

Arene carbonylation in acidic, chloroaluminate ionic liquids

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Abstract

Chloroaluminate ionic liquids formed from either 1-ethyl-3-methyl-1*H*-imidazolium-chloride (EMIM-Cl) or 1-butyl-3-methyl-1*H*-imidazolium chloride (BMIM-Cl) were examined as conversion agents for toluene carbonylation at room temperature and at pressures of 150 and 1100 psig. The effect was examined upon the toluene conversion and selectivity for changing the ratio of AlCl₃/EMIM-Cl or AlCl₃/BMIM-Cl from 1/2 to 2 mol/mol at a constant HCl partial pressure of 30 psig as well as the effect of changing the HCl partial pressure from 0 to 30 psig at a constant value of AlCl₃/EMIM-Cl or AlCl₃/BMIM-Cl = 2. The effect upon reactivity was also determined for changing the Al³⁺/toluene ratio at a constant value of AlCl₃/EMIM-Cl = 2 when the *P*_{HCl} was 30 psig for pressures of 150 and 1100 psig.

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1. Introduction

Ionic liquids (ILs) are substances that form liquids at room temperature and lower at normal, atmospheric pressures [1]. Many of these ILs are formed when organic cations, \mathcal{O}^{+n} , are mixed with either organic or inorganic anions, A^{-m} . Some ILs are hydrophilic (e.g., $A^{-m} = \text{AlCl}_4^{1-}$) while others are hydrophobic ($A^{-m} = \text{CF}_3\text{SO}_3^{-1}$). The very hydrophilic, chloroaluminate ILs, $\mathcal{O}^+[\text{Al}_n\text{Cl}_{3n+1}]^-$, are said to exhibit acidity when $n > 1$ [2,3]. These ILs may be prepared using organic cations such as the pyridinium ($\text{C}_5\text{H}_5\text{N}^+$) or the substituted imidazolium, $(\text{R}-\text{C}_3\text{N}_2\text{H}_5-\text{R}')^+$. The substituted imidazolium cation reported often in the literature is 1-ethyl-3-methyl-1*H*-imidazolium cation (EMIM⁺). Recently, it was reported that strong, Brønsted acidity could be created in the IL, EMIM⁺(Al₂Cl₇)⁻, upon exposure to dry, HCl gas [4].

Ma and Johnson [5] showed that carbocations were formed from selected arene hydrocarbons when combined with ILs derived from trimethylsulfonium bromide–AlCl₃/AlBr₃ and exposed to HBr gas. These results suggested to us that the combination of a Brønsted acid with the chloroaluminate IL might result in a potent conversion agent for reactions demanding high Brønsted acidity.

Room temperature ILs have been reported as conversion agents for arene carbonylation, [6] alkylation of benzene with dodecene, [7] Friedel–Crafts sulfonylation, [8] and Friedel–Crafts alkylations and acylations [9]. There is a continuing interest in the subject of arene carbonylation, especially in strong acids such as trifluoromethanesulfonic acid [10] and environmentally benign alternatives are sought to HF/BF₃ and to AlCl₃ as conversion agents. Moreover, it was of interest to explore the properties of the chloroaluminate/EMIM-Cl and chloroaluminate/BMIM-Cl ILs as a function of *P*_{HCl} and as a function of the *n* in the formula: $\mathcal{O}^+[\text{Al}_n\text{Cl}_{3n+1}]^-$, where \mathcal{O} is either EMIM or BMIM. The probe reaction used for these characterizations is toluene carbonylation, as it demands Brønsted acidity [10].

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2. Experimental

2.1. Chemicals

The imidazolium compounds were obtained from Sigma–Aldrich and used without further purification. Aluminum chloride (99.99%), obtained from Sigma–Aldrich, was sublimed under a vacuum before use. Toluene (anhydrous, 99.8%) was 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.

2.2. Preparation of ILs chloroaluminates/EMIM-Cl and chloroaluminates/BMIM-Cl

The weighing instrument, chemicals, and material transfers for AlCl_3 , either EMIM-Cl or BMIM-Cl were placed in an AtmosBag filled with dry Ar. AlCl_3 is weighed; either EMIM-Cl or BMIM-Cl is added to obtain the desired AlCl_3/O^+ ratio.

2.3. Reaction studies—low pressure

Low-pressure reactions were carried out in a Fisher Porter glass tube. A dried Fisher Porter tube with a stirring magnet was placed in the AtmosBag. The chloroaluminate/EMIM-Cl IL or chloroaluminate/BMIM-Cl IL was weighed into the Fisher Porter tube. Toluene was added to obtain the desired Al^{3+} /toluene ratio. The reactor was sealed, removed from the AtmosBag and purged with HCl gas before HCl gas was added to the desired partial pressure and then this mixture was stirred for 30 min at room temperature. Carbon monoxide was then added to give a total pressure of 150 psig. The reaction temperature was room temperature and the CO pressure was monitored to verify CO consumption. After the reaction was completed, the reactor was slowly vented and purged with Ar. The mixture was poured into a separatory funnel filled with an ice/distilled water mixture so as to dilute the acidic components. The organic layer was collected after it was neutralized with a saturated sodium bicarbonate solution. Previous experiments with HOTF showed that a stirring rate of 800 rpm was sufficient to overcome mass transfer resistance. Since the conversion rate in the IL is similar to that for HOTF (vide infra) when the acid/substrate = 10 mol/mol, we will use a similar stirring rate of 1000 rpm.

2.4. Reaction studies—high pressure

The high-pressure experiments were completed using the same procedure described in the low-pressure experiments, but we used a Parr Instrument Co. (Moline, IL) stirred autoclave (50 cm³) lined with Hastalloy C. The stirring rate was adjusted to 1000 RPM. The post-reaction work-up of the products after the high pressure runs was the same as that described for the low pressure runs. After the addition

of HCl, carbon monoxide was added to a total pressure of 1100 psig.

2.5. Analytical

Organic products were analyzed in a HP-5890 Series II Plus GC equipped with a HP-5972 mass spectrometer. High purity helium (99.995, Airgas) was the carrier gas and the column was 15 m long, 0.25 mm i.d., and 0.25 μm film thickness obtained from Supelco (SPB-524032). An analytical method was developed to separate all the liquid-phase products using the following GC oven protocol: initial temperature = 35 °C, hold for 5 min, then increase temperature 10 °C per min, and finally hold temperature at 180 °C for the final 5.50 min.

3. Results—activity versus intrinsic acidity

Five ILs, $[\text{Al}_n\text{Cl}_3]^-/\text{O}^+$, were prepared for which $n = 1/2, 1, 1.11, 1.5, \text{ and } 2$ when O^+ was 1-ethyl-3-methyl-1*H*-imidazolium (EMIM) cation and three more ILs for which $n = 1.11, 1.5$ and 2 when O^+ was 1-butyl-3-methyl-1*H*-imidazolium (BMIM) cation. These ILs were used as conversion agents for the low-pressure, carbonylation of toluene at room temperature using an amount of IL that would give 1 mol Al^{3+} /mol of toluene. One additional IL was prepared by the action of HCl gas contacting 3-Me-imidazole at room temperature [11]. The product of this reaction is 3-Me-imidazolium chlorohydrogenate and this IL represents the case where $n = 0$. BMIM-Cl or EMIM-Cl were not used for this case since both form solids upon reaction with HCl at room temperature. We began each of these tests with the same amount of toluene. The gas phase contained HCl gas at 30 psig and the balance was CO for a total pressure of 150 psig and the reaction was stopped after 16 h. From the literature [3], it was expected that only the acidic ILs, i.e., $n > 1$, should be active for this carbonylation and we did observe this trend (Fig. 1). Even with HCl added to the gas phase at 30 psig, no reaction product, *p*-tolualdehyde, was observed for the three ILs for which $n = 0, 1/2, \text{ or } 1$; however,

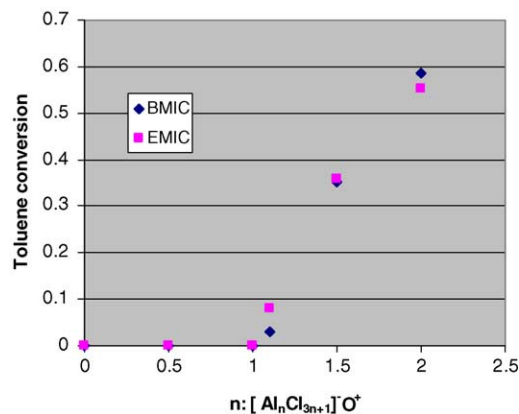


Fig. 1. Toluene conversion as a function of $n: [\text{Al}_n\text{Cl}_{3n+1}]^- \text{O}^+$.

increasing toluene conversion was observed for the three ILs having $n = 1.11, 1.5$ and 2 derived from either BMIM-Cl or EMIM-Cl. Previous authors have characterized these ILs as intrinsically acidic when $n > 1$ and our results appear to confirm this characterization when the probe reaction is toluene carbonylation, which is known to demand strong acidity.

These results also suggest that the ILs derived from either EMIM-Cl or BMIM-Cl were equally active for the toluene carbonylation reaction when the value of n was >1 . BMIM-Cl was reliably dry from the source whereas some batches of the EMIM-Cl were contaminated with water. Accordingly, we used BMIM-Cl as the organic cation in many of the remaining parts of this manuscript.

4. Results—activity versus Brønsted acidity

We were interested to know if the intrinsic acidity of the acidic chloroaluminate IL could be increased by adding a Brønsted acid, as suggested by the results of others [4,12]. The Brønsted acid was HCl gas and the acidic chloroaluminate system was EMIM⁺/Al₂Cl₇⁻. This choice of HCl as the Brønsted acid follows from (1) the fact that its concentration in the IL can be adjusted reversibly by changing the partial pressure of HCl above the IL and (2) the acidity of the resulting IL was claimed to be super acidic [4,12,13]. For these tests the Al³⁺/substrate ratio was 1 mol/mol and the dissolved HCl concentration in the IL phase was adjusted by changing the HCl gas partial pressure [13] (0, 5, 15, and 30 psig) while the partial pressure of the CO was adjusted so that the total pressure remained constant at 150 psig. All tests were completed at room temperature for varying durations from 15 min to 21 h.

Even the IL not treated with HCl gas showed some low activity for toluene carbonylation (Fig. 2, ~12% toluene conversion in 4 h); however, when HCl was added to the gas phase in little as 5 psig, the toluene conversion at 4 h was $>30\%$. Other runs for the HCl partial pressure was ≥ 15 psig showed about 40–45% toluene conversion at 4 h. Apparently, the re-

activity of the IL system for this Brønsted-initiated reaction appears to be greatly enhanced with the addition of HCl in the gas phase even at modest partial pressures. These results are consistent with the findings of others who claimed that HCl gas was absorbed by the acidic, chloroaluminate ILs developed from EMIM⁺ as the organic cation [4,7].

5. Results—activity versus Al³⁺/substrate ratio

The effect of changing the Al³⁺/substrate ratio has been reported for the Gatterman-Koch, AlCl₃-mediated carbonylation of benzene at high pressure (~1000 psig) [14]. They showed that the benzene conversion versus time curves were higher for a series of reaction isotherms in which the Al³⁺/substrate increased from 1/2 to 1. We were curious if this same result could be observed for the chloroaluminate ILs. In determining the effect of changing Al³⁺/toluene, we must be mindful of the findings of Campbell and Johnson [13] who showed the [HCl] dissolved in the IL also depended upon the intrinsic acidity of the IL (i.e., the Al³⁺/EMIM⁺ ratio). Accordingly, batch reactor data were collected at room temperature and for HCl partial pressure equal to 30 psig when the total pressure was adjusted to either 150 or 1100 psig by adding dry CO. Each run contained an acidic chloroaluminate IL [(Al_nCl_{3n+1})⁻/EMIM⁺] for which $n = 2$, but the initial amounts of IL were increased at constant initial amount of toluene so that the Al³⁺/toluene ratio was 1/2, 1, 1.5 or 2 mol/mol. The transient results are shown in Fig. 3 for each value of Al³⁺/toluene. These data show transients in the conversion versus time that are similar to the earlier work [14] for the benzene carbonylation in AlCl₃. For each ratio of Al³⁺/toluene, the toluene conversion increased rapidly at short reaction times, then, the conversion changed little at long reaction times. The ultimate toluene conversion appears to increase with increasing value of Al³⁺/toluene at low (150 psig) and high total pressures (1100 psig). The rate of approach to ultimate conversion is higher for the runs operated at 1100 psig than those completed at 150 psig.

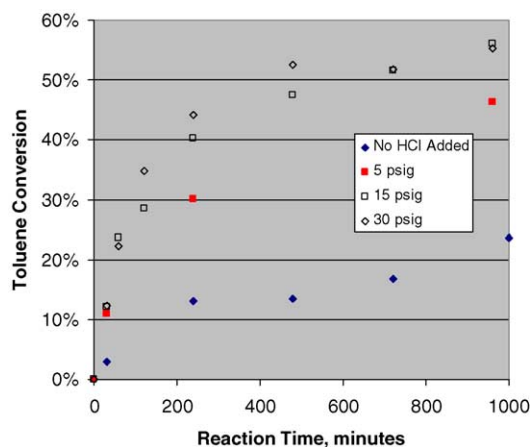


Fig. 2. Effect of HCl pressure upon reactivity.

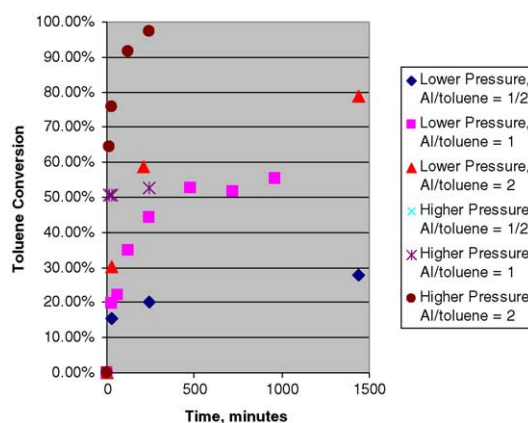


Fig. 3. Toluene conversion for changing the Al³⁺/toluene ratio.

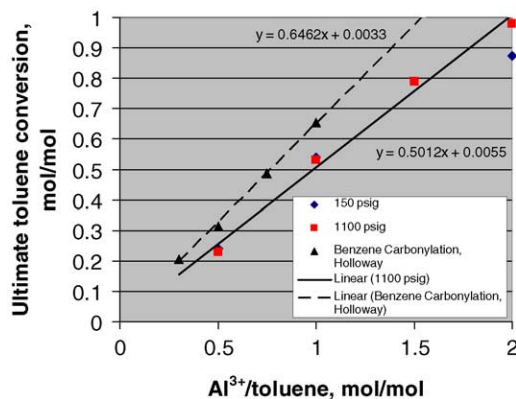


Fig. 4. Ultimate toluene conversion vs. Al^{3+} /toluene.

When Al^{3+} /toluene = 1/2, the ultimate conversion was 28% for both low and high pressure runs. For the 1100 psig run, Al^{3+} /toluene = 1, the conversion at 15 min (50%) was nearly equal to the ultimate conversion observed for this run (51%) and for the lower pressure run (~50%). When the Al^{3+} /toluene ratio was 3/2, only one run was completed for which the conversion was 79% at 21 h for the high pressure run. For the runs at Al^{3+} /toluene = 2, the ultimate conversion was 97.2% at 1100 psig (~4 h) and 87.2% at 150 psig (16 h). If the reaction had been allowed to run at these conditions for a longer time, the ultimate conversion would be nearly complete. Taken together, these data suggest that Al^{3+} is the limiting reagent in these runs.

The ultimate conversion of toluene increased linearly with increasing values of the Al^{3+} /toluene ratio, Fig. 4, showing a slope of $\sim 1/2$ and an intercept near zero. Holloway and Krase [14] observed a similar result for benzene carbonylation over AlCl_3 at 1000 psig and room temperature although the slope of their data, when plotted on the same figure, was higher (~ 0.64 mol converted/mol AlCl_3) also with an intercept near zero. For the runs where the toluene conversion < 0.8 , the reaction products remained as a liquid; however, when the conversion exceeded a value of 0.8 a slurry was formed. The data at the low and high pressure formed a single line when the conversion was less than 0.8; however, for the data at higher conversion, the data collected from the lower pressure run did not obey this same relationship. Mass transport effects could be influencing the lower pressure data at the higher conversions when the slurry was formed.

5.1. Selectivity

The regio-selectivity to the three isomers (*p*-tolualdehyde, *o*-tolualdehyde, *m*-tolualdehyde) in all of these tests was 90%/7%/3% at conversions approaching 100%. There was no substantial effect upon this distribution of regio-isomers for varying the HCl partial pressure, the Al^{3+} /EMIM-Cl ratio, the Al^{3+} /toluene ratio, or the P_{CO} when the toluene conversion of the tests were similar. The selectivity to the *para*-isomer approached 95% at lower toluene conversions. The chemical

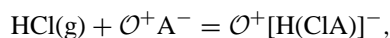
selectivity was less than $< 3\%$ to the only other products: di- and tri-tolymethanes. These regio- and chemical-selectivity for the IL systems are very similar to those we reported for the triflic acid system when the acid/substrate ratio > 6 mol/mol [10].

An additional test was completed to address the issue of isomerization of tolualdehyde after its formation. *p*-tolualdehyde was added to an acidic IL ($n = 2$) in the ratio of one mole of aldehyde per mole of Al in the IL and HCl gas was contacted with this IL at a pressure of 30 psig for 1/2 h. The HCl was vented and this mixture was stirred at room temperature for 9 h. The products were worked up per the usual procedure and analyzed by GC/MS. No other isomers of tolualdehyde were observed to form in this mixture. Apparently, the IL does not promote the isomerization of *p*-tolualdehyde at these conditions.

6. Discussion

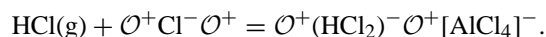
It appears that acidic, chloroaluminate, ILs formed from either BMIM-Cl or EMIM-Cl are equally strong acids that can initiate the toluene carbonylation reaction at even modest pressures. We [10] observed, initial toluene conversion rates of 2 h^{-1} in triflic acid, when the acid/substrate ratio was 10 for a total pressure of 1100 psig at room temperature. This conversion rate in triflic acid can be compared to the data from the IL (2.6 h^{-1}) having Al^{3+} /toluene = 2 also at 1100 psig and room temperature. Considering that these initial reaction rate data are free from mass transport effects, it becomes obvious that the acidic chloroaluminate ILs described here have activities that are similar to or greater than that of the triflic acid system for the toluene carbonylation reaction. One final comparison from the old literature is appropriate. Holloway and Krase [14] showed that benzene could be carbonylated in CO (1000 psig) at room temperature using a molar equivalent of AlCl_3 . Under the proper conditions, the initial benzene conversion rate was 2.4 h^{-1} which was only slightly smaller than what we report here for the initial toluene carbonylation rate in the acidic chloroaluminate/EMIM-Cl ILs (2.6 h^{-1}).

Chloroaluminate ILs, $\text{O}^+[\text{Al}_n\text{Cl}_{3n+1}]^-$, prepared with $n \leq 1$ and derived from either BMIM-Cl or EMIM-Cl are not active (Fig. 1) for the toluene carbonylation reaction even when HCl is added to the gas phase at a partial pressure of 30 psig. HCl is absorbed [13] by these basic or neutral ILs in concentrations greater than the intrinsically acidic ILs; however, the HCl does not produce Brønsted acids as indicated here and as speculated by others [13]. These authors represent HCl absorption by ILs as follows:



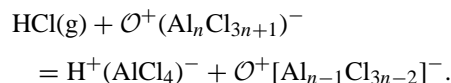
where O^+ is the organic cation (BMIM-Cl or EMIM-Cl), A^- is the chloroaluminate anion and its speciation depends upon the value of n in the formula: $\text{O}^+[\text{Al}_n\text{Cl}_{3n+1}]^-$. When $n = 1$; then they suggest that the anion A^- is the monomeric chloroaluminate anion, AlCl_4^- , and the proton in the result-

ing species $[\text{HCl}(\text{AlCl}_4)]^-$ is not labile and therefore cannot act as a Brønsted acid. Moreover, when n is less than 1, say $1/2$ then, $\text{A} = \text{AlCl}_4^-$ and the HCl absorption can be modelled as:



The anionic species $(\text{HCl}_2)^-$ also is very unlikely to surrender a labile proton. If we use this model for this system of ILs, then it becomes obvious that no carbonylation activity will result from the basic or even neutral chloroaluminate ILs notwithstanding that HCl is present in the system. The genesis of labile protons in the acidic chloroaluminate ILs will be discussed below.

The effect of n upon the formation of Brønsted acidity with the addition of HCl can also be related to its effect upon the speciation of the Al in the IL [1]. That is, when $n > 1$, a fraction of the total aluminum in the IL is a dimer, $[\text{Al}_2\text{Cl}_7]^-$ and a trimer, $[\text{Al}_3\text{Cl}_{10}]^-$. We speculate that both multimeric chloroaluminate species can form protons by interacting with HCl via a mechanism shown below.¹



An alternative formalism has been recently described by Chandler and Johnson [15]. This reaction can proceed further to form additional labile protons such that when $n=3$ originally, then two moles of protons could be produced. The toluene conversion data could be correlated with the mol fraction of the total Al^{3+} that can produce protons and weighed these mole fractions according to their reaction stoichiometry to produce protons: number protons = $\sum_i^n (i-1)X_i$; where X_i = mole fraction of chloroaluminate of nuclearity = i . That is, when $i=1$, the chloroaluminate anion is a monomer, when $i=2$, it is a dimer, etc. The result, Fig. 5, shows a linear relationship between the toluene conversion and the weighted mole fraction of the Al species [1] that are capable of forming protons when HCl is added to the IL: $\sum_i^n (i-1)X_i$. This result should not be a surprise in view of the reports reported by Campbell and Johnson who showed that the proton concentration in the same IL does change linearly with the fraction of the Al that was initially present as a dimer [13].

Consider further the finding that the slope of these curves is ~ 0.57 . The conversion of toluene is limited by the amount

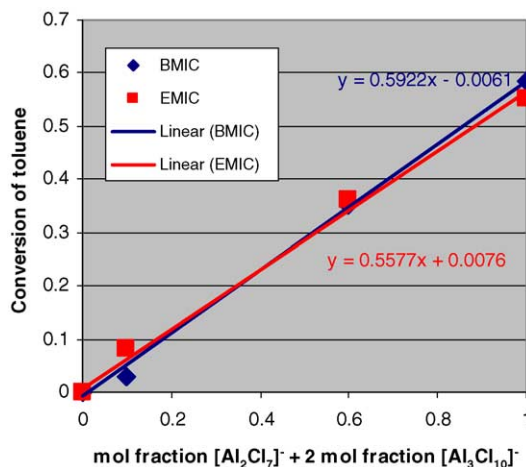
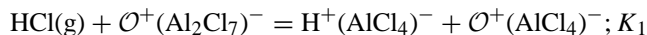


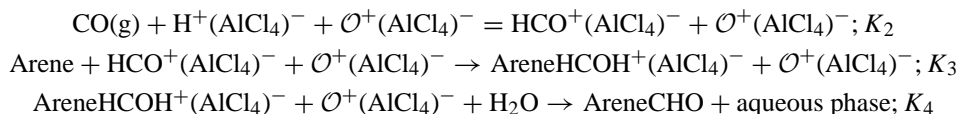
Fig. 5. Toluene conversion vs. mol fraction $[\text{Al}_2\text{Cl}_7]^- + 2 \text{ mol fraction } [\text{Al}_3\text{Cl}_{10}]^-$.

of Al^{3+} present initially here at 1 mol Al^{3+} /mol toluene. In other tests, vide supra, the ultimate conversion was 0.97 for a starting mixture having 2 mol Al^{3+} /mol toluene when the value of $n=2$. Using this final conversion of 0.97 instead of a value of 0.58, slope now becomes $(0.57 \times 0.97/0.58 = 0.95)$. This slope suggests that one mole of toluene is converted for every mole of protons that are formed by the reaction of HCl with the Al species in the IL.

The mechanism [16] for the toluene carbonylation reaction was reported to be a Brønsted-mediated reaction by electrophilic substitution of an aryl ring hydrogen. *Para*-selectivity is favored by this mechanism, which is reported to proceed by a carbocation intermediate. For the triflic acid system, the source of the proton is obvious; however, for the chloroaluminate ILs the genesis of the protons must be examined further. Consider the data and subsequent interpretation of their data by Campbell and Johnson [13] who speculated that the HCl gas became absorbed in the IL by a mechanism shown below.



They speculated that the proton associated with the chloroaluminate anion, $(\text{AlCl}_4)^-$, was labile and thus could function in the role normally associated with a labile proton. Consider now the role of this labile proton in the reaction mechanism normally advanced for arene carbonylation:



¹ Chandler and Johnson express this equation for $n=2$ by the following formalism: $\text{HCl}(\text{g}) + \mathcal{O}^+[\text{Al}_2\text{Cl}_7]^- = \mathcal{O}^+[\text{ClHAl}_2\text{Cl}_7]^-$, for the sake of clarity in the discussion here, we will use the formalism found in references [1,13].

Here the labile proton is associated with one monomeric chloroaluminate anion whereas the organic cation ($\mathcal{O}^+ = \text{BMIM}^+$) in the IL is associated with the other chloroaluminate anion. For this mechanism, the absorption of HCl and

its association with the IL species is assumed to be reversible under equilibrium constant K_1 and that the formation of the formyl cation is also reversible and governed by equilibrium constant, K_2 . The electrophilic substitution reaction is presumed to be the rate-determining step under rate constant K_3 . The product can be freed from the carbocation intermediately upon contact with water. This step is not reversible because the formed hydronium ion, H_3O^+ , is of too low acidity to catalyze the reverse step in the toluene carbonylation reaction [10]. The data shown in Figs. 3 and 4 made it necessary to derive a rate equation assuming that the Al^{3+} species was the limiting reagent. One rate law derived from this mechanism for which the chloroaluminate species is the limiting reagent is as follows:

$$\text{rate} = K P_{CO} [Al^{3+}]_0^2 [H^+] (1-f) (M-1/2f)$$

where, $M = N_{tol}^0 / N_{AlCl_3}^0$ and f is the fractional conversion of Al^{3+} . Integration of this rate law according to the isothermal, batch design equation leads to the following equation:

$$\left[\frac{1}{M-0.5} \right] \ln \left[\frac{M-1/2f}{M(1-f)} \right] = \frac{K}{2} [Al^{3+}]_0 P_{CO} [H^+] t; \quad \text{for } M > \frac{1}{2} \quad (1)$$

$$\frac{f}{1-f} = \frac{K}{2} [Al^{3+}]_0 P_{CO} [H^+] t; \quad \text{for } M = \frac{1}{2} \quad (2)$$

The conversion of the Al^{3+} species, f , is directly related to the toluene conversion using the stoichiometry revealed in Fig. 4: 1/2 mol of toluene is used in the conversion of 1 mol of Al species. The toluene conversion data (Fig. 2) were fit to Eqs. (1) and (2), using this stoichiometry for varying P_{HCl} when $M = 1$ and the total pressure was 150 psig (Fig. 6). The slopes of these curve-fits are the product: $K [Al^{3+}]_0 P_{CO} [H^+]$. For these tests P_{CO} and the temperature was nearly constant. Thus, the variation of the slope is proportional to the $[H^+]$ in the IL.

Next, these slope data were plotted, Fig. 6, versus the absolute partial pressure of HCl (psia) to determine how the product $K [Al^{3+}]_0 P_{CO} [H^+]$ responded to increasing partial pressure of HCl (Fig. 7). These results show almost a linear increase in the slopes of Fig. 6 with increasing partial pressure of HCl, when expressed as an absolute pressure. Since K , $[Al^{3+}]_0$ and P_{CO} are nearly constant in these tests, we conclude that the $[H^+]$ in the IL increases linearly with increasing partial pressure of HCl gas above the IL. A linear relationship of $[H^+]$ with HCl pressure was also reported earlier by Campbell and Johnson [13] who showed that the concentration of $[H^+]$ in an acidic, EMIM-Cl/chloroaluminate IL varied with P_{HCl} as follows:

$$[HCl], \text{ mM} = \{1.3 \times 10^3 - 1.43 \times 10^3 X_{AlCl_3}\} P_{HCl}$$

where P_{HCl} was expressed in atmospheres and X_{AlCl_3} is the mole fraction of $AlCl_3$ in the IL which equalled 2/3 for these data.

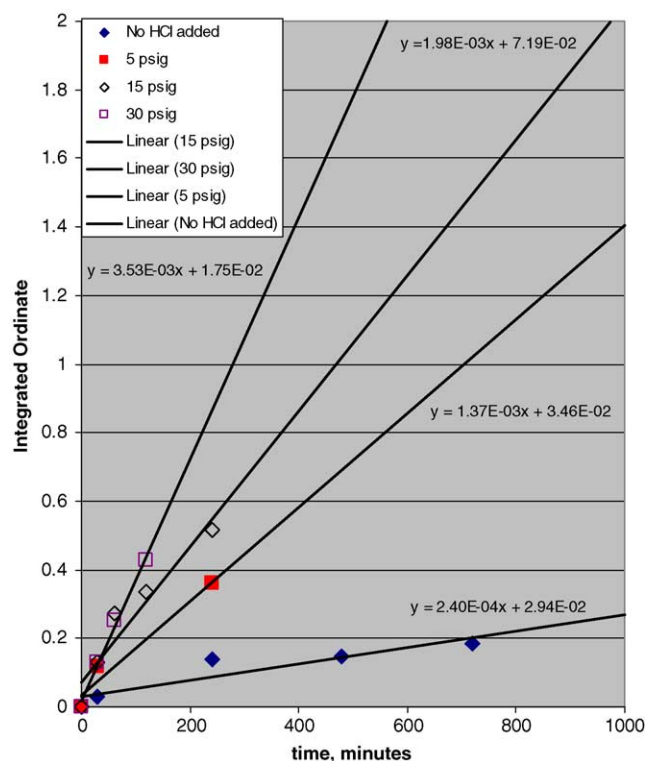


Fig. 6. Effect of P_{HCl} : integrated rate plot.

The finite but small $[H^+]$ concentration in the run without HCl added to the gas phase may be an artifact introduced by the less-than-perfectly-dry, AtmosBag in which the reagents were prepared. Others reported the finding of water in the room temperature melts in concentrations of 7.5–20 mM [17]. This adventitious water vapor [14] can react with dry $AlCl_3$ to form HCl gas that can then combine with other dry $AlCl_3$ to form a strong Brønsted acid. Holloway and Kruse [14] actually added up to 1 cm³ of water per every 60 g of $AlCl_3$ to obtain a maximum activity in their results. As with our experience [18] in other systems that have high affinity for water vapor, such as KO_2 , the attainment of nearly zero water partial pressure in a dry box is never realized.

Consider now the effect that the Al^{3+} /toluene ratio has upon the reactivity of the system. We speculate that the reac-

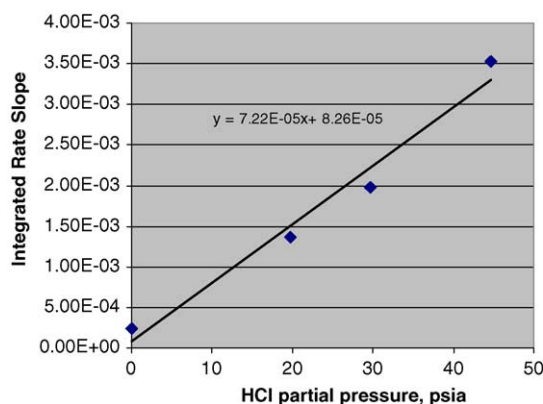


Fig. 7. Effect of HCl partial pressure upon $[H^+]$ in IL.

tion stops when 1/2 of the Al^{3+} cations initially in the mixture become associated with the product tolualdehyde molecules to form the complex $\text{CH}_3(\text{C}_6\text{H}_4)\text{CHOH}^+\text{AlCl}_4^-$ since the other 1/2 of the Al^{3+} species are needed to form the IL with the organic cation. The solid formed at high conversion could be related to this association of the chloroaluminate anion with the tolualdehyde carbocation. Holloway and Krase [14] also reported the formation of a solid during benzene carbonylation over AlCl_3 . Their system being simpler than ours, suggests that the solid formed could also be the result of the association of the benzaldehyde H^+ with AlCl_4^- .

The linear relationship of the ultimate, fractional, toluene conversion with the ratio of mol Al^{3+} /mol toluene, initially in mixture, suggests that the reaction is not catalytic and from a consideration of the slope (mol toluene converted/mol Al^{3+}) we conclude that at least two aluminum cations are needed for each toluene converted. A similar [10] result was observed for toluene carbonylation in the presence of triflic acid, except the slope of those data suggested that 10 triflic acid molecules were required for every tolualdehyde produced.

From the forgoing we believe that the reaction mechanism often cited for the triflic acid mediated arene carbonylation also explains well the data for the acidic, chloroaluminate IL system. The selectivity of the IL-based system is similar to the triflic acid system. Moreover, the way in which the Al^{3+} species limits the reactivity of the IL system is very similar to what has been observed for the Gatterman–Koch AlCl_3 system, even to the formation of solid products. It is plausible that the IL does not use any unusual chemistry for the arene carbonylation conversion. Therefore, we can speculate that the higher reactivity of the IL system is a direct consequence of it being a superior solvent for the reactants (arene and CO) and for the catalyst: H^+ . Consider a compilation of data (Fig. 8) for arene carbonylation in triflic acid,

acidic-chloroaluminate ILs, and AlCl_3 . Here, data of initial arene conversion rate (h^{-1}) were plotted versus P_{CO} for reactions completed at room temperature. The data for benzene carbonylation in AlCl_3 ($\text{Al}^{3+}/\text{benzene} = 1$) shows conversion rates of 0.5–0.7 h^{-1} over the range of pressures from 500 to 1000 psig. These data were larger than the conversion rates for the triflic acid system where the acid/substrate ratio was 2 (0.1–0.4 h^{-1}) but less than the conversion rate data for triflic acid in large excess (10 mol acid/1 mol substrate) where the conversion rate was 2 h^{-1} . Data for the IL system showed conversion rates of 0.4–1 when $\text{Al}^{3+}/\text{toluene} = 1$ and the conversion rates were 0.6 to 2.6 h^{-1} when the $\text{Al}^{3+}/\text{toluene} = 2$. The increased reactivity of the IL systems could be a direct result of the superior solvation power normally attributed to ILs in that the reactant CO and the source of protons, HCl, are readily dissolved in the IL. The reason for this better solvation power (e.g., higher acidity) cannot be ascertained from the data presented here, although sparse data in the literature suggests that the acidic chloroaluminates derived from EMIM-Cl are very strong acids showing Hammett acidity functions near -18 [3,4,19]. The high solubility of HCl gas and its formation of protons in the IL would directly influence the reactivity of these arene carbonylations.

The regioselectivity to form the isomers of tolualdehyde apparently changes little with conversion level. Moreover, it appears that p-tolualdehyde does not isomerize under reaction conditions in the IL. Sood observed the same result with triflic acid [10]. By inference, it is assumed that the other isomers of tolualdehyde do not isomerize in the IL. Thus, the regioselectivity is determined by the reaction(s) that form the tolualdehyde isomers, initially.

7. Summary

The Al^{3+} species in acidic chloroaluminate ILs interact with HCl gas to form protons and chloroaluminate species that can harbor the product aldehydes. As such, the Al^{3+} species are co-reactants with the arene and CO. The formed protons are probably very highly acidic such that the absorption of CO is favored even at modest pressures and the formation of formyl cation takes place rapidly. The role played by the proton in the IL system is not unlike that observed for protons in the perfluoroalkanesulfonic acid systems. The Al^{3+} species that are not directly associated with the organic cation in the IL system are free to sequester the product aldehydes much the same way as has been observed for AlCl_3 . The superior reactivity demonstrated by acidic, chloroaluminate ILs is probably due to their enhanced solvation power for HCl and CO.

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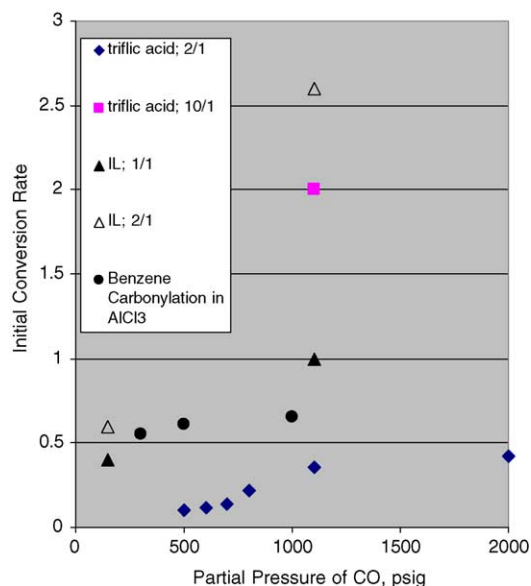


Fig. 8. Arene conversion rate for room temperature carbonylations.

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