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Invited Review

Brønsted Acids in Ionic Liquids: Fundamentals, Organic Reactions, and Comparisons

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Summary. A background for studying acids in various solvents is developed, emphasizing the importance of knowing to what extent a solvent conducts electricity and is therefore ionized, the dissociation equilibria of common molecular solvents and the acidic and basic species generated by solvent leveling. Acidity measurements in the atypical solvent water are discussed and the common method of expressing acidity in other systems – by *Hammett* values – is introduced. Representative examples of reactions involving *Brønsted* acids in ionic liquids are presented and attention paid to the questions of speciation and acidity values. It is found that the gas phase proton affinity of a base is often a better guide to the acidity of its conjugate acid in an ionic liquid than is the dissociation constant of the said acid in water.

Keywords. Ionic liquids; *Brønsted* acids.

> *I keep six honest serving men*
> *(They taught me all I knew);*
> *Their names are What and Why and When*
> *And How and Where and Who.*
>
> *– The Elephant's Child*
> *– Rudyard Kipling*

Introduction and Purpose

In this article we have adopted a broad definition of ionic liquids, namely liquids consisting of ions and ion pairs [1]. The proportion of ion pairs is considered to be small enough that the primary interactions are ion–ion forces. This definition thus embraces salts such as KCl at 800°C as well as $NaNO_3$–KNO_3 at 250°C, [*py*H][Cl] or [*py*H][picrate] at 160°C (pyridinium = *py*H), or [*bmim*][$(CF_3SO_2)_2N$] at 25°C (1-butyl-3-methyl-1*H*-imidazolium = *bmim*). Acid-base chemistry is feasible at any temperature, although *Brønsted* acids have a limited life in most liquids above ~300°C, just as organic chemistry is concentrated below 300°C.

Both inorganic and organic chemistry texts devote chapters to acid–base behavior, with the emphasis naturally on aqueous systems. It is tempting to approach *Brønsted* acid–base situations in non-aqueous systems of various ionicities with terms such as *pH* and pK_a and their aqueous system values at least in the back of one's mind. We shall consider the hydrated proton as just one cationic acidic species, whereas other cationic and various anionic acidic species are the principal reactants in systems such as pure liquid H_2SO_4, CH_3COOH, HF, or [*emim*][HCl_2] (1-ethyl-3-methyl-1*H*-imidazolium = *emim*). We will discuss attempts to compare acidities between systems and then proceed to examine a wide variety of organic reactions involving *Brønsted* acids alone, or in conjunction with *Lewis* acids, in ionic liquids, necessarily at <300°C. In conclusion we will pose

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some questions regarding reactions occurring in highly ionic *vs.* more conventional solvents.

Ions in Liquids

Self-dissociation

Simple salts such as the alkali halides are fully dissociated into ions in the liquid state as evidenced by their conductivities (Table 1); inorganic salts of larger monomeric anions are lower melting with lower conductivities but still apparently are dissociated completely [1]. However, salts of less electropositive metals and organic and semi-organic salts appear [8], from conductivities, including their temperature dependence [9] viscosities and NMR measurements, to be incompletely ionized in the liquid.

Many liquids may be described as primarily molecular but with some degree of ionicity (Table 2). Of particular interest here are the protic liquids water, the anhydrous hydrogen halides, the oxyanion acids, and the carboxylic acids.

Promoted Formation

How can we increase the ionization or ion content of a liquid? The physical approach is to increase the temperature [3, 7] and/or the pressure [2] and this has been shown to be effective. The chemical approach is to add select compounds to the system but, of course, thereby change its overall composition.

The ready solution of solid ionic NaCl or gaseous molecular HCl in water is viewed as the reaction of the base H_2O with the *Lewis* acid Na^+ to form $Na(H_2O)_n^+$ and the molecular acid HCl to form

Table 1. A selection of electrical conductivities of liquids

System	T/K	σ/Scm^{-1}	Λ/Scm^2 mol^{-1}	M/Mol dm^{-3}	Ref.
$HgCl_2$	560	8×10^{-5}			[2]
[*bpy*][BF_4]	298	2×10^{-3}	0.3	5.5	[3]
[*bmim*][CF_3CO_2]	298	3×10^{-3}	0.6	5.1	[3]
2:1 *Ac*OH/py	298	9×10^{-3}	1.6	5.5	[4]
[*emim*][Al_2Cl_7]	298	1.5×10^{-2}	4.4	3.4	[3]
[$(CH_3)_3S$][HBr_2]	298	3.4×10^{-2}	4.7	7.3	[3]
2% aq. HCl	298	0.18	325	(0.553)	[5]
20% aq. NaCl	298	0.204	52	(3.928)	[5]
$BiCl_3$	520	0.44	37	11.89	[2]
LiCl-KCl (059:0.41)	723	1.57	53	29.7	[6]
NaCl	1173	3.88	154	25.3	[7]
Na	373	1.04×10^{5}			[7]

Molarities in parentheses refer to ionic solutions. σ is the specific and Λ the molar conductivity

Table 2. Molecular liquids of limited ionic dissociation

Liquid	Equilibria	T/K	σ/Scm^{-1} [10, 11]
NH_3	$2NH_3 \rightleftarrows NH_4{}^+ + NH_2{}^-$	234	2×10^{-7}
H_3PO_4	$3H_3PO_4 \rightleftarrows H_3O^+ + H_4PO_4{}^+ + H_2P_2O_7{}^{2-}$	298	4.7×10^{-2}
$AsCl_3$	$2AsCl_3 \rightleftarrows AsCl_2{}^+ + AsCl_4{}^-$	293	1.4×10^{-7}
H_2O	$2H_2O \rightleftarrows H_3O^+ + OH^-$	298	5.7×10^{-8}
H_2SO_4	$2H_2SO_4 \rightleftarrows H_3SO_4{}^+ + HSO_4{}^-$	298	1.0×10^{-2}
HF	$2HF \rightleftarrows H_2F^+ + F^-$		
	$HF + F^- \rightleftarrows HF_2{}^-$	273	1×10^{-6}
HCl	$2HCl \rightleftarrows H_2Cl^+ + Cl^-$		
	$HCl + Cl^- \rightleftarrows HCl_2{}^-$	188	1×10^{-9}
ICl	$3ICl \rightleftarrows I_2Cl^+ + ICl_2{}^-$	>300	5.5×10^{-3}
CH_3COOH	$2CH_3COOH \rightleftarrows CH_3C(OH)_2{}^+ + H_3COO^-$	298	8×10^{-9}

$H(H_2O)_m{}^+$ ($m = 1$ through 4). Similarly, $HClO_4$ gives rise to $CH_3C(OH)_2{}^+$ in glacial acetic acid [11]. The addition of the *Lewis* acid SbF_5 to the already partially ionized HF takes a corresponding course with the ionic system $[H_2F][SbF_6]$ forming [12]. When we add a strong base to the weak electrolyte HCl (at −84°C, however) or better, HCl to the unionized liquid bases pyridine or 1-methylimidazole at 25°C, the H_2Cl^+ cation is consumed in making *py*H^+ or H*mim*$^+$ ions, respectively (3-methylimidazolium = H*mim*), leaving the $HCl_2{}^-$ as counter-ion [13].

Anhydrous carboxylic acids are also converted into conducting liquids by the addition of strong bases, with the maximum conducting liquids and the maximum azeotropic composition rich in carboxylic acid though not necessarily identical [4, 14].

Acids and Bases Defined

Definitions

The *Lewis* (or *Franklin*) definition of an acid as an electron pair acceptor and a base as an electron pair donor includes the *Brønsted* definition regarding the proton. The gas phase acidity of a protic molecule is more commonly expressed as the proton affinity (P.A.) of the conjugate base, which is equivalent to the enthalpy of dissociation of the acid [15]. This represents the intrinsic reactivity of the acid or base, which will be altered by the solvent medium it is in. Because how ionic liquids affect acid/base character is not well established, and is one of the points of this article, the intrinsic reactivity is used here as a starting point in such discussions.

$$HX\ (g) \rightarrow H^+\ (g) + X^-\ (g), \qquad \Delta H = \text{P.A. of } X^-$$

Table 4 lists the gas phase proton affinities of many of the species discussed in this article, as well as the aqueous pK_as when available. Specific gas phase examples are (in $kJ\,mol^{-1}$): 1459 for acetate, 1395 for chloride, 930 for pyridine, and 691 for water [16, 17]. Such gas phase proton affinities are far more endothermic than in aqueous solution (0 to 14 *pK* units, or 0 to 90 kJ/mol), because the solvation energetics of ions are so much stronger than for neutral species.

If acids or bases are transferred into a solvent, there are limitations on what ionized species can exist there. Any base stronger than the conjugate base of the solvent will deprotonate the solvent to create that conjugate base, known as the "lyate ion" in complex mixtures [18]. Likewise, a *Brønsted* acid stronger than the protonated solvent (its "lyonium" ion) becomes that ion. This leveling effect limits the range of acid–base reactivity in any solvent. One must examine each ionic liquid to determine what the conjugate acid and base are, and thus the range of acidities accessible.

Beyond the inherent acid/base character of a solvent, when a protic molecule is dissolved in that solvent, the question arises as to whether it will act as an acid or a base, *e.g.* acetic acid or, more appropriately, hydrogen acetate, is a weak acid in water, a strong acid in ammonia but a strong base in hydrogen fluoride.

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

$$CH_3COOH + NH_3 \rightarrow CH_3COO^- + NH_4{}^+$$

$$CH_3COOH + 2HF \rightarrow CH_3C(OH)_2{}^+ + HF_2{}^-$$

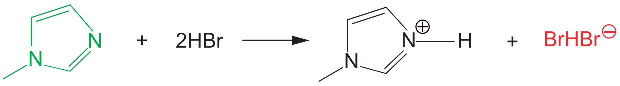
The energetics of forming a solution will include the solvation of the starting molecule and of the ions produced, *i.e.* entropies as well as enthalpies are significant. If dissociation of the solute is incomplete, as with aqueous acetic acid, then we have a concentration-dependent term. We may also find that the nature of the solvation, such as the proton coordination, is concentration dependent and this indeed becomes extreme when we deal with a mixture such as 20 mol% HCl in water *vs.* 50 mol% HCl in water [16].

Will the behavior of several conjugate acid/base pairs in one solvent necessarily follow that in another or in the reference phase, the gas? The answer is clearly NO! Thus, while we have the extensively developed chemistry of *pH* and acid and base dissociation constants (pK_as and pK_bs) for aqueous solutions, these values and their sequences are not necessarily applicable to other solvent systems. When dealing with the enormous number of modern ionic liquids, it may be propitious to start at proton affinities.

Speciation

When we write the equilibria for a polybasic acid H_nX in water, we include the several protic anions which act as base then acid as the proton activity drops; they, like the proton and H_nX, may be hydrat-

Table 3. Solvent leveling

System	Reaction
H_2O	$HCl + H_2O \rightarrow H_3O^+ + Cl^-$ $NH_3 + H_2O \rightarrow OH^- + NH_4^+$
NH_3	$CH_3COOH + NH_3 \rightarrow NH_4^+ + CH_3COO^-$
H_2SO_4	$H_2O + H_2SO_4 \rightarrow HSO_4^- + H_3O^+$ $CH_3COOH + H_2SO_4 \rightarrow HSO_4^- + CH_3C(OH)_2^+$ $HClO_4 + H_2SO_4 \rightleftarrows H_3SO_4^+ + ClO_4^-$
CH_3COOH	$HClO_4 + CH_3COOH \rightarrow CH_3C(OH)_2^+ + ClO_4^-$ $C_5H_5N + 2CH_3COOH \rightarrow C_5H_5NH^+ + (CH_3COO)_2H^-$
HBr	
ICl	$C_5H_5N + 2ICl \rightarrow C_5H_5NI^+ + ICl_2^-$ $AlCl_3 + 2ICl \rightarrow I_2Cl^+ + AlCl_4^-$
$POCl_3$	$KCl + POCl_3 \rightarrow Cl^- + K^+ + POCl_3$ $FeCl_3 + POCl_3 \rightarrow POCl_2^+ + FeCl_4^-$
HF	$SbF_5 + 2HF \rightarrow H_2F^+ + SbF_6^-$ $CH_3COOH + 2HF \rightarrow CH_3C(OH_2)_2^+ + HF_2^-$

—— Latent acid; —— acid species; —— latent base; —— basic species

ed. Likewise, nitrogen bases and their conjugate cations and hydroxide ions, will be appropriately hydrated. This leveling process means that H_3O^+ and OH^-, or their hydrates, are the operative acidic and basic species in water. Similar situations arise for other protic liquids as shown in Table 3 [15, 16]. In particular, the neutral molecule will accept or donate a proton according to the acidity of the solute in that solvent. We observe pairs of ions such as $CH_3C(OH)_2^+$ with $H(CH_3COO)_2^-$ [4], HCl_2^+ with HCl_2^- [19], $H_3SO_4^+$ with HSO_4^- and NH_4^+ with NH_2^-.

There is good evidence that ions such as HCl_2^- have integrity – they are not just solvated anions [19]. If a strong base B reacts with HCl, the liquid salt BH^+Cl^- is first formed but with more HCl, the liquids BH^+ HCl_2^- and eventually BH^+ $H_2Cl_3^-$ are obtained [20] and the $H_nCl_{n+1}^-$ ions, not the BH^+ ions, are the acidic species [13]. Similarly, the appropriate choice of added base can increase the acidity of acetic acid [4]. Reference to the proton affinities in Table 4 indicates that the salts BH^+X should revert to $B + HX$ in the vapor.

Table 4. Proton affinities and aqueous acidities

Base	Proton affinity[a]	$pK_a(H_2O)$[b]
HO^-	1633 ± 1	15.74
Imidazolide$^-$	1465 ± 8	14.4
$\mathit{Me}CO_2^-$	1459 ± 8	4.75
$\mathit{Ph}CO_2^-$	1423 ± 9	4.20
$ClCH_2CO_2^-$	1408 ± 8	2.10
Cl^-	1395 ± 0	−8 [27]
$H_2PO_4^-$	1383 ± 21	2.12
NO_3^-	1358 ± 1	−1.4 [185]
$CF_3CO_2^-$	1355 ± 12	0.68
Br^-	1354 ± 1	−9 [185]
$\mathit{Me}SO_3^-$	1343 ± 9	−0.6 [27]
$\mathit{Ph}SO_3^-$	1322[d]	−1.6 [185]
I^-	1315 ± 1	−9 [185]
HSO_4^-	1307 ± 21	−9 [185]
$CF_3SO_3^-$	1278 ± 9	−14 [27]
ClO_4^-	1259 ± 21	−10 [27]
$(CF_3SO_2)_2N^-$	1247 ± 9	<0
BF_4^- (dissoc)[c]	1222 ± 12	
1,3-di*Me*-imidazole ylide	1075[d]	
$AlCl_4^-$ (dissoc)[c]	1074 ± 12	
Methylguanidine	1022[d]	13.4 [184]
$\mathit{Me}_3N(^+)CH_2CO_2^-$	1004 ± 9	1.83
1-*Me*-imidazole	959 ± 9	7.05 [184]
2-*Me*-pyridine	948 ± 9	5.96 [184]
Pyridine	930 ± 9	5.21 [184]
*Me*CONH*Me*	889 ± 9	−0.6 [184]
NH_3	854 ± 9	9.24 [184]
H_2O	691 ± 2	−1.74

[a] ΔH^{298} for $AH \rightarrow A^- + H^+$ or $BH^+ \rightarrow B + H^+$, in kJ/mol, from the NIST Webbook (webbook.nist.gov/chemistry)

[b] pK_a of conjugate acid. Unless otherwise stated taken from Ref. [183]

[c] Dissociative proton transfer: $MX_n + H^+ \rightarrow MX_{n-1} + HX$. The MX_nH species is not stable in the gas phase

[d] No reliable experimental value exists. Computational value, using Gaussian 98 [24] at the *B3LYP*/6–311 + G(3df,3pd)//*B3LYP*/6–31 + G* level, corrected to 298 K with vibrational frequencies, unpublished results, *Bartmess* [25]

It is also possible to generate the mixed protic anions HXY^- with for example $X = (CF_3SO_2)_2F^-$, $Y = CF_3SO_3^-$ [14], $X = Cl^-$, Br^-, $Y = AlCl_4^-$, $AlBr_4^-$, $Al_2Cl_7^-$, $Al_2Br_7^-$ [20, 21]. As discussed in more detail later, systems derived from HCl or HBr and $Al_2Cl_7^-$ or $Al_2Br_7^-$ are superacidic and there is good evidence that the acidic species are the ions HXY^- not the molecules HCl or HBr nor the unknown $HAlCl_4$, $HAlBr_4$, HAl_2Cl_7 or HAl_2Br_7. The solvent systems in which these superacids have been used consist of an organic cation such as *emim*$^+$ or R_3S^+ (R = alkyl) together with a mixture of tetrahaloaluminate and heptahalodialuminate anions [20–22].

Measurements of Acidity

Gas phase proton affinities are experimentally determined by various specialized mass spectrometry techniques [23] calculated by means of *Born-Haber* cycles [15] or obtained *via* high-level *ab initio* computations [24, 25][a]. For the liquid phase the acidity is viewed as the availability of protons. What is the effective concentration or, more precisely, activity, of hydrogen ions in the system? The said hydrogen ions will be at least solvated and generally in distinct combination with basic units. For strong acid systems, parent protic molecules are essentially fully dissociated, but for weak acid systems, the incomplete ionization equilibria must be unaffected by the method(s) of assessing hydrogen ion activity.

The *Brønsted* acidity of a liquid can, in theory, be identified with the hydrogen ion activity. In practice, the $pH = -\log_{10} a_{H^+}$, is sought and, for aqueous systems, a scale constructed from one or more standards is used. This calibration is derived from measurements of e.m.f.s of cells such as

$$\mathrm{Pt, H_2(g)/acid\ solution/aqueous\ KCl/AgCl,}$$

$$\mathrm{Ag\ and\ glass\ electrode^{b}/buffer\ solution/S.C.E.}$$

and the calculation of activity coefficients by the *Debye-Hückel* theory [26]. However, the *Debye-Hückel* theory is only valid for dilute solution of ions ($I < 0.1\,M$) and liquid junction potentials are not independent of drastic composition changes, especially at higher concentrations.

There is no fundamental reason why a *pH* scale could not be developed in the same way for a nonaqueous solvent system in which a reversible hydrogen electrode can operate. This has been done in *DMSO* solvent, though for only a limited range of the possible acidity scale there [27]. In fact, a number of ionic liquids of the type HX in MX, where M^+ is a highly electropositive cation, appear to be appropriate candidates for such an exercise [20]. The hydrogen electrode reaction for such a system will take the form

$$\mathrm{H}X_2^{\,-} + \mathrm{e}^- \rightarrow \frac{1}{2}\mathrm{H}_2 + 2X^-$$

and a metal ion/metal electrode is likely to involve an anion complex also *e.g.*

$$\mathrm{Ag}X_2^{\,-} + \mathrm{e}^- \rightarrow \mathrm{Ag} + 2X^-$$

However, it is possible to connect solvent systems with common cations and different anions and to measure the thermoelectric powers of the cells if some electrode reactions are restricted to certain temperatures [28].

An alternative method for measuring acidity, one which is very commonly used for concentrated acids, is by spectrophotometry. It was successfully applied by *Rochester* [26] to a 0.189 *M* 4-*t*-butylphenol solution in several $NaHCO_3$/NaOH buffers (see fig. 1.1 of Ref. [26]). The *pH* and the acid dissociation constant are related:

$$pH = pK_{\mathrm{HA}} + \log_{10}(c_{A^-}/c_{\mathrm{HA}}) + \log_{10}(\gamma_{A^-}/\gamma_{\mathrm{HA}})$$

The ionization ratio was derived from the optical density and the activity coefficient γ_{A^-} from the *Debye-Hückel* equation while $\gamma_{\mathrm{HA}} \rightarrow 1$ provided I, the ionic strength, is <0.1 molal.

For a weak base B in any solvent, *Hammett* and *Deyrup* [29] defined the acidity function

$$H_0 = pK_{B\mathrm{H}^+} - \log_{10}\left(\frac{c_{\mathrm{BH}^+}}{c_B}\right)$$

where the cs refer to the concentrations of the conjugate acid/base pair $B\mathrm{H}^+$ and B. Further

$$H_0 = -\log_{10} h_0 = -\log_{10}\left(\frac{a_{H^+}\gamma_B}{\gamma_{B\mathrm{H}^+}}\right)$$

at low I, $H_0 \rightarrow -\log_{10} c_{\mathrm{H}^+}$ and at infinite dilution $H_0 \rightarrow pH$.

The evaluation of H_0 for the solvent depends on the difference between the spectra of the weak base and the acid. It necessitates that there is a single protonation step and that added indicator base concentration is insufficient to affect the solvent's acidity.

The results for aqueous acids have been reviewed thoroughly by *Rochester* [26]. Most relevant to our consideration of ionic liquids is the finding that H_0 of strong acids in water increases much more rap-

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[a] Computational value, using Gaussian 98^{24} at the *B3LYP*/6-311+G(3df,3pd)//*B3LYP*/6-31+G* level, corrected to 298K with vibrational frequencies. Acidities and basicities at this level agree with experimental values to within ±10 kJ/mol in most cases over hundreds of acids, and at worst to ±25 kJ/mol [25].

[b] A glass electrode is actually a soda-glass membrane which is sensitive to hydrogen ions. On the inside of the membrane is a chloride solution containing an AgCl/Ag electrode and on the outside the test solution containing a saturated calomel electrode (S.C.E.) connected by a salt bridge.

idly than the stoichiometric acid concentration (see fig. 2.4 of Ref. [22]). The acidity is independent of the anion and a function of (c_{H^+}/c_{H_2O}); indeed H_0 can be correlated with successive proton hydration equilibria up to $H_9O_4^+$ formation [30]. Interestingly, the composition of the azeotropes of HCl and H_2O (*Dalton*, 1832) and HF and H_2O are $8H_2O$:HCl and $1.8H_2O$:HF [9].

What is the appropriate protocol for determining the acidity function H_0 of any liquid and referring it to the moderately precise values of aqueous systems? The ratio of acid:base concentrations for the solutions of weak base indicators with aqueous pK_b values spanning the expected H_0 are determined spectrophotometrically. If a series of solutions of an acid added to a given solvent can be studied, then a plot of H_0 *vs.* $\log_{10}(c_{BH^+}/c_B)$ should have a slope of -1 for all the indicators. H_0 values are thus determined by an interpolative procedure.

The critical question is which bases are appropriate for a given system. Provided the bases simply undergo protonation in the acid, the series of primary nitroanilines is satisfactory (pK_bs in water range from 2.50 for 3-nitroaniline to -10.04 for 2,4,6-trinitroaniline). For superacidic systems [12, 31], defined as having $H_0 < -12$, a series of aromatic hydrocarbons may be useful [32].

Acidity functions have also been derived from NMR measurements, firstly using ^1H and ^{19}F nuclei but more recently ^{13}C. The area has been reviewed by *Farcasiu* and *Ghenciu* and will not be detailed here [33]. Suffice it to note that chemical shift differences for two atoms of an indicator can be correlated with the acidity of a solvent and the uncertainties arising from activity coefficient changes can be minimized by extrapolation to infinite dilution. A typical result is shown in fig. 4 of Ref. [33].

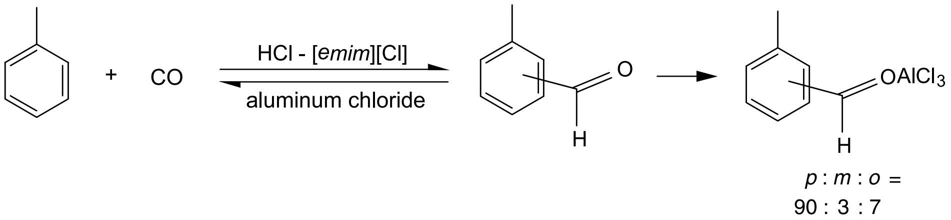
Kamlet and *Taft* have measured the electronic transitions of a series of carefully selected dyes in a series of molecular solvents [34–37]. From the λ maxima they determined, the researchers developed a set of three empirical parameters, α, β, and π^*, to characterize the dominant properties of the solvents investigated. In this scheme α represents the hydrogen bond donor acidity of the solvent, β the hydrogen bond acceptor basicity, and π^* the dipolarity/polarizability. These parameters thus are very useful in understanding how solutes are solvated in solution. Water in *Kamlet–Taft* scheme is very polar ($\pi^* = 1.09$), a very good hydrogen bond donor ($\alpha = 1.17$), and a moderate hydrogen bond acceptor ($\beta = 0.47$), while benzene is weakly polar/polarizable ($\pi^* = 0.59$), a very poor hydrogen bond donor ($\alpha = 0$), and a poor hydrogen bond acceptor ($\beta = 0.10$) [38]. These parameters have been used in a large number of ways through the years including how solvents influence optical rotations [39].

Organic Reactions in Ionic Liquids

Ionic Liquids Containing Hydrogen Halides

The most common latent *Brønsted* acids found in ionic liquids are HCl and HBr, especially in those that contain the corresponding aluminum halide. Considerable effort has been expended in measuring the acidity of these media. To begin let us consider ionic liquids consisting of mixtures of 1-ethyl-3-methylimidazolium chloride ([*emim*][Cl]) and aluminum chloride. These mixtures were in fact among the first ionic liquids synthesized and studied. Remarkably they are liquid at room temperature for a wide range of ratios of the two components. Ionic liquids with more [*emim*][Cl] than aluminum chloride are basic, with the anionic components being Cl^- and $AlCl_4^-$. When $AlCl_3$ is in excess, the liquids are acidic, with $AlCl_4^-$ and $Al_2Cl_7^-$, a very powerful *Lewis* acid, being the primary anionic components. As the amount of $AlCl_3$ in the acidic ionic liquid increases, the amount of $Al_2Cl_7^-$ also goes up. The combination of HCl and $Al_2Cl_7^-$ creates a very strong proton donor. At even higher concentrations of aluminum chloride higher aggregates of $AlCl_4^-$ and $AlCl_3$ are formed. As seen in Table 4, $AlCl_4^-$ is intrinsically a very weak base, compared to other anionic bases.

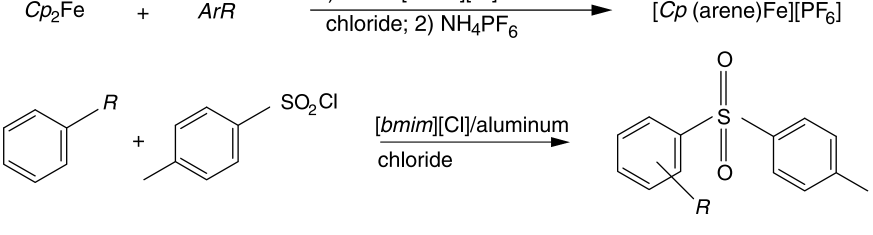
Smith and co-workers were the first to examine the acidity of HCl dissolved in *Lewis* acidic [*emim*][Cl]/$AlCl_3$ [32, 40]. This was accomplished by measuring the degree of protonation of a series of arenes of varying basicity as a function of ionic liquid composition and external hydrogen chloride pressure. Because arenes are not the traditional bases used to measure acidity functions, these researchers correlated their data with those for the protonation of the same arenes in HF/BF_3 whose acidity functions were known. This then led to acidity functions for HCl in the ionic liquids. By this criterion 0.01 atmospheres of HCl in equilibrium with an ionic liquid containing 51 mol% $AlCl_3$ has $H_0 = -12.6$, and 1 atmosphere of HC1 in equilibrium with an ionic liquid with 67 mol% $AlCl_3$ has $H_0 = -18$. Various lines of evidence suggest that these acidity functions may be too negative. For example, the acidity function of HF/BF_3 changes rapidly at low concentrations of BF_3. Furthermore, the acidity function of pure HF is not known with certainty. Nonetheless, it is fair to characterize HCl in [*emim*][Cl]/$AlCl_3$ as being superacidic.



Trulove and *Osteryoung* have studied the nature of HCl in both basic and acidic [*emim*][Cl]/$AlCl_3$ by NMR and IR spectroscopies [41]. They discovered two proton-containing species, HCl and HCl_2^-, in the basic ionic liquid, in equilibrium, with the anionic species predominating. In the acidic ionic liquids only HCl was detected. *Campbell* and *Johnson* [20] measured the solubility of HCl in the chloroaluminate liquids and studied its electrochemistry as a function of pressure. They deduced that the HCl is complexed to both $AlCl_4^-$ and $Al_2Cl_7^-$ in the *Lewis* acidic system, to $AlCl_4^-$ in the neutral one, and primarily to Cl^- in the basic one.

Subsequent theoretical calculations by *Chandler* and *Johnson* [42] strongly support this analysis and structures of the complexes were derived. Thus, the chlorine-containing superacid in [*emim*][Cl]/$AlCl_3$ is actually the complex $ClHAl_2Cl_7^-$. *Angueira* and *White* have used *Chandler*'s and *Johnson*'s results to calculate molar concentrations of the various species in solution when HCl gas is in contact with acidic [*emim*][Cl]/$AlCl_3$ [43]. The amount of $ClHAl_2Cl_7^-$ increased as the partial pressure of HCl above the liquid also increased. These authors were then able to correlate the rate of carbonylation of toluene in the ionic liquids [44] to the sum of the concentrations of $ClHAl_2Cl_7^-$ and $Al_2Cl_7^-$. Because the equilibrium between toluene (plus carbon monoxide) and tolaldehyde favors toluene, the reaction is driven to completion by the irreversible complexation of the aldehyde to $ClHAl_2Cl_7^-$ and $Al_2Cl_7^-$.

Several other reactions have been reported in ionic liquids which contain both aluminum chloride and hydrogen chloride. *Dyson* and co-workers have examined the ligand exchange on ferrocene with aromatic compounds in [*bmim*][Cl]/$AlCl_3$; the exchange only occurred when the proton source [*bmim*][HCl_2], was added to the reaction medium [45]. *Nara et al.* have shown that the sulfonylation of arenes with *p*-toluenesulfonyl chloride occurs smoothly in *Lewis* acidic [*bmim*][Cl]/$AlCl_3$ [46] Interestingly in this case [46] Al NMR spectroscopy showed that the catalytic $Al_2Cl_7^-$ present in the reaction mixture initially was replaced by $AlCl_4^-$ as the reaction proceeded. Experiments also showed that this transformation was due to the buildup of HCl in the medium which reacted with the *Lewis* acid and sulfone (*B*), the basic product of the reaction: $Al_2Cl_7^- + HCl + B \rightarrow 2AlCl_4^- + BH^+$. Because sulfones are weakly basic, this reaction shows once again the protonating power of $HCl/Al_2Cl_7^-$.

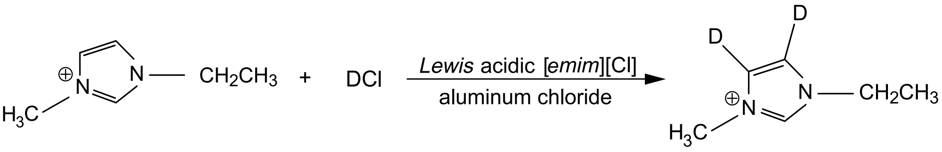


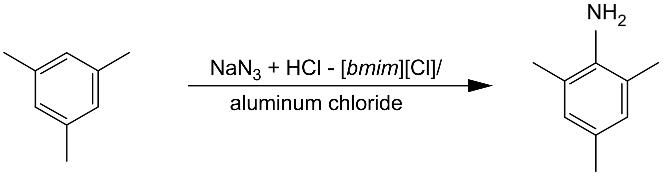
Remarkably, the *emim* cation undergoes deuterium exchange at positions 4 and 5 when *Lewis* acidic [*emim*][Cl]/$AlCl_3$ is treated with deuterium chloride, DCl [47]. The rate of this extraordinary electrophilic aromatic substitution reaction is proportional to the concentrations of both DCl and $Al_2Cl_7^-$. HCl also functions as a reagent in these *Lewis* acidic ionic liquids. Treatment of methyl-substituted benzenes in *Lewis* acidic [*bmim*][Cl]/$AlCl_3$ (3:4) with sodium azide and HCl yielded anilines in good yield [48]. Mesitylene, for example, afforded 2,4,6-trimethylaniline in 76% yield. In a different study 2-methylnaphthalene was effectively alkylated with long-chain alkenes with HCl in an ionic liquid consisting of triethylammonium chloride plus excess aluminum chloride [49]. The alkylation of benzene with 1-hexene in $Et_3NCl/FeCl_3$ and $Et_3NCl/AlCl_3$ with added HCl has been reported [50]. High catalytic activity and selectivity were observed in both solvents. The system, $HCl + Et_3NCl/AlCl_3$, was also used to isomerize the hydrocarbon, heptane [51]; the solubility of HCl in the ionic liquid as a function of temperature and external HCl pressure was also determined in this study.

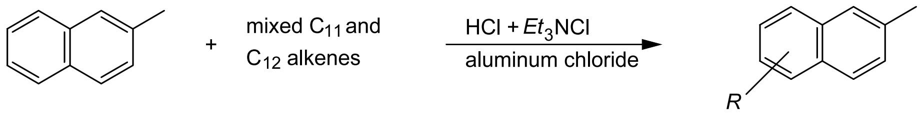
In 1990 *Melton* and co-workers first reported [52] the synthesis of a neutral buffered ionic liquid when [*emim*][Cl] and excess$AlCl_3$ are treated with solid sodium chloride. Enough of the NaCl dissolves in the liquid to neutralize the $Al_2Cl_7^-$:

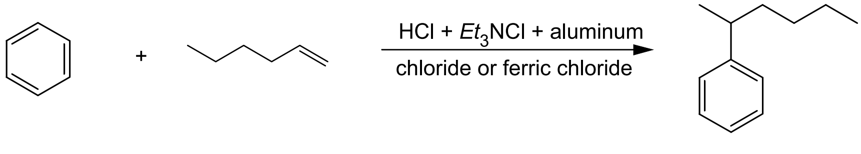
$$Cl^- + Al_2Cl_7^- \rightarrow 2AlCl_4^-$$

excess solid sodium chloride insures that the ionic liquid remains buffered. Chloroaluminate ionic liquids buffered in this manner, either with sodium chloride or other alkali and alkaline earth chlorides, have an interesting property which *Osteryoung* has termed latent acidity [53]. Acetylferrocene does not form an adduct with $AlCl_3$ in a neutral but unbuffered ionic liquid, but does when the liquid is buffered. This unusual reaction is due to the precipitation of the metal halide *via* the reaction $AlCl_4^- + B + M^+ \rightarrow MCl(s) + B : AlCl_3^-$, where M^+ and B are the metal cation and acetylferrocene, respectively. In addition to showing latent *Lewis* acidity these buffered ionic liquids also show latent *Brønsted* acidity [54]. Based on the ability of HCl to protonate 9,10-dimethylanthracene and hexamethylbenzene ionic liquids initially 55 mol% in $AlCl_3$ and buffered with









LiCl, NaCl, and KCl have different acidity functions, with the liquid containing LiCl being most acidic and that with KCl the least. Because the solubility of HCl in acid chloroaluminates had been measured [20], it was possible to quantitate the acidity functions directly. For one atmosphere of HCl over the LiCl-containing liquid $H_0 = -12.7$ and that of the NaCl-containing liquid $H_0 = -11.3$. Because the arbitrary cutoff for a superacid is an acidity function of -12, these ionic liquids are close to being superacidic. Later work demonstrated that the differences in values of the acidity functions of the ionic liquids buffered with LiCl, NaCl, and KCl are likely due to the differences in the solubility products of these salts in the ionic liquids [55].

Zawodzinski and *Osteryoung* were the first to prepare an ionic liquid containing [*emim*][Cl] and HCl and *no* $AlCl_3$ [56]. The synthesis, which was accomplished by exposing solid [*emim*][Cl] to excess gaseous HCl followed by evacuation, afforded the colorless liquid [*emim*][HCl_2]. *Campbell* and *Johnson* extended this idea by preparing a series of ionic liquids containing various mole fractions of [*emim*][Cl] and HCl [57]. When [*emim*][Cl] was in excess, the anionic components consisted mainly of Cl^- and HCl_2^-, whereas when HCl was in excess, HCl_2^- and $H_2Cl_3^-$ were the primary anionic species. As the amount of HCl in the ionic liquids increased, the mole fraction of the hydrogen chloride–chloride aggregates likewise increased. The acidity functions of some these ionic liquids have been determined [58, 59]. By measuring the extent of protonation of several nitroanilines, it was found that [*emim*][Cl]/HCl (mole fraction of HCl $= 0.49$) had $H_0 = -1.5$ and [*emim*][Cl]/HCl (mole fraction of HCl $= 0.67$) had $H_0 = -3.2$. These are strong acids but are far from being superacidic.

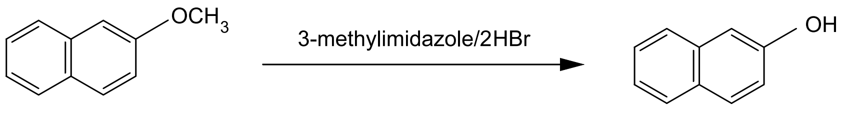
Ionic liquids containing $AlBr_3$ and HBr are also known. *Ma* and *Johnson* have prepared liquids consisting of a 2 to 1 mole ratio of $AlCl_3$ or $AlBr_3$ and trimethylsulfonium bromide (*TMSB*) plus HBr [21]. These researchers examined the extent to which a series of aromatic hydrocarbons are protonated from which the liquids' acidity functions were determined: 2:1 $AlCl_3$/*TMSB*-HBr (1 atm.) has $H_0 = -14$, while 2:1 $AlCl_3$/*TMSB*-HBr (1 atm.) has $H_0 = -16$ to -17. Both hydrogen bromide-containing superacids are more acidic than the ones containing [*emim*][Cl], $AlCl_3$, and HCl described earlier [32, 40]. The chemical behavior of triphenymethane in these *Lewis* acidic ionic liquids, with and without HBr, is most interesting. In $AlCl_3$/*TMSB*-HBr, for example, the hydrocarbon yielded protonated benzene, benzene, the triphenylmethyl cation, and surprisingly the diphenylmethyl cation. A scheme for the formation of these products is shown below. Because the hydride transfer from triphenylmethane to the diphenylmethyl cation is exothermic and irreversible, the observance of the diphenylmethyl cation in the mixture remains to be explained.

$$(C_6H_5)_3CH + H^+ \rightleftharpoons (C_6H_5)_2CH(C_6H_6)^+$$

$$\begin{aligned}(C_6H_5)_2CH(C_6H_6)^+ &\rightarrow (C_6H_5)_2CH^+ + C_6H_6\\ &\rightarrow C_6H_7^+\end{aligned}$$

$$\begin{aligned}&(C_6H_5)_3CH + (C_6H_5)_2CH(C_6H_6)^+\\ &\quad\rightarrow (C_6H_5)_3C^+ + (C_6H_5)_2CH_2 + C_6H_6\end{aligned}$$

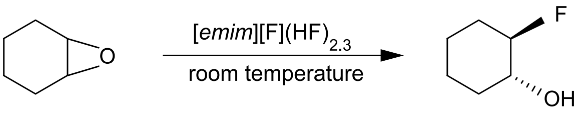
When one equivalent of 1-methylimidazole is treated with 2 moles of HBr, a still new ionic liquid is created which consists of the 3-methylimidazolium cation and an equilibrium mixture of the anions Br^-, HBr_2^-, and $H_2Br_3^-$ [13]. This new acidic ionic liquid is effective in the rapid cleavage of ethers at ambient temperatures and is estimated to have $H_0 < -4$. An example of this synthetically useful reaction is shown below:

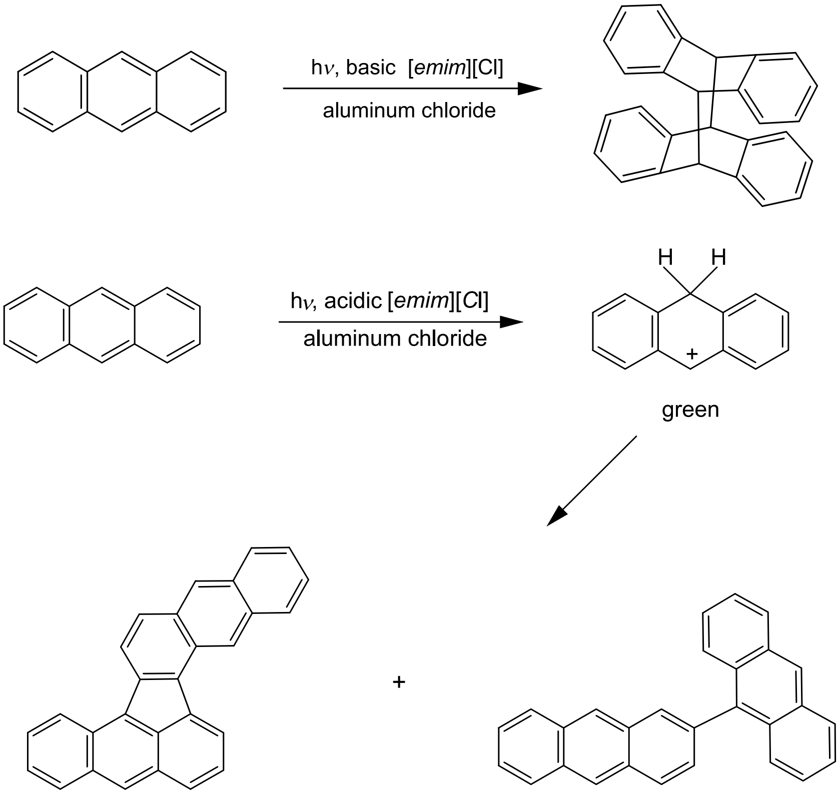


The course of photochemical reactions is also influenced by the presence of hydrogen halides in ionic liquids. It is well known that the photolysis of anthracene in most deoxygenated solvents yields a [4 + 4] dimer [60]. When anthracene is photolyzed in basic [*emim*][Cl]/$AlCl_3$ where any trace HCl present in solution is the *Brønsted* acid HCl_2^-, the hydrocarbon yields the same [4 + 4] product [61].

When anthracene is added to acidic [*emim*][Cl]/$AlCl_3$, a beautiful green solution is produced, the color of which is due to protonated anthracene [62]. The residual HCl in the acidic medium is $ClHAl_2Cl_7^-$, an excellent proton donor. Photolysis of this solution yields other dimers by a complex series of electron transfer, hydrogen atom transfer, and dimerization reactions. Subsequently, it was possible to mimic this very unusual behavior using mixtures of trifluoroacetic and trifluoromethanesulfonic acids [63].

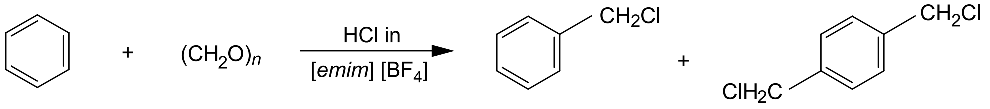
Hydrogen fluoride is effectively available from suitably substituted ionic liquids such as [*emim*][$F(HF)_{2.3}$] [65–67]. This system has been used to ring-open epoxides and deprotect silyl ethers. An example of the ring-opening reaction is shown below:





The chloromethylation of aromatic substrates using paraformaldehyde and catalytic HCl in [*emim*][BF_4] at 70°C has recently been reported [64]. Only those aromatic substrates as activated (or more) as benzene underwent electrophilic aromatic substitution; multiple substitution unfortunately also occurred commonly in the reaction.

Olah and co-workers have prepared an interesting series of hydrogen fluoride-containing ionic liquids by treating an appropriate amine such as pyridine with a large excess of liquid HF [68]. Perhaps the most noted of these ionic liquids is pyridinium poly(hydrogen fluoride), sometimes referred to as *Olah*'s reagent. *Olah*'s reagent serves as



a source of catalytic HF for alkyation and *Friedel-Crafts* reactions.

These HF systems are better termed polyfluorohydrogenates, analogous to the systems derived from HCl and HBr. The actual acids are then mixtures of $H_nF_{n+1}^-$ anions with appropriate *Hammett* acidities, not that of liquid HF. The amines used had similar proton affinities not pK_bs however.

Brønsted Acidic Ionic Liquids

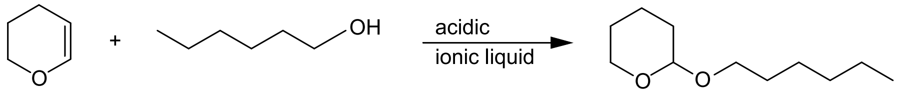
This section of the paper considers ionic liquids that are intrinsically acidic. These include solvents in which the cations contain appendages such as COOH or SO_3H. There are several solvents in which the anions such as HSO_4^-, $H_2PO_4^-$, and the phthalate anion are potentially acidic. A few other ionic liquids contain conceivably both acidic cations and anions. There are also a number of ionic liquids that contain ionizable ammonium, pyridinium, and imidazolium cations; ethylammonium nitrate, perhaps the first ionic liquid ever synthesized, fits into this category. In addition, there are several ionic liquids that behave as acids but do not fit neatly into any of the above groupings.

Liquids with Acidic Anions

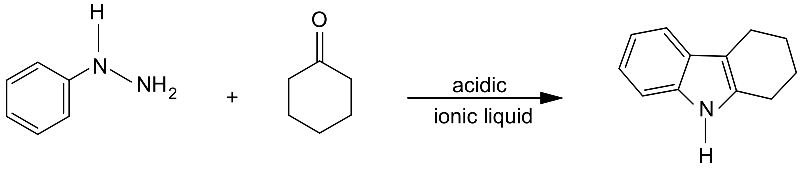
To begin, consider the potentially acidic anions which to date have appeared in ionic liquids: HSO_4^-, $H_2PO_4^-$, and the conjugate base of dicarboxylic acids. Sulfuric acid is a strong acid in water, ionizing completely in water to yield the hydronium ion and HSO_4^- which in turn is a strong acid in water, have $pK_a = 1.99$. If this ionization constant is any guide, one expects bisulfate-containing ionic liquids to be sufficiently acidic to catalyze a number of organic reactions which, as described below, is in fact the case. By the same type of reasoning, one does not expect $H_2PO_4^-$-containing ionic liquids to be sufficiently acidic to catalyze organic reactions because the ionization constant of $H_2PO_4^-$ in water is 7.20; this prediction turns out not to be true. This demonstrates that estimating acidity in ionic liquids from ionization constants in water is not trustworthy. Ionic liquids that contain monoanions of dicarboxylic acids such as tartaric acid and phthalic acid should have acidities between those that contain HSO_4^- and $H_2PO_4^-$. No reactions to date have been catalyzed by ionic liquids with monanions of dicarboxylic acids. Interestingly, ionic liquids containing anions which can donate a proton or accept a proton may serve as buffers.

At least seven different acid-catalyzed reactions have been run in ionic liquids with acidic anions including the *Friedel-Crafts* alkyation reaction [69], the *Biginelli* reaction [70], tetrahydropyranation [71, 72], the *Fischer* indole synthesis [73], the *Mannich* reaction [74], two distinct types of cyclizations [75, 76], and electrophilic aromatic substitution on indoles [77]. Rather than discuss each of these reactions the authors think it more profitable to describe three of the above reactions in which the anion in the ionic liquid was varied.

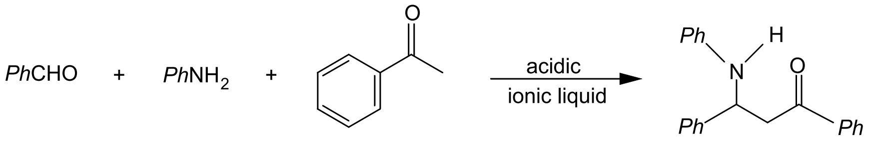
A classic manner in which to protect an alcohol is *via* its reaction with 3,4-dihydro-2*H*-pyran to form a tetrahydropyranyl ether. Reaction of neat hexanol with a slight excess of the pyran and catalytic amounts of [*bmim*][HSO_4] or [*bmim*][H_2PO_4] at 20°C afforded the protected alcohol in 96% yield in both cases [72]. Interestingly, this reaction did not work quite as well with [H*mim*][BF_4] as catalyst (71% yield), even less well when the imidazolium cation contained a carboxylic acid appendage (18% yield), and not at all when the cation contained a sulfonic acid appendage. Alcohols such as *tert*-butyl alcohol and *sec*-butyl alcohol also gave their respective protected products in high yields in [*bmim*][HSO_4], without the formation of any dehydrated products.



The *Fischer* indole synthesis involves the acid-catalyzed rearrangement of an aryl hydrazone, prepared from an aryl hydrazine and a ketone. In the intervening 125 years since its discovery, the reaction has been successfully carried out with myriad *Brønsted* and *Lewis* acids. A recent report has shown that acidic ionic liquids, serving as both solvent and catalyst, are effective as well [73]. In the reaction of phenylhydrazine and cyclohexanone, for example, [*bmim*][HSO_4], [*bmim*][H_2PO_4], and several salts of the methylimidazolium ion gave the cyclized product in yields varying from 81 to 92%. [*bmim*]-[HSO_4] worked equally well in sixteen other *Fischer* indole syntheses.



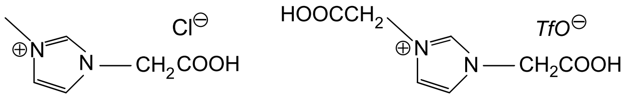
The model *Mannich* reaction of benzaldehyde, aniline, and acetophenone in several acidic ionic liquids (25°C, twelve hours) has recently been reported [74]. Surprisingly, the reaction did not occur in [*bmim*][HSO_4], but worked reasonably well in [*bmim*][H_2PO_4] (67% yield). The reaction worked best when carried out in an ionic liquid in which the cation was assumed to be acidic ([H*mim*][*Tf*O] (83% yield; *Tf*O = triflate). There is no obvious explanation for the large disparities in yield. A variety of other *Mannich* reactions were carried out in high yield in [H*mim*][*Tf*O].



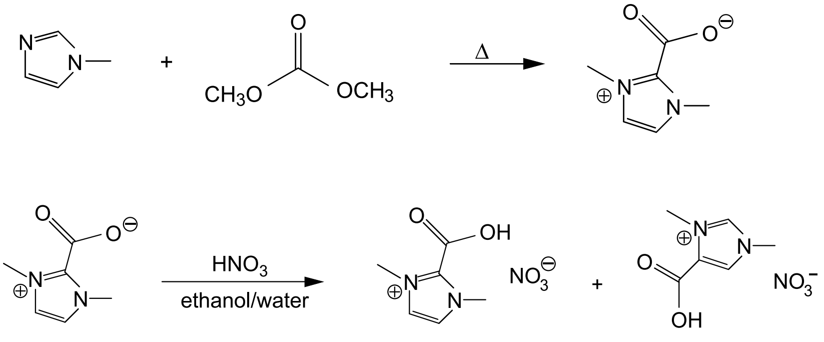
It is not clear in several of these studies if the systems were completely anhydrous nor if the salt stoichiometry in the liquids was 1:1. This raises questions as to the identity of the acidic species. It would be surprising if the 3-methylimidazolium cation ionized in the anhydrous salts, but not so if water were present. There is evidence from other measurements that $H[TfO]_2^-$ is a stable acid [14]. Since the equilibria in liquid H_3PO_4 are complex (see Table 2) the $H_2PO_4^-$ ion in [*bmim*][H_2PO_4] maybe in equilibrium with H_3O^+ and $HP_2O_7^{3-}$.

Ionic Liquids Whose Cations Contain COOH Appendages

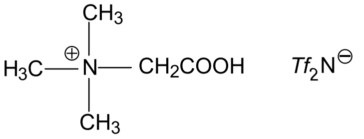
Dyson and his students in Switzerland have recently reported the synthesis and characterization of imidazolium-based ionic liquids in which the cations contain one or two carboxylic acid functionalities [78]. Two of these salts are shown below. Measurement of the ionization constants of the ionic liquids in water showed that the imidazolium cation is strongly electron withdrawing. The counterion also influences the value of the pK_a, with chloride salts being most acidic and triflate salts the least. No organic transformations were reported in this study.



Rogers and co-workers reported in 2003 that the reaction of *N*-methylimidazole with dimethyl carbonate unexpectedly afforded a zwitterionic carboxylate which was characterized by crystallography [79]. Reaction of the zwitterion with most *Brønsted* acids in ethanol/water resulted in decarboxylation, thus yielding a dimethylimidazolium salt. Treatment of the zwitterion with nitric acid in ethanol/water at various temperatures, however, resulted in the formation of two carboxylic acids, with the one containing the acid functionality between the two nitrogen atoms the kinetic product and the one containing the acid functionality next to a single nitrogen atom the thermodynamic product [80]. Both carboxylic acids could be decarboxylated on heating. To date no organic transformations have been reported to occur in these most interesting salts.



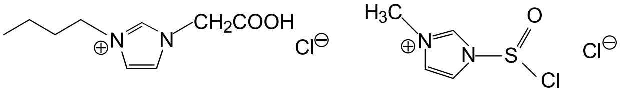
Another interesting ionic liquid, which contains a tetraalkylammonium ion with a single COOH substituent, was prepared by *Binnemans* and co-workers [81]. The ionic liquid with a melting point of 57°C has the unusual ability to dissolve a wide range of metal oxides. No organic reactions have been carried out in this fascinating liquid.



$$H_3C-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}-CH_2COOH \qquad Tf_2N^{\ominus}$$

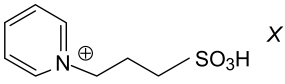
Three papers have been published in recent years in which these types of ionic liquids have been used either to catalyze organic transformations such as the acetalization of aldehydes [82] and the *Biginelli* reaction [83] or to function as scavenger to remove excess reagent in a chemical transformation [84].

Only one of these three uses will be described here. *Deng* and students have examined how a series of catalytic ionic liquids influenced the acetalization of aldehydes [82]. The butylcarboxymethylimidazolium chloride effectively catalyzed the acetalization of butyraldehyde with isoamyl alcohol, while the most unusual ionic liquid with a sulfinyl chloride substituent on the imidazolium ring was an even more effective catalyst. Numerous other aldehydes were protected using the sulfinyl chloride-containing ionic liquid.



Ionic Liquids Whose Cations Contain Sulfonic Acid Appendages

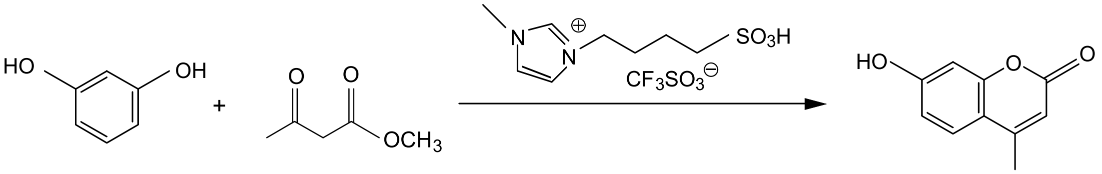
Ionic liquids whose cationic components contain side chains functionalized with sulfonic acid groups are of relatively recent vintage [85, 86] and are commonly prepared by reaction of a nucleophile such as pyridine, an alkyl-substituted imidazole, or phosphine to yield a zwitterion which is then treated with an appropriate *Brønsted* acid. *Forbes* and co-workers utilized these potentially very acidic ionic liquids to catalyze the *Fischer* esterification, the pinacol rearrangement, and the dehydration of an alcohol to an ether [85]. *Wang* and students determined the acidity functions of several pyridinium-based, sulfonic acid-containing ionic liquids [87], but, unfortunately, their samples contained several percent of water.

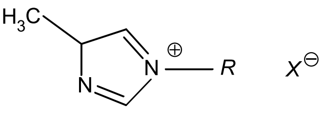


X	H_0
BF_4	–3.6
HSO_4	–3.3
*p-Ts*O	–2.1
H_2PO_4	–1.5

The more acidic of these ionic liquids catalyzed the *Fischer* esterification and the synthesis of tocopherol which will be described later in the section. Several other papers have been published which used sulfonic acid-based ionic liquids to convert carboxylic acids into esters [88, 92]. Interestingly, the H_0 values parallel the intrinsic (gas phase) basicity of the anions, but not the aqueous values, as seen in Table 4.

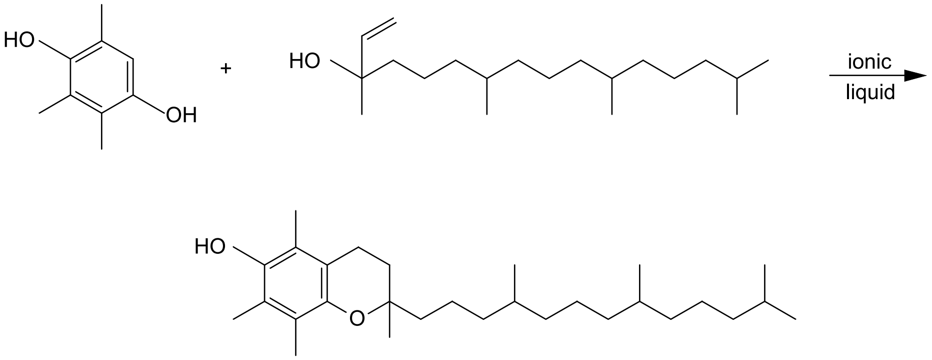
Interesting examples of electrophilic aromatic substitution have been carried out in the sulfonic acid-based ionic liquids [93–97]. They include the *Friedel-Crafts* alkylation of phenol with *tert*-butyl alcohol to give a mixture of 2- and 4-*tert*-butylphenol and 2,4- and 2,6-di-*tert*-butylphenol [93] and the *Pechmann* reaction which involves three reactions in total: a transesterification, a *Friedel-Crafts* alkylation, and a dehydration [94]. An example of the *Pechmann* reaction is shown at the end of this paragraph. It is also worth noting that the Chinese chemists who carried out the *Pechmann* reaction also measured the acidity functions of several potentially acidic ionic liquids; the structures of these liquids and their associated H_0 are also shown. It is interesting to note that the sulfonic acid-based ionic liquid was the most acidic of the four. The presence of water probably accounts for any acidity of their [H*mim*][BF_4].



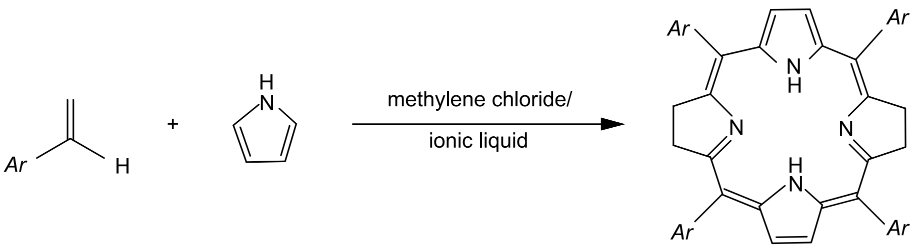


R	*X*	H_0
$(CH_2)_4SO_3H$	CF_3SO_3	0.01
$(CH_2)_3CH_3$	HSO_4	0.73
$(CH_2)_3CH_3$	H_2PO_4	2.55
H	BF_4	1.44

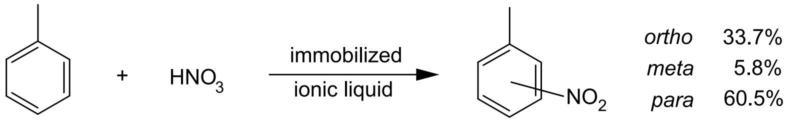
Tocopherol, also called of vitamin E, has been synthesized in a pyridinium-based sulfonic acid-containing ionic liquid by the reaction of trimethylhydroquinone and isophytol which involves a cyclization and a *Friedel-Crafts* alkylation reaction [87, 95]. The anion plays a significant role in the yield of reactions, decreasing in the order: $BF_4^- > \text{bisulfate} > H_2PO_4^- \gg p\text{-}Ts\text{O}^-$. Interestingly, the reaction gave higher yields of product when run in toluene or a mixture of propylene carbonate and *n*-heptane, with the ionic liquid serving a catalytic role only.



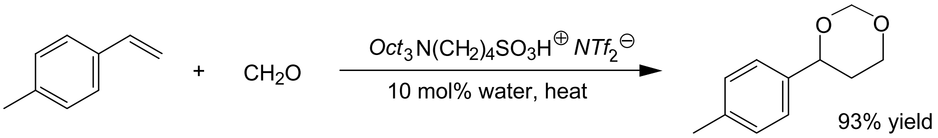
Tetraarylporphyrins have been prepared by the reaction of pyrrole and aryl aldehydes in imidazolium-based sulfonic acid-containing ionic liquids [96]. The cyclization reactions involved two phases, the first consisting of the ionic liquid and the other methylene chloride. The ionic liquid could be reused ten times without diminution of the yield of the porphyrin.

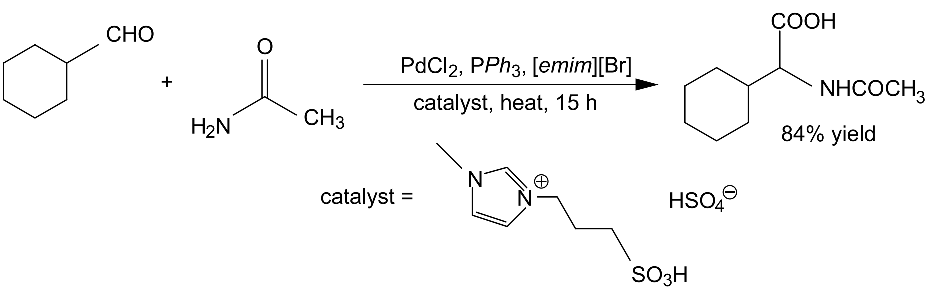


Yokoyama and co-workers have prepared a fascinating imidazolium-based sulfonic acid-containing ionic liquid which was chemisorbed to the surface of silica gel [97]. The heterogeneous material was then used to carry out the *Fischer* esterification and the nitration of arenes. A typical nitration reaction, shown below, gave the expected distribution of isomeric products. Electrophilic aromatic nitration also occurs in liquid phase sulfonic acid-based ionic liquids [97, 98].



The section will conclude with a brief discussion of other organic transformations catalyzed with the sulfonic acid-containing ionic liquids. Ionic liquids functionalized with SO_3H have been used, for example, for the oligomerization of alkenes [99] and the *Koch* carbonylation of tertiary alcohols [100]. The *Prins* reaction, which involves the cyclization of a styrene derivative with formaldehyde, has been carried out in an unusual ionic liquid based on a tetraalkylammonium cation [101], an example of which is shown immediately below. The cyclotrimerization of aliphatic aldehydes has also been successfully carried out in a disparate series of ionic liquids functionalized with sulfonic acid groups [102]. The *Mannich* reaction described earlier in the article has been carried out in moderate to excellent yield in both phosphonium- and imidazolium-based ionic liquids [103], typical reactions occur rapidly, with the phosphonium-based solvent being more effective. A clever palladium-catalyzed amidocarbonylation has been reported by *Zhu* and *Jiang* in which one ionic liquid such as [*emim*][Br] serves as solvent while a second ionic liquid with SO_3H functionality serves as catalyst [104]. One example of this intriguing reaction is also displayed below:



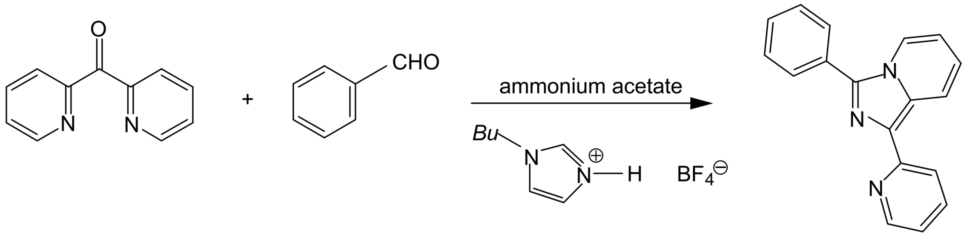


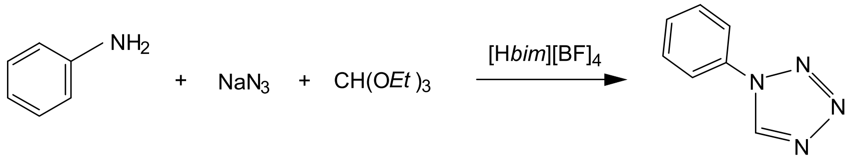
Ammonium-Type Liquids

Ethylammonium nitrate is perhaps the prototypical ammonium-type ionic liquid. This solvent was first prepared in 1914 [105] but was only considered a novelty until *Jaeger* and *Tucker* investigated the *Diels-Alder* reaction in it [106]. *Royer* in France extensively investigated organic reactions in pyridinium chloride and bromide several decades ago. A summary of *Royer*'s work may be found in a review by one the authors of this paper [107].

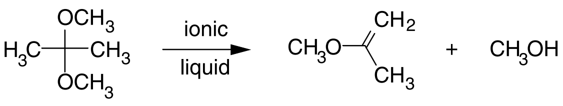
Susan et al. [108], *Noda et al.* [109], *Nakamoto et al.* [110], *Yoshizawa et al.* [111], *Greaves et al.* [112], *Nuthakki et al.* [113], *Ogihara et al.* [114, 115], *Ohno* [116], and their students have prepared and thoroughly characterized a very large number of ammonium-type ionic liquids. Two of the interests of these researchers are proton-conducting phases and fuel cell applications. No organic reactions were reported in these extensive studies.

A large number of organic transformations have been carried out in *N*-alkylimidazolium salts which are easily prepared from the corresponding *N*-alkylimidazole and a suitable *Brønsted* acid. A short summary of much of this work was reported by *Siddiqui* in 2006 [117]. Some of the acid-catalyzed reactions carried out in these media include the *Knoevenagel* condensation [118], the *Michael* reaction [119], *Fischer* esterification [120, 121] and the acetalization of aldehydes and ketones [122, 123]. Other reactions carried out in imidazolium-based ionic liquids include the elimination of HCl from an alkyl chloride [124], enamine formation from 1,3-dicarbonyl compounds [125], and the dimerization of an α-methylstyrene [126]. The synthesis of heterocyclic compounds has also been carried out in these ionic liquids [117, 127–129]. For example, the reaction of dipyridylketone, benzaldehyde, and ammonium acetate in butylimidazolium tetrafluoroborate ([H*bim*][BF_4]) at 100°C for one hour afforded 1-(2-pyridyl)-3-phenylimidazo[1,5-*a*]pyridine in 94% yield; numerous other related cyclizations also were carried out in [H*bim*][BF_4] [128]. The same group of researchers also demonstrated that primary amines react with sodium azide and ethyl *ortho*-formate in [H*bim*][BF_4] to form tetrazoles in excellent yields [129]. Again it was assumed that [H*bim*]$^+$ is ionized in the liquid state (see later).



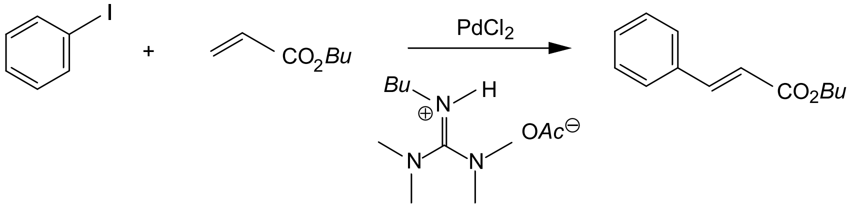


Dai et al. have prepared an unusual dendrimeric ammonium bistriflamide ionic liquid with potential applications for non-aqueous electrolytes and sensors [130]. To date no organic reactions have been carried out in this photoluminescing material. The well-characterized liquid alkylammonium formates may have applications as mobile phases in reverse-phase chromatography [131]. Not surprisingly, several acidic trialkylammonium salts have been used to catalyze the *Fischer* esterification reaction [132] and the acetalization of acetone [133]. The combination of triethylammonium chloride and aluminum chloride has been used to initiate the cationic co-polymerization of styrene and 1,3-pentadiene [134]. Several ammonium- and imidazolium-based ionic liquids have been used to crack 2,2-dialkoxypropanes at 140°C [135]. The reactions were faster in the imidazolium-based ionic liquids, but the selectivity was higher in the ammonium-based ionic liquids.



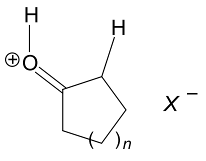
Duan et al. have prepared three acidic ionic liquids based on 2-methylpyridine: 2-methylpyridinium triflate, methanesulfonate, and trifluoroacetate [136]. The acidity functions of these liquids were determined by the indicator method with the result that the triflate salt with $H_0 = 1.53$ was most acidic, the methanesulfonate salt with $H_0 = 3.13$ the next most acidic, and the trifluoroacetate liquid the least acidic ($H_0 > 3.13$, but not quantitated). The acidity of these ionic liquids then is thus strongly influenced by the basicity of the anion, as seen in Table 4. The rates of *tert*-butylation of phenol with *tert*-butyl alcohol and the esterification of acetic acid with cyclic alkenes were correlated with the acidity of the ionic liquid, being fastest in the triflate-based liquid, slower in the methanesulfonate salt, and not occurring at all in the trifluoroacetate-based ionic liquid.

Li et al. have prepared several guanidinium-based ionic liquids and used them as media for the palladium-catalyzed *Heck* reaction [137]. The butylguanidinium acetate proved to be the most versatile medium for the coupling reaction. For example, the reaction of iodobenzene with butyl acrylate at 140°C for fifteen minutes afforded the coupling product in quantitative yield. Presumably the acetate anion is functioning as a base, a requirement of the *Heck* reaction, in these coupling reactions.



Miscellaneous

Deng and co-workers have prepared twelve new *Brønsted* acidic ionic liquids by reacting caprolactam or butyrolactam directly with a *Brønsted* acid [138]. The researchers proposed that the lactams are protonated on the amides' nitrogen atoms, but it is more reasonable to believe that the protonation occurs on the lactams' carbonyl oxygen atoms. Various physical properties of these materials were measured including the acidity functions of seven of the new ionic liquids. Unfortunately, the acidity functions were not determined on the pure ionic liquids but on solutions of the ionic liquids in methylene chloride. The values determined in this manner are shown below. The H_0 values for $n = 3$ are in the order of the intrinsic basicity of the anions, as per Table 4. The same group subsequently cleanly carried out the *Beckmann* rearrangement of cyclohexanone oxime in one of these lactam-based ionic liquids [139].



X	*n*	H_0 in CH_2Cl_2
BF_4	3	–0.22
BF_4	1	0.91
NO_3	3	2.08
CF_3CO_2	3	3.35
CF_3CO_2	1	3.48
$ClCH_2CO_2$	3	5.04
PhCO_2	3	6.07

Just this past year, the group of *Sheng Dai* prepared eight formamide type ionic liquids, all containing the bistriflamide anion [140]. These compounds were prepared by neutralizing the corresponding formamide with an aqueous solution of a *Brønsted* acid followed by addition of LiNTf_2. Phase separation from the water then yielded the triflamide ionic liquids. These liquids are thus hydrophobic and ionic. No organic reactions have been reported to date in the formamide-type ionic liquids.

Hydrogen Bond Donor Acidity of Ionic Liquids

Not surprisingly, the *Kamlet–Taft* parameters have been determined for a series of ionic liquids [141]. The parameters have also been determined for mixtures of ionic liquids and organic molecular solvents [142]. Ionic liquids containing imidazolium cations have π^* values comparable to that of water, moderate α values which depend primarily on the cation, and moderate β values determined mainly by the nature of the anion. Imidazolium cations with a CH group between the two nitrogen atoms have larger α values than those in which the connecting carbon atom has a methyl group in place of hydrogen. This suggests that hydrogen bond acidity occurs primarily through this CH group. *Ab initio* calculations [25] indicate that deprotonation at the C2 site in dimethylimidazolium cation, to form the equivalent of *Arduengo*'s carbene [143] is 87 kJ/mol more favorable than deprotonation at the benzylic 1-methyl site. This along with the sp^2 nature of the C2 site is consistent with it being the best hydrogen bond donor location. *Aggarwal et al.* have investigated the *Diels-Alder* reaction of methyl acrylate with cyclopentadiene in a series of ionic liquids and were able to correlate the diastereoselectivity of the reaction and related rate enhancements to hydrogen bonding from the imidazolium cation of the solvent to the dienophile, methyl acrylate [144]. It is well known that added *Lewis* acids have the same effect on *Diels-Alder* reactions. In an even more cogent study of the S_N2 reaction in ionic liquids *Crowhurst et al.* found a negative correlation of the second-order rate constants with α [145]. This observation was attributed to the solvent hydrogen bonding to the anion, thus reducing its nucleophilicity.

Acidity of N,N′-Dialkylimidazolium Cations

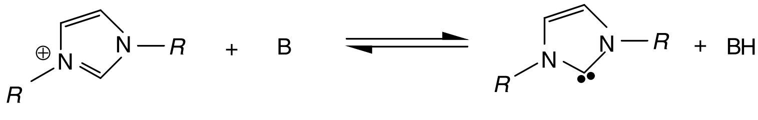
N,N′-Dialkylimidazolium cations function as very weak *Brønsted* acids in ionic liquids. Deprotonation of the site between the two nitrogen atoms yields isolable carbenes [143] which function either as very strong bases, as shown in Table 4, or ligands to transition metals. This reaction is not particularly simple. While potassium *t*-butoxide removes the C(2)H from [*emim*][Cl] [146], hydride ions attack basic [*emim*][Cl]/$AlCl_3$ but not neutral [*emim*][Cl]/$AlCl_3$ liquids [147]. Further, palladium(II) acetate forms a carbene complex with [*bmim*][BF_4] only if a halide ion is present [148]. It is noteworthy that the first stable crystalline carbene made was 1,3-diadamantylimidazolidene [149].

Alder et al. have found the pK_a of 1,3-diisopropyl-4,5-dimethylimidazolium ion to be 24 in dimethyl sulfoxide [150]. *Kim* and *Streitwieser*, on the other hand, found 1,3-di-*tert*-butylimidazolium ion to have $pK_a = 22.7$ in the same solvent [151]. Even though there is concern as to whether the ionization constants are for free or ion-paired cations or both [151], the weak acidity of dialkylimidazolium ions in ionic liquids is definite, and is consistent with their yields being the strongest neutral bases listed in Table 4.

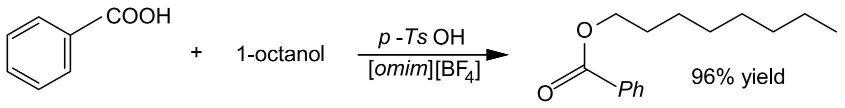
Other Acids in Ionic Liquids

It should be a surprise to no one that many *Brønsted* acids other that the hydrogen halides have been used to catalyze reactions in ionic liquids. Although the acidity of these acids in ionic liquids has not been quantitated by a dissociation constant or an acidity function, it is clear from what is described below that they are sufficiently acidic to catalyze several very important organic transformations.

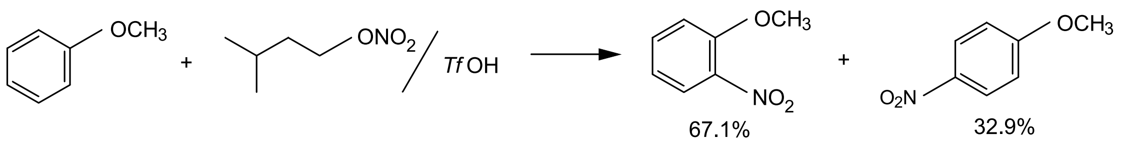
The *Fischer* esterification, which is the acid-catalyzed reaction of a carboxylic acid and an alcohol, is the best and most widely used method to prepare esters. The reaction which also generates water is reversible which means that an excess of a reagent must be used or a product removed to drive the reaction to completion. A few examples of this classical reaction have been carried out successfully in ionic liquids. *Nguyen et al.* have carried out the *Fischer* esterification in mixtures of 1-octyl-3-methylimidazolium tetrafluoroborate ([*omim*][BF_4])/*p*-toluenesulfonic acid (*p-Ts*OH), activated either by heat or microwaves [152]. What made this procedure especially advantageous was the fact that the esters, being insoluble in the ionic liquid, formed a second, easily separable phase. This not only made the isolation of products easy, it also insured that the reversible reactions were driven to completion. One example of this reaction is shown below. *Crespo et al.* have discovered another manner in which to shift the equilibrium towards the ester [153]. In their study of the reaction of (−)-borneol and acetic acid in [*bmim*][BF_4]/



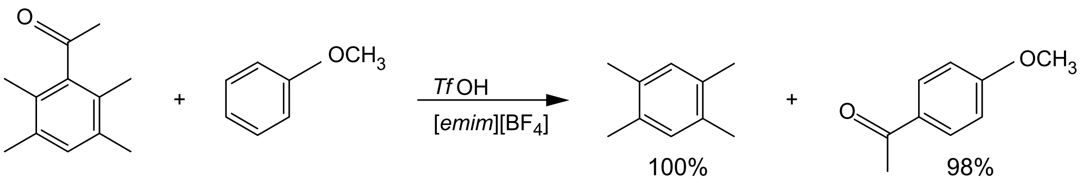
*p-Ts*OH, the water was removed from the reaction by passing through a hydrophilic membrane whose opposing side was subject to vacuum, a process the authors call pervaporation. Using this methodology the researchers were able to double the yield of bornyl acetate. The transesterification reaction, which involves converting one ester into another by treatment with acid and alcohol, has also been successfully accomplished in ionic liquids [154]. Methyl acetoacetate, for example, was converted into butyl acetoacetate in 96% yield in 1-propyl-3-methylimidazolium chloride ([*pmim*][Cl])/sulfamic acid at 80°C. Sulfamic acid (NH$_2$SO$_3$H) is a non-volatile, non-corrosive compound with moderate acidity in water, ($pK_a = 1.0$), *DMF*, and other solvents [155–157].

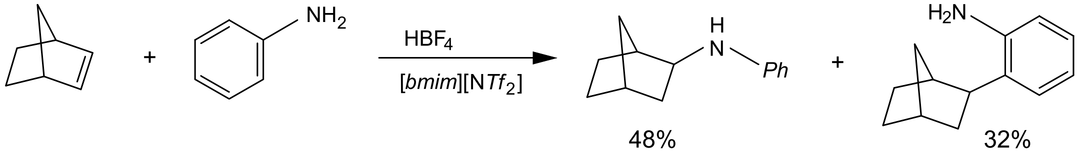


Several examples of electrophilic aromatic substitution are known to occur in mixtures of strong acids and ionic liquids. *Laali* and *Gettwert* have carried out an extensive examination of the nitration of aromatic substrates in a variety of ionic liquids and sources of NO$_2$ [158]. Germaine to the topic of the article are reactions carried out in [*emim*][O*Tf*] where the combination of isoamyl nitrate and triflic acid served as the source of the nitronium cation. One example of this procedure is shown below:

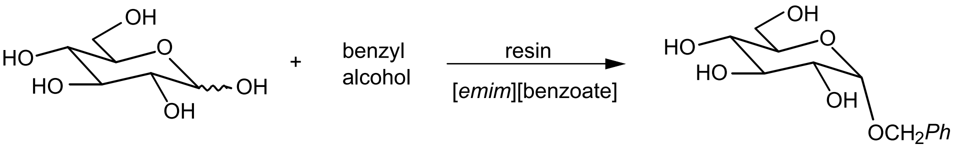


Sarca and *Laali* have shown that it is possible to transacylate or deacylate aromatic compounds in imidazolium-based ionic liquids at 70°C, with triflic acid (CF$_3$SO$_3$H; *Tf*OH) serving as catalyst [159]. A beautiful example of the transacylation reaction is illustrated below; here the sterically hindered acetyldurene serves as the source of acetyl and the activated anisole as the acceptor. *Laali* and his students have also shown that one can adamantylate [160] and benzylate [161] aromatic substrates using 1-adamantanol and benzyl alcohol, respectively, in mixtures of triflic acid and imidazolium-based ionic liquids. Interestingly, the benzylation of toluene yields mixtures of the *ortho*, *meta*, and *para* substitution products, whereas the adamantylation of toluene only yields the *para* product. The Brazilian chemists, *Jairton Dupont et al.*, have shown that the reaction of norbornene and aniline at 135°C in HBF$_4$/[*bmim*][N*Tf*$_2$] affords two products, one of which clearly is formed *via* electrophilic aromatic substitution [162]; other *Brønsted* acids also catalyzed this reaction. Surprisingly, only the *ortho* substitution product is formed in this reaction.

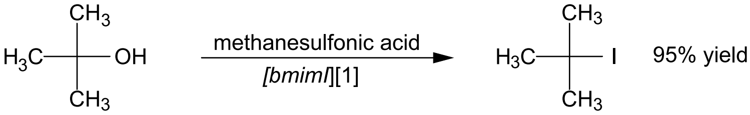




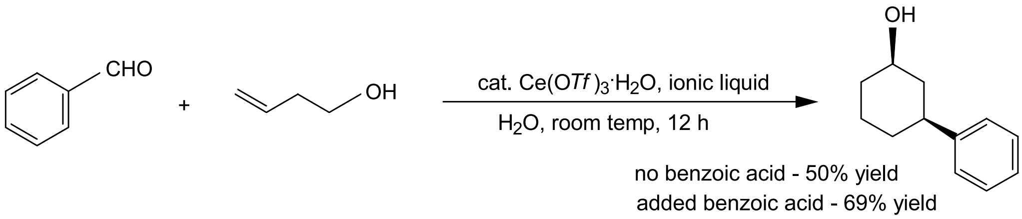
The glycosylation of carbohydrates and carbohydrate derivatives has been successfully carried out in a variety of imidazolium-based ionic liquids using bis(trifluoromethylsufonyl)imide ($HNTf_2$) [163, 164], tetrafluoroboric acid [163], perchloric acid [164], triflic acid [164], *p*-toluenesulfonic acid [165], and Amberlite IR-120 resin [165] to catalyze the reactions. The resin-catalyzed reaction of glucose with benzyl alcohol in [*emim*][benzoate] at 50°C, for example, afforded the glycosylated product in 64% yield; the reaction was α selective in every glycosylation examined.



Several other acid-catalyzed reactions occurring in ionic liquids have also been reported in the literature including the *Michael* reaction (catalyst: *p-Ts*OH) [166], the cleavage of aryl alkyl ethers to yield phenols (HBr, *p-Ts*OH, methanesulfonic acid, acetic acid, HCl, H_2SO_4) [167], the cyclization of terpenoids (FSO_3H) [168], the copolymerization of styrene and CO (*p-Ts*OH) [169], and the conversion of alcohols into alkyl halides (HCl, H_2SO_4, methanesulfonic acid) [170]. The features of two of these reactions are worth mentioning in some detail. The cleavage of the aryl alkyl ethers at 115°C, for example, used two ionic liquids, [*bmim*][BF_4] as solvent and [*bmim*][Br] and the *Brønsted* acid as reagent. The acid, presumably HBr_2^-, protonated the ether oxygen and the bromide then displaced the alkyl group *via* an S_N2 reaction. In some instances the acidic species may have been H_3O^+ or $HBrX^-$. The reactions which converted alcohols into alkyl halides were carried out with one equivalent of *R*OH and one equivalent of [*bmim*][*X*], where *X* represents the halogen to be incorporated into the molecule. The mechanism of these reactions is similar to that for the previously mentioned cleavage of ethers. The acid protonates the hydroxyl oxygen and the halide displaces the water either in an S_N1 or in an S_N2 reaction depending on the structure of the alcohol.



Keh et al. recently reported that cerium triflate in [*bmim*][PF_6] catalyzed the cyclization reaction of aryl aldehydes with homoallylic alcohols to form tetrahydropyranols, with the reaction being stereoselectively *cis* [171]. Interestingly, added benzoic acid (1 equivalent) increased the yields of products by as much as 19%. No reaction occurred when the reaction mixture contained benzoic acid, but no cerium triflate.



Liquid Salt Hydrates

Many salts exist in hydrated forms and many of these hydrates are liquids below 100°C, the artificial dividing temperature between molten salts and ionic liquids. "Almost anhydrous" tetrabutylammonium fluoride, which retains some water, is a liquid at room temperature and is useful in the fluorination of organic compounds [172]. The mono- and dihydrates of tetraethylammonium acetate are both liquids at room temperature, while the tetrahydrate is a solid [173]. Based on the pK_as of hydrogen fluoride and acetic acid, one would expect the fluoride and acetate ionic liquids to be considerably basic. The two liquid acetate hydrates in fact absorb considerable amounts of carbon dioxide which is converted into bicarbonate.

Numerous metal cations exist as hexa- or tetrahydrates in water. These hydrated cations often function as bases and reversibly accept protons from water; others are acidic and donate protons to water. $Mg(H_2O)_6^{+2}$, for example, has $pK_a = 11.44$ in water, while $Fe(H_2O)_6^{+3}$ has $pK_a = 2.19$ [174]. Because many of these cations are acidic in water, their salts in liquid form may also be quite acidic. $ZnCl_2 \cdot 4H_2O$ is a liquid at ambient temperature and has $H_0 = -2$ [175, 176]. Interestingly, when water is added to the liquid salt, the acidity of the medium is significantly reduced. Molten $Ca(NO_3)_2 \cdot 4H_2O$ is neutral, but when $Al(NO_3)_3 \cdot 9H_2O$ is added, the supercooled liquid has considerable acidity with H_0 varying from +0.5 to −0.5 depending on how much solute the ionic liquid contains [177, 178]. Added $Cd(NO_3)_2 \cdot 4H_2O$, on the other hand, has a smaller effect, with H_0 values from roughly +2.1 to +0.5. Adding nitric acid to $Ca(NO_3)_2 \cdot 4H_2O$ yields a medium with more protonating power than the ionic liquids containing the cadmium or aluminum salts. This new acid was used to hydrolyze a series of esters, the rate of which was proportional to the acidity function of the medium [178]. This particular ionic liquid thus functions as both catalyst and reagent. Although other acidity functions of liquid salt hydrates have not been measured, it is possible to estimate them from proton NMR data. *Ellis* and *Hester* were the first researchers to measure the hydrogen chemical shifts of a series of molten zinc, magnesium, and calcium nitrate hydrates at 95°C, although the data were not interpreted in terms of acidity [179]. *Duffy* and *Ingram*, on the other hand, have shown that the proton chemical shift of aqueous HCl and HNO_3 and the previously described $ZnCl_2 \cdot 4H_2O$ correlate with their respective acidity functions [180]. Based on its hydrogen chemical shift, molten $Al(NO_3)_3 \cdot 10H_2O$, for example, should have an acidity function between −2 and −3. Estimates of the acidity of the hydrates of magnesium, cadmium, silver, calcium, lithium, and sodium salts were also made on this basis; these liquids are predicted to have acidity functions between approximately −0.2 and +0.8. It is not clear what protic species are responsible for acidity in these systems. While $H(H_2O)_n^{+}$ is the obvious candidate, HCl_2^{-} and $H(NO_3)_2^{-}$ should be considered.

Related Hammett H_0 Measurements

Thomazeau et al. [181] have determined H_0 values for a number of *Brønsted* acids, notably Tf_2NH and *Tf*OH, in [*bmim*][N*Tf*$_2$]. Values of H_0 range from −3.3 at low Tf_2NH concentration, to −5.0 at *ca.* 0.3 *M* Tf_2NH. *Tf*OH is comparable in H_0 values to Tf_2NH. In [*bmim*][BF_4], Tf_2NH shows an H_0 value of −7.0.

Crowhurst and *Welton* [182] confirmed these results and found that H[N*Tf*$_2$] gave dilute solutions with H_0 of −5.0 to −6.2 in [*bmim*][SbF_6] but very concentration-dependent values of H_0 for solutions in [*bmim*][BF_4].

Conclusions

It is clear that an extensive literature has developed quickly for this area and we apologize to authors who feel their significant work has been overlooked. Close inspection suggests that most of the reactions are classical ones, carried out in new solvents with inherent high ionic strengths. The conditions for these reactions are often less severe and excellent yields are reported in various instances. Acid speciation is seldom determined however and too often it is assumed that aqueous pK_a values are not just a guide in comparing quantities! Of course, if the systems are not anhydrous, then H_3O^+ may be the operative acidic ion.

We find that many of the results can be accounted for if we assume that the acid/base character in liquid salts correlates with the gas phase proton affinity. Table 4, which we deliberately include in this section, shows the P.A. *vs.* pK_a relationship for many of the species discussed. *Hammett* acidity measurements have been attempted for a number of liquid salts. Values quoted for the salts dissolved in other solvents seem pointless.

The number of organic and semi-organic liquid salts that can be synthesized is indeed enormous. So far the number of cation types and anion types used has been fairly small and this augers well from the biodegradability and toxicity perspective. Nevertheless, more deliberate choices of ions for reactions of given solutes, *e.g.*, aromatic cations for aromatic solutes and aliphatic ones for aliphatic solutes, would likely sharpen the chemistry achievements. It is important to realize that most of these liquids consist of, at least, the constituent cations and anions as well as their combinations or ion pairs: each of these components has a distinct chemistry *vis a vis* each other and any solute. If *Brønsted* acids are involved we must remember that THE PROTON LIKES COMPANY – IT WILL NEVER WALK ALONE.

Acknowledgements

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