Super acidic ionic liquids for arene carbonylation derived from dialkylimidazolium chlorides and MCl₃ (M = Al, Ga, or In)

E.J. Angueira [a,c,1], M.G. White [b,c,*]

[a] *Ciba Specialty Products, P.O. Box 113, McIntosh, AL 36553-0113, United States*
[b] *Dave C. Swalm School of Chemical Engineering, 330 President's Circle, Mississippi State University, Mississippi State, MS, United States*
[c] *School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, United States*

Abstract

Ionic liquids, formed by combining 1 mol of 1-butyl-3-methyl-1*H*-imidazolium chloride, bmim⁺-Cl⁻, with 2 mol of a Group IIIA metal chloride (Al, Ga, In), were examined for toluene carbonylation reactivity to determine the effect for changing the M(III) cation. These ionic liquids were characterized for Brønsted acidity indirectly by ^{13}C NMR of labeled acetone, $CH_3-{}^*CO-CH_3$. These results were explained by a mechanism where the Brønsted acidity of the ionic liquid was influenced by the strength of the Lewis acid: $M^{3+}Cl_3$.
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1. Introduction

Room temperature ionic liquids (RTILs) can be formed by combining certain organic chlorides with metal chlorides. One pair of compounds often reported in the literature is 1-ethyl-3-methyl-1*H*-imidazolium chloride and aluminum chloride, but combinations of other organic compounds, such as pyridinium chloride, and other metal halides, such as indium chloride, have also been reported [1]. These strongly acidic RTILs are conversion agents for Brønsted-demanding reactions such as toluene carbonylation [2] and isobutane/butene alkylation [3–5]. We have become interested in that sub-family of RTILs that shows strong, intrinsic Lewis acidity and when HCl was added to the gas phase above the RTIL, as these materials also demonstrated strong Brønsted acidity [6]. For example, we showed that the reactivity of a Brønsted acid-demanding reaction could be adjusted by changing the HCl partial pressure above the RTIL prepared by mixing one equivalent of

1-R′-3-methyl-1*H*-imidazolium chloride (R′ = ethyl or butyl) with two equivalents of aluminum chloride [7]. Subsequently, it was shown that when the cation structure was adjusted by changing the length of the alkyl substituent group, R′, the reactivity towards the toluene carbonylation reaction decreased with increasing chain length of R′ [8].

The choice of elements in Group IIIA for the chlorometallate anion was guided from a consideration of the strength of the resulting Lewis acids that were formed. It is known that the strength of the chlorometallate Lewis acids decreases with increasing radius of the metalloid. Thus, for the Group IIIA series, one would expect that the strength of the Lewis acid MCl₃ would decrease in the following manner: Al > Ga > In. It was of interest here to determine if the properties of the IL derived from bmim⁺Cl⁻/2(MCl₃) could also be adjusted by changing the metal chloride, chosen from some members of Group IIIA (Al, Ga or In) so that the reactivity of the toluene carbonylation reaction under HCl at room temperature could be likewise adjusted.

2. Experimental

2.1. Chemicals

The dialkylimidazolium compounds were obtained from Sigma–Aldrich and used without further purification. Alu-

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* Corresponding author at: Dave C. Swalm School of Chemical Engineering, 330 President's Circle, Mississippi State University, Mississippi State, MS, United States. Tel.: +1 662 325 5797; fax: +1 662 325 2482.

E-mail addresses: ernesto.angueira@cibasc.com (E.J. Angueira), white@che.msstate.edu (M.G. White).

[1] Tel.: +1 251 436 2000.

minum chloride (99.99%), obtained from Sigma–Aldrich, was sublimed under a vacuum before use. Gallium chloride, indium chloride, and toluene (anhydrous, 99.8%) were obtained from Sigma–Aldrich and used without further purification. Carbon monoxide, CP grade, and HCl (anhydrous, >99%) were obtained from Airgas and Sigma–Aldrich, respectively. Acetone, enriched in ^{13}C in the 2-position (99%), was purchased from Sigma–Aldrich and used without further purification.

2.2. Preparation of RTILs

The detailed synthesis of the RTILs was described earlier [7–9]. We attempted to prepare samples having the M^{3+}/bmim$^+$ ratio equal to 2 mol/mol for M^{3+} = Al, Ga, or In. We were successful in preparing clear liquids for M^{3+} = Al and Ga when the ratio of chlorometallate anion/imidazolium cation, r, was 2; however, an insoluble precipitate was formed for M^{3+} = In when the ratio $r > 1.07$.

2.3. HCl absorption

The total HCl equilibrium absorption was determined volumetrically for each of the three chlorometallate ILs, $r = 2$ mol/mol, by a procedure reported earlier [7–9]. Our measurements of HCl absorption at room temperature over [emim]$^+$/[Al$_2$Cl$_7$]$^-$ RTIL showed the same equilibrium absorption coefficient as that reported by Campbell and Johnson for the same IL [10].

2.4. Probe reaction

The protocol was reported elsewhere for the toluene formylation in an isothermal autoclave [7–9]. It must be emphasized here that classical tests were completed to confirm the absence of mass transport effects in these reaction rate data.

2.5. ^{13}C NMR

The carbon external standard was a capillary filled with deuterated dimethyl sulfoxide (99%, DMSO) obtained from Sigma–Aldrich. The capillary tube was approximately 76.2–88.9 mm long 1.5 mm diameter and was filled to approximately 50.8–63.5 mm of the tube's length with the standard. This capillary was sealed so that HCl gas could not enter the capillary tube before it was secured inside the NMR tube. The RTILs were examined in a pressure valve sample NMR tube (obtained from NEW ERA Enterprises, Inc.; size = 5 mm o.d. × 130 mm long; model number NE-PCAV-5-130), which was filled in the Atmosbag^{TM} along with the different RTILs and standards. Only RTILs forming clear liquids were examined for their ^{13}C NMR spectra. The capillary tube containing the standard was placed inside the NMR tube and the RTIL or acid (sulfuric or triflic acid) was added.

The NMR tube was sealed, evacuated and filled with the desired gas to the required pressure, and contacted with this gas for 30 min. During the gas addition, the sample was shaken to promote mixing of the gas with the liquid, and bubbling of

the liquid was observed to indicate that good mixing had been achieved. All data were recorded on a Bruker 300×, with a 5 mm multinuclear probe. Typically, 256 scans were obtained for ^{13}C. The spectrometer settings for these analyses were standard settings already established by the scientists at the Georgia Tech NMR Center.

3. Results

3.1. HCl absorption

The absorption of HCl in the [bmim]$^+$[M$_2$Cl$_7$]$^-$ ILs at room temperature was determined by a classical volumetric device for M = Al, Ga, and In. The data of HCl mole fraction in the liquid versus partial pressure of HCl (atm) were fit to linear isotherms to develop the equilibrium adsorption coefficients, K (atm^{-1}), shown in Table 1. The uncertainty in these measurements suggest that the HCl absorption was the same for ILs derived from M = Al and Ga, but the HCl absorption was greater for the IL synthesized from M = In. It must be remembered that the total HCl absorption is not necessarily a reliable indicator of the potential for the IL to demonstrate Brønsted super acidity since some of the HCl can be sorbed into an IL without creating reactive sites for the toluene carbonylation reaction [7–9].

3.2. Reactivity

The fractional conversion of toluene versus time in an isothermal batch reactor at 298 K is shown in Fig. 1 for an IL derived from 1 mol of bmim$^+$ chloride with 2 mol of MCl$_3$ (M = Al, Ga, or In). The CO partial pressure was 11 atm, and the HCl partial pressure was 3 atm. The highest reaction rate was realized in the RTIL derived from the chloroaluminate anion; whereas, the RTIL derived from the chloroindate anion was inactive. The

Table 1
Equilibrium absorption coefficients for HCl into [bmim]$^+$[M$_2$Cl$_7$]$^-$ ILs

[bmim]$^+$[M$_2$Cl$_7$]$^-$	M^{3+} = Al	Ga	In
K (atm^{-1})	0.0323	0.0284	0.0422 ± 0.002
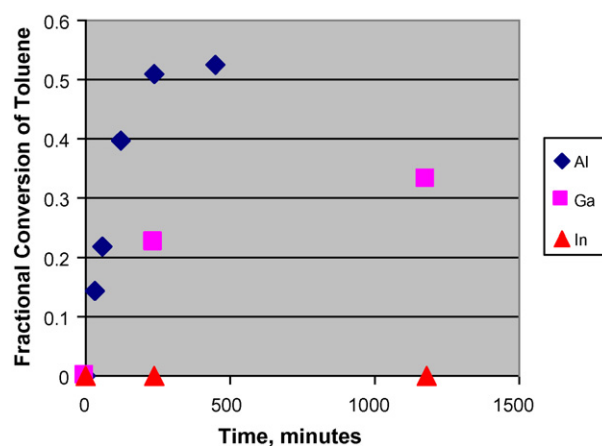
Fig. 1. Toluene conversion in [bmim]$^+$M$_2$Cl$_7$$^-$, M = Al, Ga, or In.

chlorogallate RTIL system showed an activity intermediate to these two extremes. The chloroindate RTIL was tested further using a control reaction demanding a lower Brønsted acidity: the reaction of toluene with benzoic anhydride [11]. This test showed results identical to those in the literature suggesting that the chloroindate RTIL prepared here is authentic but it could be lacking the super acidity required of the toluene with CO. This speculation of insufficient acidity generated in the chloroindate RTIL must be confirmed by an independent interrogation for the strength of the Brønsted acidity.

3.3. Probe of super acidity

One could directly probe the Brønsted acidity of the ionic liquids using ^{1}H NMR so as to infer the acidity of the protons from knowledge of the proton chemical shift. This direct approach proved unsuccessful [12] in the present work in that only very small peaks were detected upon admission of HCl gas to the IL, which prompted us to seek another method to characterize the ILs. One indirect method to characterize the acidity in such systems is to measure the effect of the acid upon the NMR spectrum of a weak base. Previous workers [13,14] showed that the ^{13}C NMR resonance of the carbonyl carbon in acetone was a sensitive indicator of Brønsted acidity by the following equilibrium:

$$(CH_3)_2-{}^{13}C=O + H^+A^- \Leftrightarrow [(CH_3)_2-{}^{13}C\text{-}OH^+]A^-$$
$$\Leftrightarrow [(CH_3)_2-{}^{13}CH^+=O]A^-$$

The nuclear environment of the carbonyl carbon in acetone becomes depleted of electron density when a strong acid is brought into contact with the weak base. The sensitivity of the characterization method could be improved by using acetone enriched with ^{13}C in the 2-position $(CH_3)_2-{}^{13}C=O$. Initial calibration of the NMR spectrometer at the Georgia Institute of Technology NMR Center for Excellence employed labeled acetone in dichloromethane using deuterated DMSO as the standard, to give an observed resonance for the labeled carbon at 205.9 ppm, which compares well with the resonance reported in the literature [13] (205 ppm). Further calibration standards included concentrated sulfuric acid and trifluoromethanesulfonic acid (triflic acid) as the standard Brønsted acids with deuterated DMSO as the external standard (Table 2). A single resonance was observed for the carbonyl carbon in each of these two acids at the following values of the chemical shifts: 243.4 and 245.7 ppm, respectively. Researchers [13] also reported a single resonance at 244 ppm for concentrated sulfuric acid that compares well to the value we observed: 243.4 ppm. These data permit us to distinguish between liquids having super acidic protons (e.g., triflic acid) and strong acids that do not have super acidic protons (concentrated sulfuric acid). Even for the super acidic species, only a single ^{13}C NMR resonance was observed in the carbonyl region of chemical shifts >225 ppm.
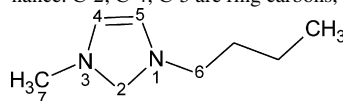
Some have expressed concern that acetone may undergo either a trimerization or a condensation reaction to form a species that might give multiple resonances in the carbonyl region under these conditions. The trimerization of acetone [15] is only
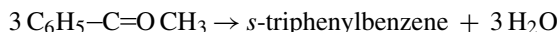
Table 2
^{13}C NMR resonances of labeled acetone/[bmim]$^+$[chloroaluminate]$^-$ IL before and after addition of HCl gas

Chemical shifts of acetone-2-^{13}C in bmim-Cl/AlCl$_3$ (1:2)

Peak identification	Before HCl	After HCl
H$^+$-acetone	No peak	246.65
H$^+$-acetone	243.10	243.02
H$^+$-acetone	240.28	240.09
C-2	133.83	133.75
C-5	123.46	123.38
C-4	122.18	122.10
N—CH$_2$—CH$_2$—CH$_2$—CH$_3$	49.66	49.57
DMSO	40.96	40.96
N—CH$_3$	36.36	36.27
N—CH$_2$—CH$_2$—CH$_2$—CH$_3$	31.16	31.07
N-CH$_2$—CH$_2$—CH$_2$—CH$_3$	18.80	18.71
N-CH$_2$—CH$_2$—CH$_2$—CH$_3$	12.87	12.78

Underlined carbon designates the atom interrogated by the corresponding resonance. C-2; C-4; C-5 are ring carbons, see figure below.

observed under strongly basic conditions, which will not be realized in the present system. One might expect a condensation reaction to occur since acetophenone undergoes a condensation reaction in HCl at 55 °C [16].

$$3\,C_6H_5-C=O\,CH_3 \rightarrow s\text{-triphenylbenzene} + 3\,H_2O$$

The products of this condensation reaction could frustrate the use of the acetone as a probe of super acidity because some of the peaks observed in the ^{13}C NMR spectrum might be ascribed to the protonated mesitylene. The ^{13}C NMR spectrum for mesitylene shows resonances at: 137.66, 126.99, and 21.17 ppm [17].

We have examined the complete ^{13}C NMR spectrum of the chloroaluminate-IL before and after addition of HCl gas and have assigned all of the peaks to those recognized for the carbons in the organic cation and the protonated acetone (Table 2). We see no peaks in the ^{13}C NMR spectrum either before or after addition of HCl gas that suggests that mesitylene was formed. Moreover, we see only a single, peak far downfield for the protonated acetone when triflic acid was interrogated by this method. Since the acidity of triflic acid is similar to that of these ILs, the multiple peaks observed when the ILs are examined, suggests that this criticism of the technique is not valid for our system and that these multiple peaks are characteristic of Brønsted sites having different acid strengths.

Consider the part of the ^{13}C NMR spectrum that characterizes the protonation of labeled acetone in contact with an RTIL synthesized from [bmim]$^+$[chloroaluminate]$^-$ and [bmim]$^+$[chlorogallate]$^-$ (1 mol bmim-Cl/2 mol MCl$_3$) after contact with dry HCl gas (Fig. 2a and b). The chemical shifts observed in the Fig. 2a–c were corrected using the observed and literature values of the chemical shift of DMSO standard (40.96 ppm) to determine the corrected chemical shifts which are reported here. For example the chloroaluminate RTIL in Fig. 2a showed a peak at 249.2 ppm which when compared to the observed chemical shift of the DMSO standard produced a
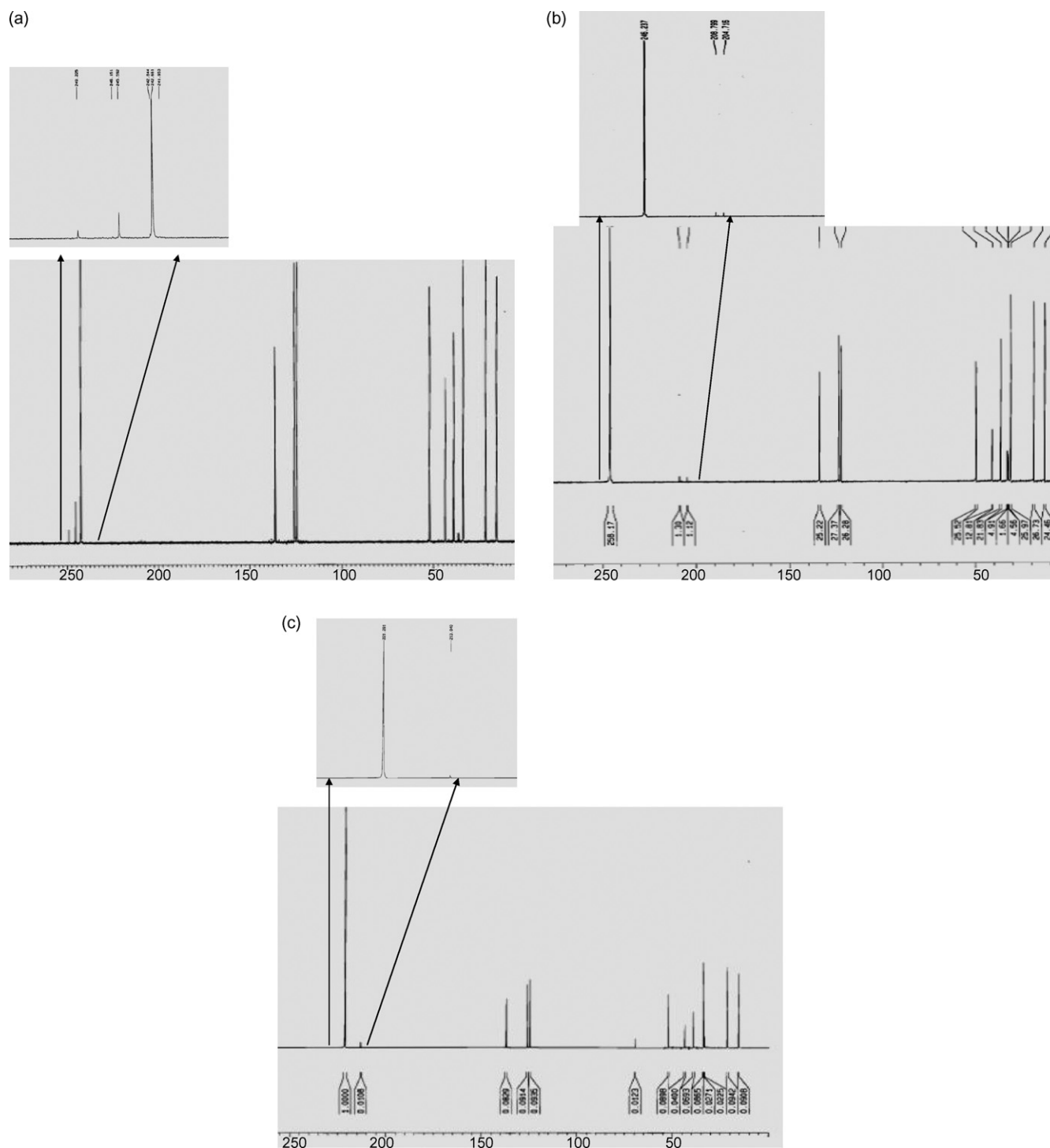
(a)

(b)

(c)

Fig. 2. (a) ^{13}C NMR of [bmim]$^+$[Al$_2$Cl$_7$]$^-$. (b) ^{13}C NMR of [bmim]$^+$[Ga$_2$Cl$_7$]$^-$. (c) ^{13}C NMR of [bmim]$^+$[In$_2$Cl$_7$]$^-$.

corrected chemical shift of 246.7 ppm, which is the value we report here in Table 3. In a similar manner, all of the observed chemical shifts were corrected using the observed and literature values of the DMSO standard.

Notice that the chloroaluminate RTIL (Fig. 2a) showed ^{13}C NMR peaks at 246.7 ppm, 243.8 and 240.5 ppm relative to the ^{13}C atom in the standard (DMSO) and the chlorogallate RTIL (Fig. 2b) showed a strong peak at 245.85 ppm and two

small peaks at 204.33 and 208.41 ppm, relative to DMSO. The chloroindate RTIL showed a single resonance at 218.44 ppm after HCl was added (Fig. 2c). For each spectrum, the data were shown magnified with the scale expanded to reveal more clearly the detail of the spectra.

In Table 3 we report these resonances of the labeled acetone as a probe of the acidity of the [bmim]$^+$[chloroaluminate]$^-$, −[chlorogallate]$^-$, and −[chloroindate]$^-$ RTILs before and after

Table 3
^{13}C NMR resonances of labeled acetone in [bmim]$^+$[chlorometallate]$^-$ RTIL after addition of HCl gas and evacuated

Sample	^{13}C-chemical shift(s) acetone (ppm)				Hammett acidity function, $-H_o$		
Sulfuric acid (100%)				243.4		12	
Trifluoromethanesulfonic acid (100%)				245.7			14.1
bmim-Cl:2AlCl$_3$ IL after HCl exposure (1/2 h)			240.1	243	246.7	9.2	11.8	14.9
bmim-Cl:2AlCl$_3$ IL evacuated after HCl exposure			240.3	243.1		9.4	11.8
bmim-Cl:2GaCl$_3$ IL after HCl exposure (1/2 h)	204.3	208.4			245.9	–		14.2
bmim-Cl:2GaCl$_3$ IL evacuated after HCl exposure		208.3	236.5			–	5.7
bmim-Cl:1.07InCl$_3$ IL after HCl exposure (1/2 h)		218.4				–	

Literature values of the Hammett acidity function, $-H_o$, together with the observed chemical shifts, CS, for sulfuric and trifluoromethanesulfonic acids were used to establish the correlation: $-H_o = a[CS] + b$.
This correlation was used to determine the values of the Hammett acidity function for the ILs shown in the table from the knowledge of the CS observed for these ILs.

exposure to dry HCl and estimates of the Hammett acidity functions for these RTILs. These estimates of Hammett acidities were developed by correlating the chemical shift data for triflic and sulfuric acid with assigned values for the Hammett acidity function of −12.0 for concentrated sulfuric acid and −14.1 for triflic acid so as to determine the coefficients in a linear equation expression the Hammett acidity as a function of the chemical shift, CS, observed for protonated acetone enriched in the 2-position with ^{13}C. We conclude that these chloroaluminate RTILs show at least three separate environments of Brønsted acidity of which one environment supports super acidity after the HCl was added to the IL (i.e., CS > 245 ppm from DMSO). Only the resonance at 246.7 ppm appears to be super acidic, $H_o = -14.93$, and thus can be attributed to the fast toluene carbonylation reaction in these samples. Upon evacuation of this sample, the observed chemical shift returns to near its original value before HCl was added for a H_o of −11.83. This RTIL showed very slow toluene carbonylation rate (*vide infra*) [7]. Thus, one may change the acidity and reactivity of the RTIL by over three orders of magnitude by changing the HCl partial pressure from 3 atm, absolute to a few milli-Torr.

From these results, we conclude that the chlorogallate RTIL shows one environment supporting super acidity, $H_o = -14.23$, and two other environments, which are only weakly acidic after the addition of HCl to a pressure of 3 atm. Evacuation of the HCl from the chlorogallate IL reduces the Hammett acidity function to a value of 5.66 showing a variation in the acidity of nearly eight orders of magnitude. Such variation in the acidity by evacuation of HCl could lead to a commercial process whereby the RTIL can be freed from the product aldehyde with heating *in vacuo*. The chloroindate shows only a single resonance upon addition of HCl, which is not super acidic after addition of HCl to a pressure of 3 atm. All of the RTILs show acidic protons before HCl gas was admitted which is probably the result of the reaction of adventitious water with the chlorometallate in the IL to form nascent HCl, which in turn is absorbed by the RTIL. This behavior was reported by others [18].

The ranking of acidity in these RTILs, as inferred from the Hammett acidity function, appears to mimic the ranking of reactivity towards the toluene carbonylation. To understand better these results, we show the observed rate constants at room tem-

perature for the toluene carbonylation over these RTILs versus the Hammett acidity function, estimated from the chemical shift of the carbonyl carbon in labeled acetone (Fig. 3). We also show the reactivity of the carbonylation in triflic acid [19] which shows a value of $H_o = -14.1$. When the HCl was evacuated from [bmim]$^+$[Al$_2$Cl$_7$]$^-$ we showed that the reactivity of the arene formylation was much lower [7] and that the estimated H_o was also less acidic as determined from the ^{13}C NMR data of labeled acetone. We did not plot the data for the RTIL formed from InCl$_3$, which was inactive for the toluene carbonylation ($k \sim 0$).

It comes as no surprise that these data describe a single line. Consider the following equation which was derived by combining the definition for the Hammett acidity function together with the expression of the pseudo, first-order rate constant reported here, $k_{observed} = k_{instrinsic}(Ka_{CO}a_{H^+})^\alpha$.

$$\log k_{observed} = \log \left[k_{intrinsic} \left(\frac{Ka_{CO}\gamma_{BH^+}}{\gamma_B} \right)^\alpha \right] + \alpha(-H_o)$$

where K is the equilibrium absorption coefficient for CO gas into the RTIL, a_{CO} is the activity of CO gas and α is the exponent of proton activity, a_{H^+}. The activity coefficients for the protonated and unprotonated acetone are γ_{BH^+} and γ_B, respectively. The value of α for the present case is 0.96 indicating a proton activity exponent of 1. If we may relate α to the molecu-
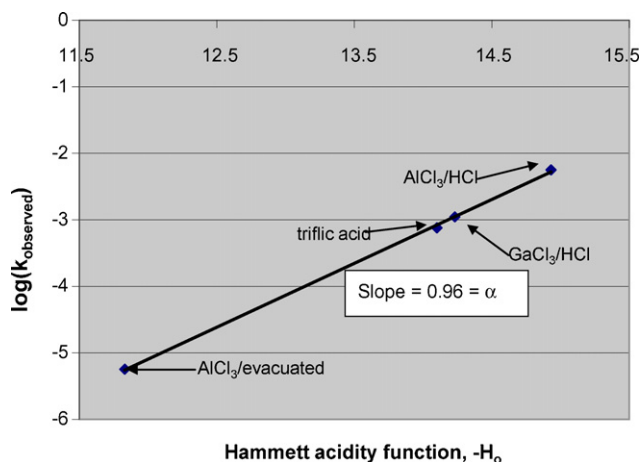

Fig. 3. Toluene carbonylation activity vs. Hammett acidity function.

larity of the rate-determining step, then these results suggest that one proton would be needed to produce the super acidity in the IL and this proton would be required to produce the formyl cation needed for the reaction resulting in a rate equation that is first order in the activity of the formyl cation. The traditional electrophilic substitution reaction, often used to explain the formylation of arenes, requires a single proton in the rate-determining step and shows a rate equation that is first order in the formyl action, thereby reinforcing our findings here [2].

4. Discussion

Others [20] have attempted to model the siting of HCl in chloroaluminate RTILs derived from 1-ethyl-3-methyl-1*H*-imidazolium chloride using quantum mechanical methods. These researchers attempted this modeling using only the chloroaluminate anion without the cation present and they found only one optimized geometry for the siting of the HCl. The HCl molecule was attached to the $Al_2Cl_7^-$ anion by hydrogen bonding to one of the terminal Cls. We extended this approach, using semi-empirical methods, to determine the optimized geometry of HCl in the *anion/cation pair* to find three locations for the HCl in the chloroaluminate RTIL prior to it being ionized into H^+-Cl^- [8]. One of the locations (b) was the same as that predicted by Chandler and Johnson [20], another location was wholly within the anion (a) and the last location was wholly within the cation (c). The software used here did not predict the activation of the HCl molecule since we did not attempt a transition state calculation, but this activation must surely occur to produce facile protons needed for the toluene formylation reaction.

The predicted ^1H NMR chemical shifts were 15.4, 14.4, and 2.6 ppm downfield from tetramethylsilane (TMS) for the HCl sited in the three positions (a, b, and c, respectively) suggesting that one site would show very weak acidity (2.6 ppm) and the other two sites should be much more acidic [12]. The predicted ^1H NMR of isolated, gaseous HCl was 1.68 ppm. Calculations of free energy of absorption showed that the lowest acidity sites (c) would be present in the largest amount and that the highest acidity sites (a) would be present in the smallest amount [12]. The third site (b), having intermediate acidity, was predicted to be in an abundant intermediate to the other two. These ^1H NMR predictions for the HCl located in the IL can be used to understand better the observed ^{13}C NMR spectra of ^{13}C-enriched acetone. That is, these data suggest that the ^{13}C resonance at 246.7 ppm would be characteristic of the most acidic site and this site might be implicated in the toluene carbonylation that requires super acidity. This conclusion appears to be confirmed by literature data, which suggest that enriched ^{13}C acetone in contact with $AlCl_3$ shows a chemical shift of 246 ppm and aluminum chloride is a known conversion agent for arene carbonylation [21]. We know that 100% sulfuric acid is not a conversion agent for arene carbonylation and its chemical shift (244 ppm) would seem to mark a lower limit on the acid strength needed to initiate the arene carbonylation reaction. Therefore, the peaks observed at chemical shifts of 244 ppm and

lower may not be sufficiently acidic to cause rapid carbonylation of the arene.

Reported elsewhere [12], we showed quantum mechanical predictions that the chlorogallate and chloroindate ILs also can host the HCl molecules in three different environments having different free energies of absorption. Moreover, the ^1H NMR chemical shifts of the HCl predicted for the most acidic sites in these ILs were 15.1 and 10.7 ppm downfield from TMS. Thus, these calculations predict an effect upon the HCl acidity as a result of changing the Lewis acid in the following order: $Al > Ga \gg In$. This ranking of Brønsted acidity, as inferred from the predicted proton chemical shifts, appears to be confirmed by the observed chemical shifts in the ^{13}C NMR of labeled acetone where the chloroaluminates showed the largest chemical shift for the acetone protonated by the most acidic site ($\sim$246.7 ppm) followed chlorogallate IL which showed a chemical shift of 245.9 ppm. The chloroindate ILs show only one resonance in the ^{13}C NMR spectra when HCl was absorbed at 218.4 ppm and we infer from these data that HCl was hosted by only one type of site in these ILs and this environment produced a very weak, Brønsted acid site. While the amount of HCl absorption in the chloroindate ILs was the largest, the Hammett acidity function was the least acidic of the three ILs that we tested here and it was apparently not sufficiently acidic to support toluene carbonylation although the same IL was active for another reaction: toluene reacting with benzoic anhydride [11].

The proposed hypothesis advanced earlier is that the strengths of the Lewis acids determine the strength of the Brønsted acidity resulting from contacting the IL with HCl gas. The strength of Lewis acids is often explained in terms of the hard–soft acid properties as defined by Pearson [22] who introduced the concept of hard and soft acids and bases (HSAB) in order to explain affinities between acids and bases that do not depend on electronegativity or other related macroscopic properties. This theory may be attractive in characterizing the properties of ILs formed from the interaction of one cation with a family of anions such as $M_2Cl_7^-$. This HSAB theory predicts decreasing Lewis acidity for the family of chlorometallate anions developed from the series of members from Group IIIA metalloids: Al, Ga, and In. The anions are considered "softer" as the size of the metalloid increases from Al, to Ga, to In. The resulting Brønsted acid strengths of these ILs appear to mimic the decreasing Lewis acidities.

The successful correlation of the apparent rate constant for toluene carbonylation with proton activity (i.e., $-H_o$) is consistent with the reaction mechanism whereby proton acidity is the controlling factor when all other reaction conditions are constant (CO partial pressure and temperature) [2]. The variation of Brønsted acidity in response to the strength of the Lewis acid partner in the RTIL suggests that activation of HCl to form a facile proton occurs with participation of the Lewis acid. Our modeling suggests that two of the three possible sites for HCl activation are in the proximity of the Lewis acid and these two sites are predicted to be the most acidic. Moreover, this molecular modeling successfully predicted the observed ranking of Brønsted acidity when HCl was added to ILs developed from MCl_3 having different Lewis acidities.

5. Conclusions

These data show how the activity of the ILs can be tuned by varying either the HCl partial pressure and/or the MCl_3. Moreover, the acidity of the ILs is lower for M^{3+} chlorides that show "softer" cations. This science can be used to tailor an acidic IL for the demands of a reaction.

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