

Ionic liquid structure effect upon reactivity of toluene carbonylation: 1. Organic cation structure

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Abstract

Acidic, chloroaluminate ionic liquids (IL's) formed from combining two moles of AlCl_3 with 1 mol of 1-R-3-methyl-imidazolium-chloride (RMIM-Cl, R = ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, or benzyl) were examined as conversion agents for toluene carbonylation at room temperature when HCl and CO were present in the gas phase at partial pressures of 3.04 and 8.16 atm, respectively. The solubility of HCl and CO into the ionic liquids was measured at room temperature in separate experiments to determine the effect, if any, of the cation structure upon gas solubility. Molecular modeling by semi-empirical methods (AM-1; PM3, and MNDO) were used to simulate the absorption of HCl into the IL's when R was changed.

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1. Introduction

Mixtures of AlCl_3 and certain organic halide salts form room temperature, ionic liquids. The organic halide salts can be substituted pyridinium halides, or disubstituted imidazolium chlorides, $(\text{R}-\text{C}_3\text{N}_2\text{H}_5-\text{R}')\text{Cl}$, and those reported often reported in the literature are 1-ethyl-3-methyl-1*H*-imidazolium-chloride (EMIM-Cl) and 1-butyl-3-methyl-1*H*-imidazolium-chloride (BMIM-Cl). Chloroaluminate ionic liquids are designated as basic, neutral, and acidic depending on the $[\text{O}^+\text{Cl}^-]/\text{AlCl}_3$ ratio where O^+ is the organic cation. It has been observed that when a strong, Brønsted acid, such as HCl, was dissolved in acidic chloroaluminate ionic liquids, a super acid was created [1]. These types of acidic, ionic liquids have been reported as conversion agents for arene carbonylation [2], alkylation of benzene with dodecene [3], Friedel–Crafts sulfonylation [4], and Friedel–Crafts alkyla-

tions and acylations [5]. Reactivity data showed that increasing HCl partial pressure above the acidic, chloroaluminate, IL increased the initial reactivity of the toluene carbonylation reaction [6,7].

It had been established that the structure of these ionic liquids may influence the transport processes [8] and the physical properties of the ionic liquid [9,10] as a result of the intimate association between the organic cation and the anion(s). It has been shown that the cation, the R-groups on the cation, and the anion can be chosen to enhance or suppress the solubility of other compounds in the ionic liquid [10]. For example, Waffenschmidt [11], showed how the solubility of octene increased in tosylate IL's prepared from tri-*n*-R-methyl ammonium cations where R was *n*-butyl, *n*-pentyl, and *n*-hexyl. The olefin was miscible in the IL prepared from the tosylate where R = *n*-octyl. They explained the increasing olefin solubility in the IL as a result of the decreasing dipole moment when R was replaced with alkyl groups of increasing chain length.

Ohlin et al. reported the solubility of CO in several ionic liquids derived from 1-R-3-methyl-1*H*-imidazolium-chloride (RMIM-Cl) at room temperature for which the R-

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group was changed from methyl to octyl when the anion was either bis(trifluoromethylsulfonyl)imide or BF_4^- [12]. They showed that the CO Henry's law constant, $K_H = P_{\text{CO}}/x_{\text{CO}}$, decreased from a value of 1.34 kbar with R=methyl to a value of 0.67 kbar for R=octyl. When R was benzyl, the Henry's law constant was 1.41 kbar suggesting that the π -electron system of the benzyl group leads to decreased CO solubility in the IL. The CO solubility in these IL's was similar to that observed for CO in toluene at room temperature ($K_H = 1.29$ kbar) which results in very small mole fractions of CO in the toluene under a CO partial pressure of 1 atm ($x_{\text{CO}} \sim 0.001$).

For the toluene carbonylation reaction in IL's for which a gaseous Brønsted acid (HCl) was added, the solubilities of toluene, CO, and HCl were important to the reactivity in the IL. Thus, one might imagine that an optimum "design" for the IL could exist which considers the solubility of gaseous species, such as CO and HCl, as well as the solubility of liquid species, such as toluene, in the ionic liquid. Apart from reactant solubility, one must also consider other factors that influence the formation of reactive species in the IL, such as strongly acidic species.

Carey and Sundberg [13] reported in their book that the strength of association between species depended upon LUMO and HOMO energies and the symmetries of the orbitals. Researchers studied the effect of changing structure and its effect on the MOs using the approach of the perturbation molecular orbital theory [14], and the interactions of orbitals in reacting molecules by incorporating the concept of frontier orbital control, which proposes that the most important interactions will be between a particular pair of orbitals [15]. These considerations have led investigators to examine the molecular environment of ionic liquids so as to understand better the experimental characterizations of these systems. Dieter et al. showed that the imidazolium cations and the chloroaluminate anions with the chlorides are closely associated to form layers in the neutral and basic IL's. [16] Moreover, Chandler and Johnson, showed how the formation of certain reactive chloroaluminate species, such as the Brønsted super acid ($\text{HAl}_2\text{Cl}_8^-$) and the Lewis super acid (Al_2Cl_7^-) depended upon the free energy of formation of the species in the melt [17] and Angueira [18] showed how the partial pressure of HCl above the melt determined the relative mole fractions of the Brønsted to Lewis super acid species. Several structures (monomeric [1] and dimeric [17,18] Al species) have been proposed for the Brønsted super acid species; therefore, it is appropriate to model these and other structures that might be present in the IL to determine how the solubility of HCl may be influenced by the structure of cation present in the IL.

We hypothesize that the structure of IL can (1) control the solubility of the gaseous reactants, (2) promote the formation of reactive species, and (3) therefore influence the reactivity of system towards a substrate. This hypothesis will be tested by experimental and by molecular modeling efforts in which the IL's would be formed from AlCl_3 (2 mol) and members of

a family of 1-R-3-methyl-imidazolium-chloride (RMIM-Cl, 1 mol), where R = ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, or benzyl. The modeling of HCl solubility in these IL's will describe the free energy for the formation of HCl-adducts with the IL's when R is changed. Where appropriate, the molecular modeling may indicate when more than one HCl-adduct can be formed. These model predictions will be compared to experimentally determined, room temperature, absorption equilibrium constants for HCl in the ionic liquids as a function of R for gas pressures up to 3.04 atm. Finally, we will determine by experiment the effect of R upon the reactivity of a toluene carbonylation probe reaction completed at room temperature in the presence of HCl (3.04 atm) with CO added to a total pressure of 11.2 atm.

2. Experimental

2.1. Chemicals

The imidazolium compounds 1-ethyl-3-methyl-imidazolium-chloride (EMIM-Cl), 1-butyl-3-methyl-imidazolium-chloride (BMIM-Cl), and 1-hexyl-3-methyl-imidazolium-chloride (HMIM-Cl), were obtained from Sigma–Aldrich; whereas, 1-octyl-3-methyl-imidazolium-chloride (OMIM-Cl), 1-dodecyl-3-methyl-imidazolium-chloride (DoMIM-Cl), and 1-benzyl-3-methyl-imidazolium-chloride (BeMIM-Cl), were obtained from Merck Chemicals and used without further purification. Aluminum chloride (99.99%), obtained from Sigma–Aldrich, was sublimed under 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 IL's

The weighing instrument, chemicals, were placed in a AtmosBag filled with dry Ar. AlCl_3 was weighed, and $\text{RMIM}^+\text{-Cl}^-$ was added so as to obtain the desired $\text{AlCl}_3/\text{RMIM}^+\text{-Cl}^-$ molar ratio. Details of the preparation can be found elsewhere [7].

2.3. Absorption of HCl gas in IL's

The amounts of HCl gas absorbed by the IL's were determined using a volumetric apparatus from a measurement of the system volumes, gas pressures, and temperatures. The moles absorbed were computed using the ideal gas law. A calibrated stainless steel vessel (150 cm^3) was filled initially with HCl at room temperature and the pressure was measured to the nearest 0.1 psia (0.0068 atm) using a 750B Baratron Pressure Transducers with a type LDM-B display module. This level of uncertainty in measuring the gas pressure leads to a minimum detection limit of 0.003 in the mole fraction of the absorbate in the IL. The gas in this vessel was expanded into the Fisher–Porter reaction tube that contained a known

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