition cannot be attained in either the $AlCl_3$–BuPyCl or the $AlCl_3$–ImCl system, even though the organic cation reduction potential is much more negative in the latter than the former (Figure 1). At a tungsten electrode the aluminum nucleation overpotential is very small, and a monolayer of aluminum is deposited in an acidic melt at potentials more positive than the potential of the Al(III)/Al couple (Figure 2). These results suggest that either the formal potential of the Al(III)/Al couple is very negative in basic melts or the electrode process leading to Al deposition in this system is irreversible.

The open-circuit potential of an aluminum electrode in a 0.9:1 $AlCl_3$–ImCl molten salt was ca. −1.4 V; it is however strongly dependent on solvent impurities (vide infra). If a potential is applied to this electrode that is less negative than the open-circuit potential, an aluminum oxidation current is observed (Figure 1, curve 3), but cathodic current flowing at potentials more negative is very small. An aluminum deposition process is not observed before the potential of the Im cation reduction (Figure 1, curve 3). This shows that $AlCl_4^-$ reduction is very irreversible, and the open-circuit potential of an aluminum electrode measured in these basic chloroaluminates is not an equilibrium potential of the Al(III)/Al couple, but rather a mixed potential with only an anodic process being due to aluminum oxidation. A cathodic process at an aluminum electrode could be a reduction of any substance present in a solution reducible at the aluminum oxidation potential. As shown previously[4,9] in $AlCl_3$–BuPyCl molten salts, the $BuPy^+$ reduction potential is less negative than the aluminum oxidation potential. Voltammograms recorded with a tungsten electrode in both $AlCl_3$–BuPyCl and AlCl–ImCl melts reveal cathodic currents at potentials more negative than ca. −0.8 V (Figure 1). These currents are due to a reduction of products formed in the reaction of water with tetrachloroaluminate melts.[10] The cathodic current observed at an aluminum electrode in the potential range between the aluminum oxidation and Im^+ reduction (Figure 1, curve 3) is probably due to the same process. Thus, the cathodic process that, with the aluminum oxidation, gives rise to the mixed

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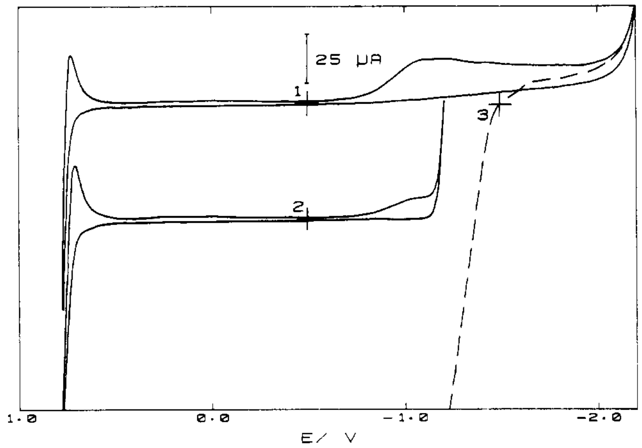

Figure 1. Cyclic voltammograms for 0.9:1 $AlCl_3$–ImCl (1) and $AlCl_3$–BuPyCl (2) at a tungsten electrode and voltammetric curve for the aluminum electrode in 0.9:1 $AlCl_3$–ImCl (3) (v = 0.1 V/s).

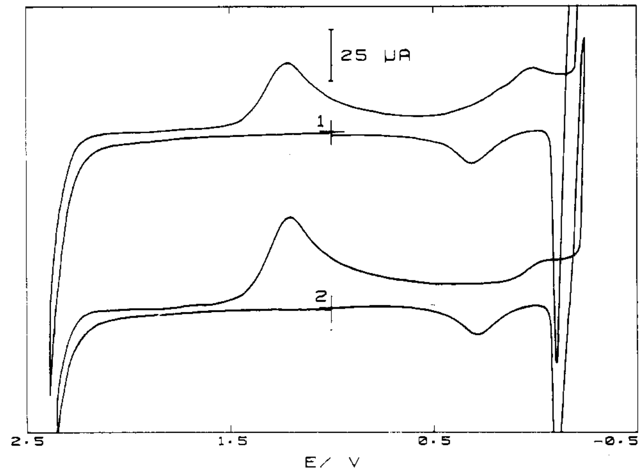

Figure 2. Cyclic voltammograms for 1.5:1 $AlCl_3$–ImCl (1) and $AlCl_3$–BuPyCl (2) at a tungsten electrode (v = 0.1 V/s).

potential of an aluminum electrode in basic chloroaluminate melts may be due to HCl reduction. In any case, aluminum oxidation potentials observed in voltammetric experiments (Figure 1, curve 3) set the least negative limit for the reversible potential of an aluminum electrode.

Discussion

A comparison of the chlorine evolution and reduction potentials in basic and acidic $AlCl_3$–BuPyCl and $AlCl_3$–ImCl melts (Figures 1 and 2, Table I) shows the respective potentials do not differ by more than 20 mV for the same $AlCl_3$:RCl mole ratio. This indicates similar chloride ion activities in the respective $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids; thus, the equilibrium constants for reaction 1 are similar in both systems. A calculation of the values of these equilibrium constants requires not only an estimate of the chlorine electrode equilibrium potentials but also a knowledge of the actual stoochiometric equilibria for this electrode. For acidic melts the electrode reaction can be written as

$$Cl_2 + 2Al_2Cl_7^- + 2e^- = 4AlCl_4^- \qquad (3)$$

and the reversible chlorine electrode potential is given by

$$E_a = E^\circ_{Cl_2/Cl^-} + \frac{RT}{2F}\ln [Cl_2]_a + \frac{RT}{F}\ln\left[\frac{[Al_2Cl_7^-]}{[AlCl_4^-]^2}\right]_a - \frac{RT}{F}\ln K \qquad (4)$$

If for basic melts the electrode reaction is

$$Cl_2 + 2e^- = 2Cl^- \qquad (5)$$

then

$$E_b = E^\circ_{Cl_2/Cl^-} + \frac{RT}{2F}\ln [Cl_2]_b - \frac{RT}{F}\ln [Cl^-]_b \qquad (6)$$

and finally at 40 °C

$$\log K = \frac{E_b - E_a}{0.062} + \frac{1}{2}\log\frac{[Cl_2]_a}{[Cl_2]_b} + \log\left[\frac{[Al_2Cl_7^-]}{[AlCl_4^-]^2}\right]_a + \log [Cl^-]_b \qquad (7)$$

where subscripts a and b indicate acidic and basic melt compositions and K is the equilibrium constant for reaction 1.

The chloride ion oxidation process in these basic room-temperature tetrachloroaluminates is presently being studied in this laboratory.[11] Preliminary results indicate that the stability of the Cl_3^- ion, which may be a chloride ion oxidation product, is not high, and a value of log K estimated from eq 7 would not differ from a value calculated for a chlorine electrode reaction, $Cl_3^- + 2e^- = 3Cl^-$, by more than 0.5.

An accurate determination of chlorine electrode equilibrium potentials could not be obtained from the voltammetric results. Only an estimate of these potentials could be made. The values of E_a' calculated as an average of chlorine evolution and reduction potentials in the acidic melts may differ from the equilibrium chlorine electrode potentials by more than 100 mV. In basic melts the electrode reaction for the Cl_2/Cl^- system at a tungsten electrode is much faster (Figure 1); cyclic voltammograms recorded at low chloride concentrations indicate that this system is quasi-reversible.[11,12] Thus, errors involved in estimating the equilibrium chlorine electrode potentials from voltammetric results are much smaller in basic than in acidic melts.

To estimate the values of E_b' in basic melts, an average of chlorine evolution and reduction potentials was taken from the curves shown in Figure 1. This approximate procedure gave the values of E_b', which differ by ca. 20 mV between $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids (Table I). The observed potential difference may indicate differences in chloride ion–organic cation association equilibria between the two ionic solvents. More detailed analysis of these association equilibria would require accurate measurements of the chlorine electrode potentials in basic melts; however, analysis of conductivity data for basic $AlCl_3$–BuPyCl and $AlCl_3$–ImCl systems[13] also suggests similar differences in the interionic interactions.

The values of log K were calculated from eq 7 by using estimated E_a' and E_b' (Table I) and $[AlCl_4^-]_a$, $[Al_2Cl_7^-]_a$, and $[Cl^-]_b$ calculated from stoichiometry of the reaction $AlCl_3$ + RCl at different $AlCl_3$:RCl mole ratios. In 1.5:1 melts $[AlCl_4^-] = [Al_2Cl_7^-]$ and is 1.75 mol dm^{-1} in $AlCl_3$–BuPyCl and 1.92 mol dm^{-3} in $AlCl_3$–ImCl melts. Chloride concentration equals 0.42 and 0.47 mol dm^{-3}, respectively, in 0.9:1 $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids.

The estimated values of log K for both $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids are compared with literature data in Table I. Despite errors involved in the estimation of chlorine electrode equilibrium potentials from the irreversible voltammetric curves, the results obtained show that the equilibrium constants of reaction 1 in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids are of the same order of magnitude. Lack of any interfering processes in the positive potential range suggests

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that in potentiometric experiments equilibrium chloride electrode potentials can be measured throughout the entire melt acidity range and more accurate values of the equilibrium constant of tetrachloroaluminate ion dissociation should be obtainable.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research.

Registry No. $AlCl_4^-$, 17611-22-2; BuPyCl, 1124-64-7; ImCl, 65039-09-0.

Additions and Corrections

1983, Volume 22

E. Canadell* and O. Eisenstein: Structure and Stability of One-Dimensional $(MX_2)_n$ Polymers. A Band Structure Analysis.

Page 3858. In the paragraph above structure **9**, read SS_3 (**6**), SS_1 (**8**), SS_2 (**7**) for SS_3 (**5**), SS_1 (**7**), SS_2 (**6**) and $(\sigma_x + \sigma_y)$ for $(\sigma_x - \sigma_y)$. The fourth sentence of this paragraph should be read "Decreasing θ decreases the bonding interaction between σ_x and σ_y."—E. Canadell

1984, Volume 23

Lawrence A. Dominey and Kenneth Kustin*: Kinetics and Mechanism of Iron(II), Cobalt(II), and Nickel(II) Mono Complex Formation with Acetohydroxamic Acid.

Page 106. In Table IV, the rate constants in column 1 should read k_L, k_{-L}, k_{HL}(exptl), k_{HL}(predicted), k_{-HL}. The units remain the same.—Kenneth Kustin