

Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis

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I. Introduction

Chemistry is dominated by the study of species in solution. Although any liquid may be used as a solvent, relatively few are in general use. However, as the introduction of cleaner technologies has become a major concern throughout both industry and academia, the search for alternatives to the most damaging solvents has become a high priority. Solvents are high on the list of damaging chemicals for



Tom Welton was born in London in January 1964. He studied Chemistry at the University of Sussex, where he graduated in 1985. He stayed at the University of Sussex to study for his DPhil on "Chemistry and Spectroscopy in Ionic Liquids", with Dr. K. R. Seddon (now Prof. Seddon of The Queen's University of Belfast). After three years as a post-doctoral fellow, he moved to Exeter University as the Demonstrator in Inorganic Chemistry. In 1995, he obtained a fellowship from the Lloyds of London Tercentenary Foundation which he used at Imperial College, where he now works as a Lecturer in Inorganic Chemistry and is a member of the Catalysis and Materials research group. Tom's research interests continue to include the use of ionic liquids as solvents for synthesis and catalysis. He also has interests in the use of metallodendrimers in catalysis.

two simple reasons: (i) they are used in huge amounts and (ii) they are usually volatile liquids that are difficult to contain.

Fused salts are liquids containing only ions, ionic liquids. It is possible, by careful choice of starting materials, to prepare ionic liquids that are liquid at and below room temperature. It is these *room-temperature ionic liquids*¹ that are the subject of this review.² Ionic liquids are not new; some of them have been known for many years, for instance [EtNH₃]-[NO₃], which has a melting point of 12 °C, was first described in 1914!³ For some time, it has been proposed that these ionic liquids provide a useful extension to the range of solvents that are available for synthetic chemistry. However, it is only in the past few years that significant literature has become available in this area. Some more recent reviews showing an overview of the potential of ionic liquids as solvents for synthesis and catalysis are available.⁴ Reviews of the use of higher melting salts in synthesis are also available.⁵

Some simple physical properties of the ionic liquids that make them interesting as potential solvents for synthesis are the following: (1) They are good solvents for a wide range of both inorganic and

organic materials, and unusual combinations of reagents can be brought into the same phase. (2) They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet noncoordinating solvents. (3) They are immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water. (4) Ionic liquids are nonvolatile, hence they may be used in high-vacuum systems and eliminate many containment problems. They do not evaporate!

The development of ionic liquids that are air and moisture stable has provided renewed vigor in ionic liquid chemistry, and the emerging use of these ionic liquids will be considered first. However, during the period covered by this review, the halogenoaluminate(III) and the closely related alkylhalogenoaluminate(III) ionic liquids have been by far the most widely studied and they will be considered separately. Where it is of interest, some salts that are only liquid above room temperature will also be included in the discussion.

II. Preparation

Until recently room-temperature ionic liquids were considered to be rare, but it is now known that many salts form liquids at or close to room temperature. Invariably, these ionic liquids are either organic salts or mixtures consisting of at least one organic component. The most common salts in use are those with alkylammonium, alkylphosphonium, *N*-alkylpyridinium, and *N,N*-dialkylimidazolium cations (see Figure 1). There is no reliable way to predict the precise melting point of organic salts, and identification of new room-temperature ionic liquids is a somewhat hit and miss affair. After all, there is nothing special about room temperature, it just happens to be the temperature at which rooms are, and salts with melting points of 20 °C and 30 °C are unlikely to have great differences in their structures and interionic interactions.

There are two basic methods for the preparation of ionic liquids: metathesis of a halide salt with, for instance, a silver, group 1 metal or ammonium salt of the desired anion and acid–base neutralization reactions.

Many alkylammonium halides are commercially available or they can be prepared simply by the reaction of the appropriate halogenoalkane and amine. Preparation of the pyridinium and imidazolium halides can be achieved similarly.^{6,7} For volatile halogenoalkanes, the low boiling points lead to preparations requiring either a sealed tube, such as in the synthesis of [emim]Cl (where [emim]⁺ is the 1-ethyl-3-methylimidazolium cation),⁸ or an elaborate reaction still. Hence, the use of salts with longer chain substituents, such as [bmim]Cl (where [bmim]⁺ is the 1-butyl-3-methylimidazolium cation), that can be prepared in conventional glassware by heating under reflux has become popular.⁹

In 1992 the first of the new ionic liquids, [emim][BF₄], was prepared via metathesis of [emim]I with Ag[BF₄] in methanol.¹⁰ This salt also has a melting

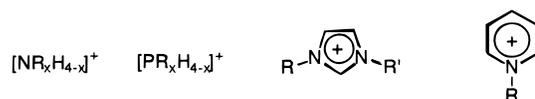


Figure 1. (a) Alkylammonium, (b) alkylphosphonium, (c) *N,N*-dialkylimidazolium, and (d) *N*-alkylpyridinium cations.

point of 12 °C and may be prepared considerably more cheaply using [NH₄][BF₄] in acetone.¹¹ This ease of preparation, together with its relative moisture stability and its immiscibility with a number of organic solvents is leading to its increasing use in biphasic catalysis (see below). The preparation of [emim][PF₆] shortly followed; this time it was prepared by reaction of [emim]Cl with HPF₆.¹² This salt has a melting point of 60 °C, which makes it slightly less attractive than the [BF₄][−] salt, if room temperature working is desired. Since then, thiocyanate, nonafluorobutanesulfonate, bis((trifluoromethyl)sulfonyl)imide, tris((trifluoromethyl)sulfonyl)methide, trifluoroacetate, and heptafluorobutanoate salts have all been prepared by metathesis reactions.^{13–15} These metathesis reactions are good candidates for those preparing new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials.¹⁶

Tetraalkylammonium tetraalkylborides are usually prepared by the metathesis reaction of the tetraalkylammonium bromide and the lithium tetraalkylboride.^{2,17} Since both the ammonium cation and the boride anion are asymmetrically substituted, the starting materials are usually made rather than purchased. Reaction of a trialkylborane with the appropriate alkyl lithium reagent in dry hexane yields the required lithium tetraalkylboride.¹⁸

Other ionic liquids are made by the quarternerization of the appropriate amine. This has been used to prepare a number of 1-alkyl-3-methylimidazolium trifluoromethanesulfonate salts.¹⁵ Methyl triflate is reacted with a stoichiometric amount of the 1-alkylimidazole in 1,1,1-trichloromethane. Since the methyl triflate is sensitive to moisture, the reaction must be carried out under anhydrous conditions.

Monoalkylammonium nitrate salts are best prepared by the neutralization of aqueous solutions of the amine with nitric acid.^{3b,13} The ionic liquids are isolated by removing excess water in vacuo. In a similar reaction, tetraalkylammonium sulfonates have been prepared by mixing equimolar amounts of the sulfonic acid and the tetraalkylammonium hydroxide.¹⁹ Again, excess water was removed in vacuo. To ensure the purity of the ionic liquids, they were dissolved in either acetonitrile or tetrahydrofuran and treated with activated charcoal for at least 24 h, and finally the organic solvent was removed in vacuo.

The final method for the synthesis of ionic liquids is direct combination of a halide salt with a metal halide. This is how the halogenoaluminate(III) (see below) and the chlorocuprate(I) ionic liquids are prepared.^{2,20} The chlorocuprate(I) ionic liquids are particularly sensitive to oxygen and have not found widespread use in synthesis.²¹

III. Handling

It is widely claimed that many of the new ionic liquids are both air and moisture stable; some are even hydrophobic. While it is true to say that the new liquids are free from many of the hydrolysis problems that make the halogenoaluminates(III) so difficult to handle, most ammonium and imidazolium salts are hygroscopic and if used in open vessels, hydration will almost certainly occur. The degree to which this is a problem will depend on the use to which the ionic liquid is being put and what solutes are being used. For instance, the small amounts of highly reactive species that are used as catalysts can be deactivated by even the smallest amounts of water.¹⁶ I would recommend handling under an inert atmosphere if the ionic liquids are to be used for air- or moisture-sensitive solutes. Nonetheless, these new ionic liquids are much easier to handle than the halogenoaluminate(III) systems and are opening up new avenues for research, particularly in homogeneous catalysis.

Among the room-temperature ionic liquids that are currently receiving attention are [EtNH₃][NO₃], [emim][NO₃], and [emim][ClO₄]. Organic nitrates and perchlorates are potentially explosive, especially when rigorously dried. Although no problems have been reported, care should be used at all times when handling them.

IV. Solvent Properties

Solvent polarity is the most commonly used solvent classification. Even when considering molecular solvents it is poorly understood and often confused. Terms such as polar, apolar, and nonpolar are used indiscriminately to apply to values of dielectric constants, dipole moments, and polarizabilities, even though none of these are directly correlated in a simple way. The simplest qualitative definition is that a polar solvent is one that will dissolve and stabilize dipolar or charged solutes. It is widely thought, though yet to be generally demonstrated, that under this definition, ionic liquids will be highly polar solvents.

The longest wavelength absorption band of Reichardt's dye (2,4,6-triphenylpyridinium *N*-4-(2,6-diphenylphenoxide) betaine shows one of the largest solvatochromic shifts known (375 nm between diphenyl ether and water).²² It can register effects arising from the solvent dipolarity, hydrogen bonding, and Lewis acidity and is considered to be a good general polarity scale. The E_T^N values of a small number of alkylammonium nitrate,²³ thiocyanate,²³ and sulfonate¹⁹ salts have been recorded. Values of ca. 0.95–1.01 for monoalkylammonium nitrates and thiocyanates are close to that of water (1.00, by definition), whereas quaternary ammonium sulfonates give lower values of ca. 0.45–0.65 which are more typical of polar organic solvents such as DMSO. An attempt was also made to separate dipole–dipole polarizability effects from hydrogen-bonding effects by using the π^* scale of dipolarity/polarizability, the α scale of hydrogen-bond-donor acidity, and the β scale of hydrogen-bond basicity.¹⁹ Although some difference was seen between the π^* values for monoalkylammo-

nium salts and the quaternary ammonium salts, the difference in the hydrogen-bond acidities and basicities was far more marked.

The solvent properties of these ionic liquids have also been investigated using chromatographic techniques.^{19,23,24} It was generally found that the ionic liquids could be considered to be polar phases with the solvent properties being largely determined by the ability of the salt to act as a hydrogen-bond donor and/or acceptor and the degree of localization of the charge on the anions. However, the ammonium and phosphonium salts that were used would not have had large differences in the delocalization of charge on the cation, and this may be an important effect for other salts, such as the pyridinium- and imidazolium-based ionic liquids. Furthermore, it was found that increasing the chain length of alkyl substituents on both cations and anions leads to greater lipophilicity of the ionic liquids.^{23,25} Also, the influence of hydrogen bonding can be diminished by fluorinating the ionic liquids.²⁶

V. Organic Reactions

A. Diels–Alder Reactions

The possibility of using ionic liquids as a substitute for water, which has become a popular solvent to carry out Diels–Alder cycloaddition reactions, has been explored. The first study was of the reaction of cyclopentadiene with methyl acrylate and methyl vinyl ketone in [EtNH₃][NO₃].²⁷ These reactions lead to a mixture of *exo* and *endo* products, and the solvent influences on the *endo/exo* selectivity of the reaction are well understood. The effect can be attributed to solvophobic interactions that generate an “internal pressure” and promote the association of the reagents in a “solvent cavity” during the activation process. The reactions showed a strong preference for the *endo* product and an acceleration of the reaction in comparison to nonpolar organic solvents. Although the increased rate and selectivities were not as great as those seen in water, the ionic liquid has the advantage that moisture-sensitive reagents may be used, Figure 2.

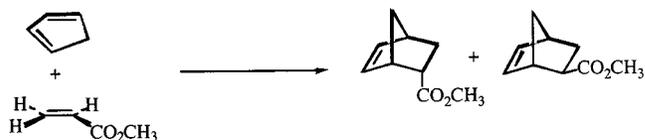


Figure 2. Diels–Alder cycloaddition of cyclopentadiene and methyl acrylate.

The same reaction has been investigated in a number of different ionic liquids ([emim][BF₄], [emim][ClO₄], [emim][CF₃SO₃], [emim][NO₃], and [emim][PF₆]), all of which showed the same general trend.²⁸ The effect was slightly weaker in these ionic liquids, and this may be due to stronger (N–H) hydrogen bonding leading to stronger solvophobic effects in [EtNH₃][NO₃].

B. Alkylation of Sodium β -Naphthoxide

The C vs O alkylation of sodium 2-naphthoxide in simple molten phosphonium and ammonium halides

(which are molten at temperatures of ca. 110 °C) has been studied to compare their properties with conventional organic solvents.²⁹ The regioselectivity of the reaction is reliant on the nature of the counterion of the 2-naphthol salt and the solvent. In dipolar aprotic solvents, O-alkylation favored. The use of *n*-Bu₄PBr, *n*-Bu₄NBr, [emim]Br, and *n*-Bu₄PCl as solvents led to the high regioselectivity of the O-alkylation product in every case (between 93% and 97%), showing the polar nature of the ionic liquids. Analysis by ¹H and ³¹P NMR showed that the ionic liquids were unaffected by the reaction and could be reused to achieve the same results.²⁹ Almost identical results were obtained for the alkylation of 2-naphthol in a [bmim][PF₆] ionic liquid, and indole showed almost exclusive N-alkylation.³⁰

VI. Transition-Metal-Mediated Catalysis

A. Hydrogenation of Homogeneous Catalysts

Transition-metal homogeneous catalysis is seen as one of the most promising routes to the improvement of the "atom economy" of a wide range of chemical processes, that is to maximize the number of atoms of all raw materials that end up in the products. The great advantage of homogeneous catalysis over heterogeneous catalysis is that all of the metal centers are available to the reagents, and so it is inherently more efficient. However, it does have the major drawback that it can be difficult to separate the catalyst from the products of the reaction. This leads to a waste of precious resources and to the danger of passing highly reactive chemicals into the environment.

Biphasic catalysis represents a method to heterogenize a catalyst and product into two separate and immiscible phases without losing the selectivity and efficiency inherent in homogeneous catalysis.³¹ The catalyst resides in solution in one of the two phases, and the substrate resides in the other phase. During reactions, the two layers are vigorously stirred, thus allowing suitable interaction of catalyst and substrate; once the reaction has reached the appropriate stage, the stirring is stopped and the mixture of phases separates into two layers, one containing the product and the other containing the catalyst. Separation is carried out by simple decantation, and in principle, the catalyst solution is available for immediate reuse.

There are three main areas of interest in biphasic catalysis. The main biphasic system used is comprised of an aqueous-organic mixture, and such processes are very effective and have been implemented in commercial processes for both oligomerization and hydroformylation reactions. While this has many advantages, it precludes the use of water-sensitive reagents or, often more importantly, catalysts. Also, trace amounts of organic materials are particularly difficult to remove from water. Another system uses fluorinated solvents to generate fluororous-organic biphasic reaction conditions.³² Here, the affinity of the fluororous phase for highly fluorinated solutes is used to isolate the catalysts in the fluororous layer. This allows the use of water-sensitive

materials but requires the use of specially prepared catalysts (that are not always available) and expensive solvents. The third system, whose use I describe below, is the ionic liquid-organic system.

B. Hydrogenation Reactions

The hydrogenation reaction of C=C bonds catalyzed by transition-metal complexes is probably one of the most widely studied reactions of homogeneous catalysis; however, the separation of products from reactants remains problematic. Initial experiments using [Rh(nbd)PPh₃][PF₆] (where nbd = norbornadiene) as the catalyst for the hydrogenation of pent-1-ene in a variety of ionic liquids showed their potential as solvents for isolating the catalyst.¹⁶ For both [SbF₆]⁻ and [PF₆]⁻, ionic liquids hydrogenation rates significantly greater than seen for the same catalyst in acetone were observed, presumably due to the stabilization of the Rh(III) intermediate. When cyclohexa-1,3-diene was used as the substrate in the [emim][SbF₆] ionic liquid, cyclohexene was generated with 98% selectivity at 96% conversion. However, the results using a [bmim][BF₄] ionic liquid were disappointing. This was attributed to the presence of dissolved chloride ions in the ionic liquid which coordinate to the metal center and deactivate the catalyst. As is common with rhodium catalysts, it was also found that isomerization of pent-1-ene to pent-2-ene occurred under the reaction conditions. Unlike traditional homogeneous systems, where it has little effect, the *cis/trans* selectivity of the isomerization was dependent upon the anion. In the ionic liquids, the cationic catalyst is in direct contact with neighboring anions, whereas in a conventional solvent they will be solvent separated. It is probably this close contact that leads to the influence of the anion on the product distribution.

RhCl(PPh₃)₃ and [Rh(cod)₂][BF₄] (where cod = cyclooctadiene) have also been used for the hydrogenation of cyclohexene in [bmim][BF₄].³³ Although RhCl(PPh₃)₃ gave higher turnover rates, the use of [Rh(cod)₂][BF₄] lead to higher overall conversion of cyclohexene to cyclohexane. It is also notable that ionic [Rh(cod)₂][BF₄] showed greater solubility in the ionic liquid than RhCl(PPh₃)₃.

RuCl₂(PPh₃)₃ is also an effective hydrogenation catalyst in the [bmim][BF₄] ionic liquid.³⁴ Hex-1-ene, cyclohexene, and 1,3-butadiene, producing a mixture of but-1-ene, but-2-enes, and *n*-butane, are all reduced. Use of [bmim]₃[Co(CN)₅] to hydrogenate 1,3-butadiene leads to 100% selectivity for but-1-ene.³⁴ The chiral catalyst [RuCl₂-(S)-BINAP]₂·NET₃ has been used to asymmetrically hydrogenate 2-phenylacrylic acid and 2-(6-methoxy-2-naphthyl)acrylic acid, Figure 3.³⁵

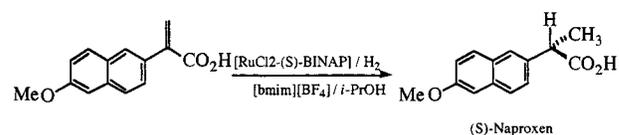


Figure 3. Formation of (s)-naproxen in a [bmim][BF₄] ionic liquid.

Palladium(II) chloride has been used in molten [bu₄N]Cl (mp = 42 °C) to hydrogenate CCl₄ to give a

mixture of C₁–C₅ paraffins and C₂–C₄ olefins and small amounts of partially hydrogenated products.³⁶ The catalyst quickly deactivates, but its life can be extended if CoCl₂ or CuCl₂ is added to the reaction mixture. Almost certainly [PdCl₄]²⁻ is formed on initial dissolution of the PdCl₂ in the [bu₄N]Cl.

The hydrogenation of carbon monoxide at 220 °C and 430 atm pressure has been investigated in a variety of quaternary group 15 halides.³⁷ The addition of either ruthenium(IV) oxide or ruthenium(III) acetylacetonate led to solutions that would catalyze the reaction to yield mixtures of ethylene glycol, its monoalkyl ethers (up to propyl), methanol, and ethanol. The best results were achieved with quaternary phosphonium salts. Evidence suggested that the active catalytic species in solution were the anionic cluster [HRu₃(CO)₁₁]⁻ and, after multicycling, [H₃Ru₄(CO)₁₂]⁻, [HRu₃(CO)₁₃]⁻, and possibly [HRu₃(CO)₁₁]⁻.

C. Hydroformylation

Rh(acac)(CO)₂ with PPh₃ in a range of ionic liquids ([PF₆]⁻, [SbF₆]⁻, [AsF₆]⁻, [BF₄]⁻) from a solution that will catalyze the hydroformylation of olefins.^{16,38} Although the solution showed high catalytic activity and could be reused, some of the catalyst was lost with each run. To avoid this, sulfonated triphenylphosphine derivatives were used as the phosphine; however, this led to reductions in reaction rates. This highlights the possibility of using these ligands, which are widely used to solubilize transition-metal complexes in water, for the same purpose in ionic liquids. This will greatly extend the range of materials that can be investigated.

Solutions of ruthenium clusters in quaternary ammonium and phosphonium salts have also been used as hydroformylation catalysts.^{39,40} Improved yields were reported when bidentate N-donor or P-donor ligands were added to the reaction mixtures and the principal catalytic species were [HRu₃(CO)₉(L–L)]⁻ (where (L–L) = bidentate ligand).

D. Dimerization of Butadiene

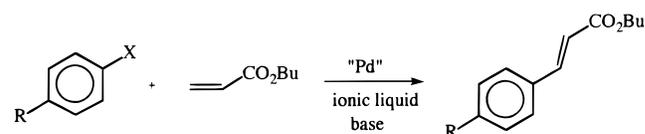
Palladium dichloride, acetate, and acetylacetonate in the [bmim][BF₄] or [bmim][PF₆] ionic liquids have been used for the hydrodimerization of butadiene to form octa-2,7-dien-1-ol as the major product and 1,3,6-octatriene as the minor product.⁴¹ The reaction mixture was homogeneous under the reaction conditions (70 °C), but the products could easily be separated by cooling the mixture to below 5 °C. Again, the recovered ionic liquid and catalyst could be reused. In this reaction system hydrodimerization was achieved in the absence of CO₂, which is necessary for reaction to occur in conventional molecular solvents, although both the degree of conversion of the 1,3-butadiene and the turnover frequencies were greatly improved by its addition. In this case, the active catalyst is the neutral *trans*-bis(methylimidazole)palladium(II) dichloride, which is formed from the ionic precursor [bmim][PdCl₄] when water is added to its solution in the ionic liquid.⁴¹

The cyclodimerization of butadiene to 4-vinylcyclohexene using Fe(NO)₂ in [bmim][AF₆] (A = P or

Sb) ionic liquids has been reported to show a remarkable solvent effect.^{4,42} Fe(NO)₂ was produced by the chemical or electrochemical reduction of Fe₂(NO)₄Cl₂ to yield the catalyst for this Diels–Alder dimerization.

E. Heck Reactions

Palladium(II) chloride and acetate have also been used as precatalysts in a number of tetraalkylammonium and phosphonium bromide salts for palladium(0)-catalyzed C–C coupling, Heck, reactions.⁴³ Since the reactions were conducted at 100 °C, it did not matter if the solvents were liquids at room temperature. In the Heck reaction, C–C coupling of aromatic and vinylic systems occurs. The palladium-catalyzed reaction of bromobenzene with *n*-butyl acrylate in phosphonium salts in the presence of triethylamine at 100 °C formed *trans*-cinamic *n*-butyl ether in good yields; 5% of the *cis*-isomer was synthesized when sodium acetate was added to the reaction mixture, Figure 4.⁴³



where R=H, OCH₃, NO₂ and X=Br, Cl

Figure 4. Heck coupling reactions in tetraalkylammonium and phosphonium bromide salts.

When the complexes dichlorobis(triphenylphosphine)palladium(II) and palladium(II) acetate were used as the catalyst precursors, stable solutions were formed which could be reused after the reaction without loss of catalytic activity for at least two further runs. The products were removed from the solution by distillation. High levels of conversion were observed in these ionic liquids (over 99% in some cases). When palladium(II) chloride was used, precipitation of a palladium cluster which was deactivated toward the catalysis, occurred after some hours.

VII. Halogeno and Alkylhalogenoaluminate(III) Ionic Liquids

Although this is changing, the halogenoaluminate(III) ionic liquids remain by far the most widely studied of all of the room-temperature ionic liquids and justify separate treatment here. The first halogenoaluminates(III) to be liquid at room temperature were mixtures of 1-alkylpyridinium bromides with aluminum(III) chloride where $X(\text{AlCl}_3) = 0.66$.^{7,44} However, in other compositions, these mixtures were solid at room temperature. By using 1-butylpyridinium chloride ([*n*-bpy]Cl), a system which was liquid over a range $X(\text{AlCl}_3) = 0.43$ – 0.66 was obtained.⁴⁵ Further improvements in liquid ranges were achieved by using a mixture of 1-ethyl-3-methylimidazolium chloride with aluminum(III) chloride ([emim]Cl–AlCl₃).^{46,47} Since the first use of imidazolium salts, they have become the ionic liquids of choice. In addition to the chloroaluminate(III) systems, [emim]-

Br–AlBr₃ ionic liquids have also been prepared.⁴⁸ Often 1-butyl-3-methylimidazolium ([bmim]⁺) salts are used.

A. Preparation

Preparation of the halogenoaluminate(III) ionic liquids is simple: an imidazolium or pyridinium halide salt is mixed directly with the appropriate aluminum(III) halide in the ratios necessary to generate the composition required. Upon mixing, an exothermic reaction occurs and the two solids melt into a liquid. If the mixture is allowed to get too hot or hot spots occur, decomposition of the organic component may occur,⁶ which will lead to degradation of the ionic liquid. Many workers prefer to add the ingredients to a small amount of the liquid from a previous preparation; this allows efficient stirring and heat dissipation.

Spectroscopically pure ionic liquids require that the aluminum(III) chloride be sublimed several times before use. However, recently commercial aluminum(III) chloride has been used to prepare a solvent that was used for synthesis with no apparent loss of function.⁴⁹ It must, however, be noted that the introduction of proton and oxide impurities can have dramatic effects on the chemistry of the ionic liquid (see below).

B. Handling

The room-temperature halogenoaluminate(III) ionic liquids are extremely sensitive to moisture and must be handled either in vacuo or under an inert atmosphere at all times. Although it is possible to use standard Schlenk techniques, most workers in this field prefer the use of high-integrity gloveboxes. The halogenoaluminate(III) ionic liquids are corrosive to many materials, and care must be taken in the selection of equipment. All-glass apparatus is used when possible, and PTFE is the preferred lubricant for ground-glass joints. The equipment must be thoroughly cleaned and dried before use. In our experience, the use of glassware washed with acetone often leads to the discoloration of the liquids, particularly in acidic compositions. It is well-known that acetone is difficult to remove from glassware, even with prolonged heating, and that residual acetone will stick to the surface of the glass. The discoloration is possibly caused by a Lewis-acid-catalyzed condensation reaction of the acetone with trace amounts of unreacted imidazole in the ionic liquid, such reactions are well-known for the related pyrroles.

Little is known of the toxic effects of halogenoaluminate(III) ionic liquids. In a study of the effects of a basic ($X(\text{AlCl}_3) = 0.40$) [emim]Cl–AlCl₃ ionic liquid on the skin of rats,⁵⁰ it was shown that the ionic liquid induced significant skin irritation, leading to ulceration in severe cases. Penetration of the top layer of the skin of toxic material, assumed to be aluminum(III) chloride, and damage to the underlying cells was observed. It was shown that washing the area of skin contact with water led to a reduction in the degree of damage incurred. This study demonstrates that these ionic liquids are potentially

hazardous; it does *not* provide safe exposure limits nor does it recommend treatment procedures.

As stated above, the halogenoaluminate(III) ionic liquids react rapidly with water generating HCl, itself a toxic and irritant gas. Therefore, care is required to minimize exposure, particularly when destroying used ionic liquid.

It must be assumed that the ionic liquids are *at least* as hazardous as their component materials and decomposition products, for which the handling procedures are well-known.

C. Chloroaluminate(III) Species

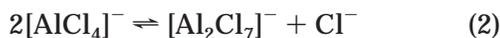
Upon fusion, aluminum(III) chloride almost doubles in volume, giving a liquid of low electrical conductivity ($<3 \times 10^{-7} \Omega \text{ cm}^{-1}$).⁵¹ X-ray analysis of the pure melt reveals a molecular liquid consisting of [Al₂Cl₆] dimers,⁵² comprising two tetrahedra sharing an edge. However, when mixed with chloride salts, the melts formed are conducting, indicating of the presence of ions.⁴⁷

Raman,⁵³ ²⁷Al NMR,⁵⁴ and mass spectra^{55,56} all indicate that when $X(\text{AlCl}_3) < 0.5$ in a pure ionic liquid, [AlCl₄][−] is the only chloroaluminate(III) species present. These observations confirm the formation of the single compound [cat][AlCl₄] (where cat = [emim]⁺ or [*n*-bpy]⁺), that is indicated by the local maxima in the phase diagrams^{7,47} of the chloroaluminate(III) systems when $X(\text{AlCl}_3) = 0.5$. Ions with the aluminum coordination number greater than four do not form, and excess Cl[−] ions remain uncoordinated.

²⁷Al NMR spectra of [*n*-bpy]Cl–AlCl₃ ionic liquids as a function of composition⁵⁷ at temperatures in the region 28–55 °C consist of a single peak, which broadens considerably as more aluminum(III) chloride is added. At temperatures of 65 and 76 °C the spectrum of a $X(\text{AlCl}_3) = 0.58$ ionic liquid resolved into two peaks, one broad and the other sharp, attributable to [Al₂Cl₇][−] and [AlCl₄][−], respectively. Similar results have been obtained for [emim]Cl–AlCl₃ ionic liquids.⁵³ Negative-ion FAB mass spectra of [emim]Cl–AlCl₃ ionic liquids have also shown peaks due to both [AlCl₄][−] and [Al₂Cl₇][−] ions.⁵⁸ X-ray diffraction studies of the [*n*-bpy]Cl–AlCl₃ ionic liquids ($X(\text{AlCl}_3) = 0.5$ and 0.67) demonstrate the presence of the tetrahedral [AlCl₄][−] ion and the [Al₂Cl₇][−] ion constructed from two corner-sharing (AlCl₄) tetrahedra.⁵⁹

Unambiguous evidence for the presence of the [Al₃Cl₁₀][−] ion in [emim]Cl–AlCl₃ ionic liquids has been provided by the negative-ion FAB mass spectrum ($X(\text{AlCl}_3) = 0.66$)⁶⁰ and by the infrared spectrum ($X(\text{AlCl}_3) = 0.75$, $T = 200$ °C).⁶¹ In addition, the infrared spectrum⁶¹ demonstrated the presence of the molecular species [Al₂Cl₆], indicating that it is unlikely that chloroaluminate(III) species heavier than [Al₃Cl₁₀][−] make any contribution to the structure of these ionic liquids at any composition.

Clearly, the chemistry of these chloroaluminate(III) ionic liquids is dependent upon the specific composition of the ionic liquid. The anionic chemistry of the addition of a chloride salt to aluminum(III) chloride can be described simply by reactions 1–3.



The equilibrium constant for eq 2 has been measured several times for both the [emim]Cl–AlCl₃ and [n-bpy]Cl–AlCl₃ systems and lies in the range from 10⁻¹⁶ to 10⁻¹⁷ at 40 °C.^{62–64} Heerman and D'Olieslager⁶⁵ measured potentiometric titration curves for [n-bpy]Cl–AlCl₃ ionic liquids containing a large excess of aluminum(III) chloride and calculated the equilibrium constant for eq 3 to be 2.09 ± 0.06 × 10⁻³ at 40 °C.

In the ionic liquid, an analogy is often made between equilibrium 2 and the autosolvolysis reaction of water. Since Cl⁻ is a Lewis base and [Al₂Cl₇]⁻ and [Al₃Cl₁₀]⁻ are both Lewis acids, the Lewis acidity/basicity of the ionic liquid may be manipulated by altering its composition. This leads to a nomenclature of the liquids in which compositions with an excess of Cl⁻ (i.e., X(AlCl₃) < 0.5) are called basic, those with an excess of [Al₂Cl₇]⁻ (i.e., X(AlCl₃) > 0.5) are called acidic, and those at the compound formation point (X(AlCl₃) = 0.5) are called neutral.

²⁷Al NMR spectra of the closely related ethylchloroaluminate(III) system [emim]Cl–EtAlCl₂ have also been measured and used to propose the presence of [EtAlCl₃]⁻ ions and molecular Et₂Al₂Cl₄ in neutral compositions of the ionic liquid with an additional small amount of [Et₂Al₂Cl₅]⁻ in acidic (X(EtAlCl₂) = 0.6) compositions.⁶⁶ However, both ¹H NMR and Raman spectroscopy of [bmim]Cl–EtAlCl₂ ionic liquids have shown that the distribution of the ethylchloroaluminate(III) species follows the same pattern as that found in chloroaluminate(III) ionic liquids.^{67,68} Hence, in basic ionic liquids Cl⁻ and [EtAlCl₃]⁻ ions are found, in moderately acidic ionic liquids [EtAlCl₃]⁻ and [Et₂Al₂Cl₅]⁻ ions are present, and in highly acidic compositions [Et₃Al₃Cl₇]⁻ and finally Et₂Al₂Cl₄ become important components. Similar results are found for [bmim]Cl–Et₂AlCl ionic liquids.⁶⁸ This simple model of the ethylchloroaluminate(III) ionic liquids does not, however, give the full picture. Closer inspection of the Raman spectra of acidic [bmim]Cl–EtAlCl₂ ionic liquids reveals that the ions [AlCl₄]⁻ and [EtAl₂Cl₆]⁻ and the molecular species Et₂AlCl and Et₃Al₂Cl₃ are present.⁶⁸ Hence, exchange of ethyl and chloride ligands must be taking place,⁶⁸ e.g.,



This behavior is well-known for the molecular species, and it is quite likely that the liquids are complex mixtures containing ions of the type [Et_xAlCl_{4-x}]⁻, [Et_xAl₂Cl_{7-x}]⁻, and [Et_xAl₃Cl_{10-x}]⁻. In two-phase systems, the molecular ethylchloroaluminate(III) species EtAlCl₂, Et₂AlCl, and Et₃Al₂Cl₃ are extracted into the organic phase, leading to a reduction in the acidity of the ionic liquid and an increased concentration of the chloroaluminate(III) species.⁶⁸

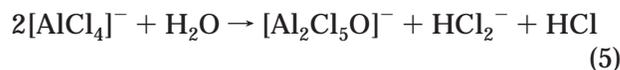
VIII. Reactions with Water

Aluminum(III) halides are extremely sensitive to even the smallest amounts of water. Hence, when water is added to a chloroaluminate(III) ionic liquid of any composition, an exothermic reaction occurs with the evolution of HCl. The reaction produces oxide- and proton-containing species, both of which can interact with other solutes.

A. Oxide-Containing Species

¹⁷O NMR spectra of the [emim]Cl–AlCl₃ ionic liquids with added ¹⁷OH₂ show a single signal in basic compositions, the chemical shift of which is dependent on the amount of ¹⁷OH₂ added and the exact composition of the ionic liquid.⁶⁹ If proton impurity is removed by the addition of ethylaluminum(III) dichloride,⁷⁰ then a single resonance appears, the chemical shift of which is both composition and concentration independent.²⁰ These data suggest that in basic ionic liquids, there is a single chlorooxoaluminate(III) species that, in the presence of proton, is in equilibrium with a chlorohydroxoaluminate(III) species with the former being dominant at lower concentrations of oxide.⁶⁹

Negative-ion FAB mass spectra of basic [emim]Cl–AlCl₃ and [n-bpy]Cl–AlCl₃ ionic liquids show the presence of [Al₂Cl₅O]⁻ ions,⁷¹ and this is clearly the chlorooxoaluminate(III) species seen in the ¹⁷O NMR spectra.¹⁹ However, no hydroxo-containing species was observed; in particular, there is no evidence for the [AlCl₃(OH)]⁻ ion. The absence of [AlCl₃(OH)]⁻ in the FAB experiments indicates that the initial reaction of the basic ionic liquid with water is that shown in eq 5. At higher concentrations of proton, a second reaction becomes important, leading to the formation of the hydroxo species, possibly [Al₂Cl₆(OH)]⁻.



In acidic ionic liquids, the ¹⁷O NMR spectra⁶⁹ clearly show three oxide-containing species whose relative concentrations are sensitive to both the precise composition of the ionic liquid and the amount of ¹⁷OH₂ added. Again, using EtAlCl₂ to remove proton, one of these can be shown to be a chlorohydroxoaluminate(III) species ([Al₂Cl₆(OH)]⁻). The other two signals were attributed to [Al₂Cl₅O]⁻ and [Al₃Cl₆O₂]⁻ ions.

Negative-ion FAB mass spectra of oxide-free [emim]Cl–AlCl₃ ionic liquids have been recorded and the hydrolysis of the liquids in the spectrometer observed.⁷² After 30 min in the spectrometer, six oxide-containing ions were visible in the spectrum. The formation of [Al₃Cl₈O]⁻ ions (the structure of which has been determined crystallographically⁷³) directly from [Al₃Cl₁₀]⁻ was clearly demonstrated, as was that of [Al₂Cl₅O]⁻ from [Al₂Cl₇]⁻. These initial reactions were shown to be followed by others, leading to [Al₂Cl₆(OH)]⁻ as the dominant chlorohydroxoaluminate(III) ion and to [Al₄Cl₉O₂]⁻, [Al₃Cl₇O(OH)]⁻, and [Al₃Cl₆O₂]⁻ ions as the amount of water is increased.

Given that the amount of water added in the NMR experiment is likely to have been much greater than the amount that the ionic liquid was exposed to inside a high-vacuum mass spectrometer and that mass spectrometry is sensitive to the smallest amounts of sample, these observations do not necessarily contradict each other.

Since the presence of water is ubiquitous, in even the most carefully controlled systems oxide impurities are universally present. However, it has been clearly demonstrated that phosgene (COCl_2) will remove all oxide contamination from both basic and acidic chloroaluminate(III) ionic liquids.⁷⁴ It has also been shown that the solid, bis(trichloromethyl) carbonate (triphosgene), will do the same, at least in basic compositions.⁷⁵

B. Proton-Containing Species

The discovery that in acidic compositions of the chloroaluminate(III) ionic liquids protons become superacidic has stimulated a considerable amount of interest in their speciation.^{76,77} The Brønsted acidity varies as both a function of proton concentration and precise composition of the ionic liquid, with Hammett acidities of up to -18 for the most acidic ionic liquids.

In basic oxide-free $[\text{emim}]\text{Cl}-\text{AlCl}_3$ ionic liquids, the formation of the $[\text{HCl}_2]^-$ ion has been clearly demonstrated over a range of compositions and concentrations.⁷⁸⁻⁸¹ When the amount of HCl added exceeds the amount of available Cl^- , species such as $[\text{H}_2\text{Cl}_3]^-$ and $[\text{H}_3\text{Cl}_4]^-$ can form.⁸⁰

Some workers have claimed that in oxide-free acidic chloroaluminate(III) ionic liquids, HCl is the only proton containing species,⁷⁹ whereas the formation of the hydrogen-bonded species $[\text{AlCl}_4-\text{HCl}]^-$ and $[\text{Al}_2\text{Cl}_7-\text{HCl}]^-$ have also been suggested.⁸⁰ It is likely, since it has been shown that $[\text{AlCl}_4]^-$ and $[\text{Al}_2\text{Cl}_7]^-$ are only poor hydrogen-bond acceptors,⁸² that the bond is relatively weak. Hence, it would probably be a mistake to think of the species as long-lived isolable ions. It is better to view the situation as highly dynamic, with the HCl being solvated by the best hydrogen-bond acceptor ions available in the ionic liquid.

In addition to these protic species, ionic liquids with oxide impurities have been shown to contain chlorohydroxoaluminate(III) ions.⁶⁹⁻⁷²

Complete removal of proton-containing impurities from the chloroaluminate(III) ionic liquids has been demonstrated using ethylaluminum(III) dichloride.⁷⁰ Care is required and the EtAlCl_2 must be titrated into the ionic liquid, because an excess of this reagent cannot be removed. Moreover, EtAlCl_2 must be handled with caution. However, it has more recently been shown that it is possible to remove all proton impurity from both basic and acidic ionic liquids by prolonged (overnight) pumping (10^{-6} – 10^{-7} Torr).⁸³ This also confirms that free HCl is present in the liquids, as it is the species that is actually removed.

Complete removal of contamination of the ionic liquids by the adventitious water present in, even the best, anhydrous systems can now be achieved by first treating with phosgene⁷⁴ or triphosgene⁷⁵ and then evacuating overnight.⁸³

IX. Transition-Metal Halide Chemistry

One of the most common uses of the halogenoaluminate(III) ionic liquids is in the investigation of the spectroscopy and electrochemistry of transition-metal halide complexes, and the area has been well reviewed.⁸⁴ Much of this work has focused on the precise measurement of redox couples or electronic absorption spectra rather than the in situ preparation of the ions used and is not of direct relevance to this review. However, these ionic liquids have been shown to stabilize a variety of species that usually demonstrate only transient existence in most molecular solvents, and a number of species have been observed in solution for the first time.

When MoCl_5 or $[\text{Et}_4\text{N}][\text{MoCl}_6]$ are dissolved in a basic chloroaluminate(III) ionic liquid, a one-electron reduction to the $[\text{MoCl}_6]^{3-}$ ion (confirmed by electronic absorption spectroscopy) is observed.⁸⁵ Clearly, the species that is found in the ionic liquid is the product of the spontaneous reduction of Mo(V) to $[\text{MoCl}_6]^{2-}$. This species cannot usually be observed in solution because either it hydrolyses in water, it yields to coordination by the solvent in polar solvents, or its salts are insoluble in nonpolar solvents. Similarly, if WCl_6 (oxidation state (VI)) or KWCl_6 (oxidation state (V)) are dissolved in a basic ($X(\text{AlCl}_3) = 0.44$) ionic liquid, identical solutions of the complex $[\text{WCl}_6]^-$ are formed which can be reduced to $[\text{WCl}_6]^{2-}$ and $[\text{WCl}_6]^{3-}$.⁸⁶ The W(III) metal-bonded cluster ion $[\text{W}_2\text{Cl}_9]^{3-}$ undergoes a one-electron oxidation to give $[\text{W}_2\text{Cl}_9]^{2-}$ but on exhaustive electrolysis yields $[\text{WCl}_6]^{2-}$. This is proposed to be the result of the disproportionation of the $[\text{W}_2\text{Cl}_9]^{2-}$ ion in the presence of excess chloride ion in the ionic liquid.⁸⁶

A wide range of chlorometalate species have been observed in the chloroaluminate(III) ionic liquids. In basic ionic liquids, well-defined anionic halogenometalate species were formed in all cases.⁸⁴ In acidic ionic liquids, it was only after extended debate that the tetrachloroaluminate(III) ion was shown to act as a ligand, Figure 5.^{87,88} With simple M(II) complexes, bidentate coordination was preferred.

Not surprisingly, several people have used the ionic liquids as solvents for the electrodeposition of metals. Aluminum has been deposited from a variety of ionic liquids,⁸⁹ as have a number of other metals.⁹⁰ The chloroaluminate(III) ionic liquids have also been used to deposit several aluminum–transition-metal alloys.⁹¹ Neat $[\text{emim}]\text{Cl}$ at 120°C has even been used to deposit a Bi–Sr–Ca–Cu superconductor.⁹² When

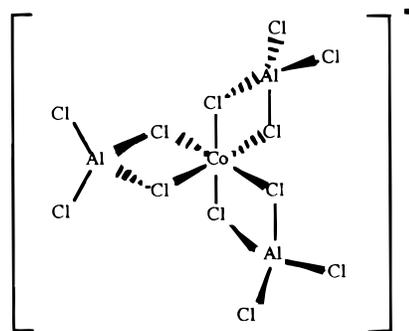
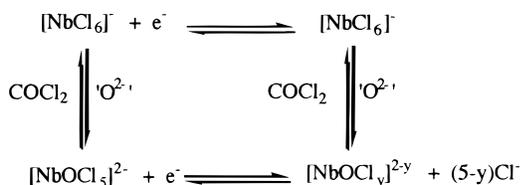


Figure 5. Tris(tetrachloroaluminate)cobalt(II) ion.

Scheme 1. Oxoexchange Chemistry of Niobium Halides in a Basic [emim]Cl–AlCl₃ Ionic Liquid



aluminum(III) chloride containing ionic liquids were used, aluminum co-deposited with the alloy.

Despite the widespread interest in the ionic liquids as solvents for halogenometalate species, very few chemical transformations of these complexes have been studied in the ionic liquids. The only real exception to this has been the investigation of the oxo-exchange chemistry.^{75,93,99} The use of phosgene as a deoxygenation agent combined with electrochemistry has been used to generate both Nb(IV) and Nb(V) complexes, Scheme 1.⁹²

More recently triphosgene, which is a solid and much easier to handle, has been used to deoxygenate both $[\text{VOCl}_4]^{2-}$ and $[\text{VO}_2\text{Cl}_2]^-$.⁷⁵ In this study the deoxygenation was accompanied by spontaneous reduction of the products to $[\text{VCl}_6]^{3-}$ and $[\text{VOCl}_4]^{2-}$, respectively. It was also found that mild oxidants could be used to generate $[\text{VOCl}_4]^{2-}$ from $[\text{VCl}_6]^{3-}$, but the stronger oxidizing agent iodobenzene was required to produce $[\text{VO}_2\text{Cl}_2]^-$.

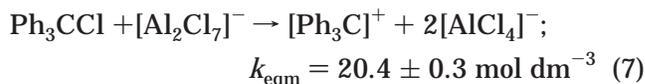


X. Organic Reactions in Chloroaluminate(III) Ionic Liquids

A. Electrophilic Substitutions

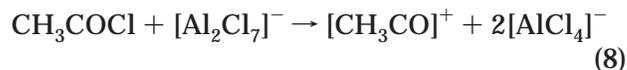
It is unsurprising that electrophilic aromatic substitutions were the first organic reactions to be investigated in the room-temperature chloroaluminate(III) ionic liquids.⁹⁵ The high concentration of chloroaluminate(III) species coupled with the good solubility of simple arenes in the acidic ionic liquids makes them ideal solvents for these reactions, and it is possible to combine their function as a solvent and a catalyst. Of the arenes tested by reaction with 1-chloropropane, only nitrobenzene failed to react. As with conventional systems, polyalkylation was common, e.g., reaction between an excess of chloroethane and benzene led to the formation of a mixture of mono (12%), di (11%), tri (33%), tetra (24%), penta (17%), and hexa (2%) substituted products. Polyalkylation can be minimized by use of a large excess of the arene but not totally eliminated. Basic ionic liquids do not provide adequate catalytic activity for alkylation and acylation reactions to occur.

In order for the Friedel–Crafts reactions to occur, it is necessary to be able to form an electrophile in the ionic liquid. Luer and Bartak⁹⁶ demonstrated that even in a moderately acidic ($X(\text{AlCl}_3) = 0.52$) ionic liquid, dissolution of chlorotriphenylmethane leads to the formation of the triphenylmethyl carbonium ion.



Reactions with 1-chloropropane and 1-chlorobutane lead to the formation of products resulting from secondary carbonium ions, which implies that alkylation occurs via the dissociated carbonium ions.⁹⁵ Mixing benzene and hexamethylbenzene in an acidic ionic liquid did not lead to the formation of toluene, xylenes, mesitylenes, etc., showing that there is no dissociation of the methyl substituents when the ionic liquid does not contain protic impurities.

Friedel–Crafts acylation reactions of aromatic compounds have also been carried out in the [emim]Cl–AlCl₃ ionic liquids.⁹⁵ For the reaction of acetyl chloride with benzene, it was determined that the rate at which acetophenone was produced was dependent on the Lewis acidity of the ionic liquid, which is in turn dependent on the ionic liquid composition. The reaction between acetyl chloride and the acidic ionic liquid was followed by ¹H NMR. The results suggested a stoichiometric reaction between CH₃COCl and $[\text{Al}_2\text{Cl}_7]^-$.⁹⁵



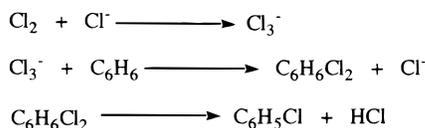
Indeed, it is possible to isolate solid $[\text{CH}_3\text{CO}][\text{AlCl}_4]$ from the ionic liquids.

The alkylation of coal has been investigated in a pyridinium chloride based ionic liquid ($X(\text{AlCl}_3) = 0.65$).⁹⁷ The coal chosen for study was a high-sulfur, high-volatile C bituminous coal, and the alkylating agent employed was 2-propanol. Autoalkylation of 2-propanol yielded a series of high molecular weight polymers, most of which were nonvolatile. No alkylated pyridines, from reaction with the ionic liquid itself, were formed. Reaction between the demineralized coal and 2-propanol was attempted, and the Friedel–Crafts alkylation was accompanied by depolymerization of the coal.

Isobutane alkylation has also been investigated in ionic liquids. Again, it was the adjustable nature of the Lewis acidity of the systems that made them attractive.⁹⁸ The process involved a reaction mixture consisting of isobutane, butane, and but-2-ene (mixture of cis and trans) in a [bmim]Cl–AlCl₃ ionic liquid. The products of the reaction included 2,2,4-trimethylpentane, 2,5-dimethylhexane, light ends (C₅–C₇ isoparaffins), and heavy ends (C₉+ isoparaffins). The rate and selectivity of the alkylation reaction was found to be dependent on the precise composition of the ionic liquid, reaction temperature, feed rate into the reactor, and residence time of the mixture in the ionic liquid.

In an investigation of the electrochemical oxidation of hexamethylbenzene in mixtures of an acidic ($X(\text{AlCl}_3) = 0.67$) ethylpyridinium bromide–aluminum(III) chloride ionic liquid with benzene,⁹⁹ it was found that a product mixture containing penta-, tetra-, and trimethylbenzene and diphenylmethane was formed. The authors postulated that the mixture was formed by a series of Friedel–Crafts reactions initiated by a two-electron oxidation of hexamethylbenzene.

Scheme 2. Proposed Mechanism for Chlorination of Benzene in a Basic [emim]Cl–AlCl₃ Ionic Liquid



Carbocations are not the only electrophile that can be generated in the chloroaluminate(III) ionic liquids, and both chlorination and nitration reactions have been observed in [emim]Cl–AlCl₃ ionic liquids.¹⁰⁰ Chlorination occurs in both acidic and basic ionic liquids but not in pure molten [emim]Cl, which indicates that chloroaluminate(III) ions are required for reactions to occur. However, almost certainly reactions proceed via different mechanisms in acidic and basic ionic liquids. In both reactions, the primary product was chlorobenzene. In acidic compositions, large amounts of at least two dichlorobenzene isomers were synthesized, as well as some trichlorobenzene products. In basic compositions, there was no formation of polychlorobenzenes but significant amounts of tetrachlorocyclohexene isomers and hexachlorocyclohexane isomers were observed.

In acidic compositions, it is obvious that a very reactive electrophile is observed, suggested by the substantial polychlorination and the authors propose the formation of Cl⁺.¹⁰⁰



Simple electrophilic chlorination via Cl⁺ is less likely in basic ionic liquids, since reaction with Cl[–] would almost definitely destroy the electrophile. Hence, Cl₃[–], formed by the reaction of Cl₂ with Cl[–], was proposed as the chlorination agent, Scheme 2.

Nitration of aromatic compounds in [emim]Cl–AlCl₃ ionic liquids used KNO₃ as the source of NO₂⁺, which acts as the electrophile and resulted in a 55% yield of nitrobenzene.¹⁰⁰ NH₄NO₃ and NO₂BF₄ were also tried as nitrating agents but gave much lower yields.



B. Reactions with Protons in Acidic Chloroaluminate(III) Ionic Liquids

It has been demonstrated that protons present in [emim]Cl–AlCl₃ ionic liquids are superacidic, with Hammett acidities up to –18.⁷⁶ Hence, they are expected to be highly reactive.

Initial investigations⁷⁶ showed the ability of [emim]Cl–AlCl₃–HCl systems to protonate aromatic substrates and generate cationic species. Anthracene has been shown to exchange deuterium with DCl in acidic [emim]Cl–AlCl₃ ionic liquids.¹⁰¹ It is, therefore, unsurprising that it has been shown that the [emim]⁺ cations undergo H–D exchange in acidic [emim]Cl–AlCl₃ solutions of DCl.¹⁰² Since the exchange occurs

by an electrophilic substitution mechanism, the exchange occurs at the 4 and 5 positions of the imidazolium ring rather than the 2 position, which has a greater positive charge.

Carbocation formation by protonation of arenes has been observed, using both electronic absorption and ¹H NMR spectroscopies, for a number of substrates in trimethylsulfonium bromide–aluminum(III) chloride and trimethylsulfonium bromide–aluminum(III) bromide (*X*(AlCl₃) = 0.67) ionic liquids with added HBr.¹⁰³ As one would expect, the all-bromide system proved to be the more acidic solvent. Also observed were the formation of the 1,1-diphenylethyl cation by protonation of 1,1-diphenylethene and the diphenylmethyl cation from chlorodiphenylmethane in the all-bromide ionic liquid. All of the solutions of carbocations were shown to be stable in the absence of moisture for at least several days.

Protonation of benzene is also probably the first step in the chemical synthesis of polyphenylene.¹⁰⁴ The reaction requires the addition of CuCl₂ which acts as the oxidizing agent in this dehydropolycondensation of benzene. Alternatively, polyphenylene can be prepared by the electropolymerization of benzene in neutral and acidic ionic liquids.^{105–107} Varying the precise composition of the ionic liquid had a minimal effect on the polymerization potential, suggesting that there is little interaction between benzene and chloroaluminate(III) species in the ionic liquid. This reaction has also been carried out in a novel [*n*-bpy]Cl–AlCl₂(OC₂H₃) ionic liquid.¹⁰⁸

Protons in acidic chloroaluminate(III) ionic liquids have been known to catalyze the formation of oligomers, with molecular weights characteristic of a cationic reaction, from olefins. Indeed, attempts to avoid this reaction lead to the first preparation of alkylchloroaluminate(III) ionic liquids.¹⁰⁹ The electrochemical oligomerization of ethene and propene in the three room-temperature ionic liquids [*n*-bpy]Cl–AlCl₃, [pyH]Cl–AlCl₃, and [emim]Cl–AlCl₃ have also been investigated.¹¹⁰ The main products of oligomerization were C₃–C₆ hydrocarbons. The results indicated that the [emim]Cl–AlCl₃ ionic liquid leads to much greater selectivity of unsaturated C–C hydrocarbons than the more acidic [*n*-bpy]Cl–AlCl₃ ionic liquids, in the case of both ethene and propene conversion. The [emim]Cl–AlCl₃ and [pyH]Cl–AlCl₃ ionic liquids gave similar selectivities during propene oligomerization. However, the [pyH]Cl–AlCl₃ ionic liquid shows by far the best catalytic stability and is therefore the best system for these conversions.¹¹⁰ The average conversion of propene is greater than that of ethene in this ionic liquid, but this is expected as propene is generally more reactive than ethene. Similar electrochemical polymerization has been utilized to synthesize polyaniline using [emim]Cl–AlCl₃ ionic liquids.¹¹¹

This chemistry has led to a number of patent applications for the polymerization of raffinate gas (mixtures of butenes)^{112–114} and the preparation of branched oligomeric fatty acids from linear fatty acids.¹¹⁵

XI. Organometallic Reactions in Chloroaluminate(III) Ionic Liquids

Another interesting Friedel–Crafts reaction performed in room-temperature ionic liquids is the acylation of ferrocene.⁴⁹ The acylation of ferrocene with acetic anhydride in a [emim]I–AlCl₃ ionic liquid and in the liquid clathrate, prepared from the addition of toluene to the ionic liquid, was investigated. Interestingly, the authors used commercial aluminum(III) chloride, without further purification, to prepare their ionic liquids. It was claimed that monoacetylferrocene was the only product of the acylation reaction using both reaction media, with the highest yields being acquired using the liquid clathrate.

Arene exchange reactions of ferrocene are well-known to be catalyzed by aluminum(III) chloride. Hence, the acidic ($X(\text{AlCl}_3) = 0.65$) [bmim]Cl–AlCl₃ ionic liquid has been used to prepare a number of arene(cyclopentadienyl)iron(II) complexes, [Fe(C₅H₅)(arene)]⁺, from ferrocene.¹¹⁶ The ionic liquid acts as both a solvent and Lewis acid source. However, since the ionic liquids used were completely aprotic, the products were only formed on addition of a proton source, [bmim][HCl₂]. This would probably have been unnecessary if commercial aluminum(III) chloride had been used without sublimation, Figure 6.

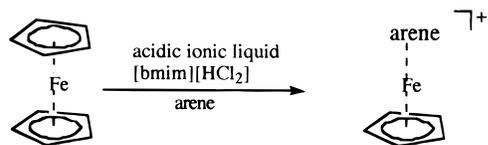
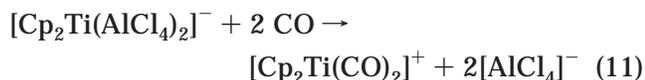


Figure 6. Arene exchange reactions of ferrocene.

The reductive carbonylation of titanocene dichloride (Cp₂TiCl₂) in an acidic ($X(\text{AlCl}_3) = 0.60$) [emim]Cl–AlCl₃ ionic liquid has also led to the formation of a metal–carbon bond.⁴⁹ A reducing mixture was prepared by adding sodium metal to the ionic liquid. This led to the precipitation of aluminum from the ionic liquid in a form that was more reactive than commercial granular aluminum. Initial dissolution of titanocene dichloride in the [emim]Cl–AlCl₃ ionic liquid has been shown¹¹⁷ to lead to the formation of Cp₂Ti(AlCl₄)Cl. In the reducing mixture used in this process, this rapidly reduces to the Ti(III) species ([Cp₂Ti(AlCl₄)₂][−]). [AlCl₄][−] is a labile ligand and is easily substituted by CO by passage of CO gas through the solution formed.



Further reduction of this complex led to the formation of Cp₂Ti(CO)₂, which precipitated from solution.

XII. Transition-Metal-Mediated Catalysis in Chloroaluminate(III) Ionic Liquids

In homogeneous catalysis, the solvent can often control the course of a reaction by affecting reaction rates and improving chemo-, regio-, stereo-, and

enantioselectivities of reaction products. In transition-metal-based catalysis, it is important for the solvent to solubilize and stabilize the active catalytic species but remain unreactive toward the active catalytic site, i.e., to behave as a noncoordinating solvent. Hence, acidic compositions of the chloroaluminate(III) ionic liquids, with their poorly coordinating anions, offer a potentially exciting novel medium for catalysis.

A. Olefin Dimerization

The chloroaluminate(III) ionic liquids were first used as solvents for the dimerization of propene to hexenes using nickel(II) complexes as the catalysts.¹⁰⁹ In these reactions, the product hexenes separated from the ionic liquid phase and could easily be removed by decantation. It was found that only catalysts with a nickel–carbon bond were active and that the products were contaminated with the products of a cationic side reaction. By using ethylaluminum(III) dichloride-based ionic liquids, both of these problems were avoided. This allowed a greater number of potential catalysts to be employed for the reaction, particularly nickel phosphine dihalides.

Cationic π -nickel(II) complexes containing phosphine ligands are useful catalysts for the dimerization of propene in solution in chlorinated or aromatic hydrocarbons.¹¹⁸ The nature of the phosphine ligand determines the regioselectivity of the dimerization reaction, sterically demanding ligands lead to the formation of 2,3-dimethylbutenes (tail-to-tail dimers), which can be utilized as starting alkenes for the production of fine chemicals, whereas catalysts with undemanding ligands yield oligomers with uncontrolled regioselectivity.

A number of air-stable NiCl₂·2L complexes (L = P(Bu)₃, P(i-Pr)₃, P(cyclohexyl)₃, and pyridine) have been successfully used as catalysts for the regioselective dimerization of propene in chloroaluminate(III) and ethylchloroaluminate(III) ionic liquids.¹¹⁹ A cosolvent of heptane is used to improve product separation. The upper layer containing the products can be removed easily, and the catalyst remains in the ionic phase and can be reused. However, deactivation of the system is observed if pure ethylchloroaluminate(III) ionic liquids are used as the solvent due to the extraction of the dimeric [Et₄Al₂Cl₂] into the organic layer. This is avoided by the use of the [bmim]Cl–AlCl₃ ionic liquid with a small amount of dichloroethylaluminum(III) added.

This work has been extended to the oligomerization of butenes¹²⁰ and to the selective dimerization of ethene.¹²¹ In this latter example, quantitative analysis of the nickel content of the two phases indicated that over 98% of Ni remained in the ionic layer.

Optimum dimerization activity and selectivity is achieved when toluene is used as the cosolvent for the reactions.^{119,121} When other organic solvents such as heptane are used or a cosolvent was omitted, a mixture of high molecular weight ethene oligomers was synthesized. It is feasible that this occurs as a result of coordination of AlCl₃ to the aromatic ring.¹²² This would reduce the acidity of the ionic liquid, so attenuating the activity of the catalyst.

B. Olefin Polymerization

In two studies of titanium chemistry in chloroaluminate(III) ionic liquids to which alkylchloroaluminate(III) drying agents had been added, ethene polymerization has been observed. When AlEtCl_2 and TiCl_4 are added to an acidic ($X(\text{AlCl}_3) = 0.52$) ionic liquid, a deep red solution is formed which will polymerize ethene to give poly(ethene) with a melting point in the region 120–130 °C.¹²³ Better yields were obtained with solutions of Cp_2TiCl_2 in the same composition ionic liquid with $\text{Al}_2\text{Me}_3\text{Cl}_3$ acting as the alkylating agent.¹²⁴ Interestingly, neither Cp_2ZrCl_2 or Cp_2HfCl_2 were catalytically active in the ionic liquids. Unfortunately, this work does not seem to have been followed up.

C. Olefin Hydrogenation

Another example of the use of this system is the catalytic hydrogenation of cyclohexene by rhodium complexes.³³ The use of an acidic chloroaluminate(III) ionic liquid ($X(\text{AlCl}_3) = 0.54$) leads to the polymerization of cyclohexene (see above). However, upon dissolving Wilkinson's catalyst ($\text{RhCl}(\text{PPh}_3)_3$) in a basic ($X(\text{AlCl}_3) = 0.45$) ionic liquid, the cyclohexene undergoes hydrogenation,³³ and the product collects in a separate phase, which can easily be decanted. Wilkinson's catalyst forms a stable solution, and the active species (more than 98%) is retained in the ionic phase.

XIII. Conclusions

The chemistry of room-temperature ionic liquids is at an incredibly exciting stage in its development. No longer mere curiosities, ionic liquids are beginning to be used as solvents for a wide range of synthetic procedures. The advent of systems that are easy to handle will allow those without specialist knowledge of the field to use them for the first time. The small number of reactions that have been investigated so far show the potential of the ionic liquids but are just a beginning. The solvent environment that is provided by the ionic liquids is quite unlike any other available at or close to room temperature. Already, startling differences have been seen between reactions in ionic liquids and molecular solvents. As the number of investigations increases, we will be able to tell if there is any general "ionic liquid effect". Potentially any reaction may produce interesting results in ionic liquids, and the discovery of the new chemistry waiting to be found will be a mammoth task. It has been 15 years since Chuck Hussey wrote the first major review of room-temperature ionic liquids,² I hope that this review has in some way updated that work and look forward with excitement to the next.

XIV. References

- (1) Note on nomenclature: room-temperature ionic liquid, nonaqueous ionic liquid, molten salt, liquid organic salt, and fused salt have all been used to describe salts in the liquid phase. With the increase in electronic databases, the use of keywords as search tools is becoming ever more important. While authors are free to choose any name that they wish for their systems, I would suggest that they at least include the term ionic liquid in

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