

Super acidic ionic liquids for arene carbonylation derived from dialkylimidazolium chlorides and MCl_3 ($M = Al, Ga, \text{ or } In$)

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Introduction

Ionic liquids (IL's), formed by combining 1 mole of 3-butyl-1H-methylimidazolium chloride with two moles of a Group III-A metal chloride (Al, Ga, In), were examined for toluene carbonylation reactivity to determine the effect changing the M(III) cation. These ionic liquids were characterized for acidity indirectly by ^{13}C -NMR of labeled $CH_3-^{13}C(=O)-CH_3$. These results were correlated by a mechanism where the Brønsted acidity of the ionic liquid was regulated by the $M^{3+}Cl_3$.

Results

The fractional conversion of toluene *versus* time in an isothermal batch reactor at 298 K is shown in Fig

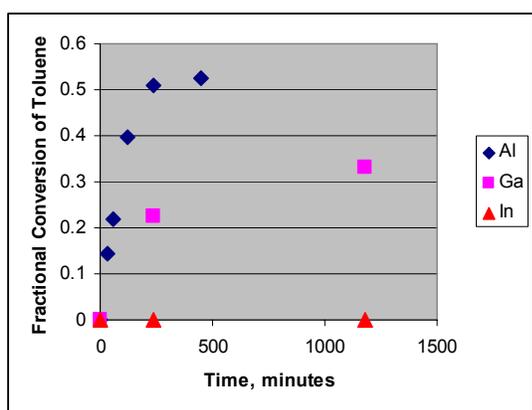


Fig 1 Toluene Carbonylation in BMIM- MCl_3 IL's

1 for an IL derived from 1 mole of 3-butyl-1H-methylimidazolium chloride with 2 moles of MCl_3 ($M = Al, Ga, \text{ or } In$). The CO partial pressure was 11 atm, and the HCl partial pressure was 3 atm. The highest reaction rate was realized with the chloroaluminate anion; whereas, the chloroindate anion was inactive and the chlorogallate system showed intermediate activity. The acidity of these IL's were characterized indirectly by recording the chemical shift in the ^{13}C -NMR spectrum of labeled acetone which was protonated by the Brønsted acid developed upon absorption of HCl into the IL at room temperature. The strength of the Brønsted acid can be correlated with the chemical shift of the carbonyl carbon of the acetone. We show how the first-order rate constants of the toluene carbonylation reaction in IL's can be correlated with the Hammett acidity function of the same IL's as inferred from the ^{13}C -NMR

chemical shifts of labeled acetone (Fig 2). The Hammett acidity function of BMIM- Al_2Cl_7 (-13.92) is more acidic than the H_0 of BMIM- Ga_2Cl_7 IL's (-13.72) in contact with HCl. We also show the reactivity of the carbonylation in triflic acid¹ which shows a $H_0 = -13.65$. When the HCl was evacuated from BMIM- Al_2Cl_7 we show that the reactivity of the arene formylation is much lower and that the H_0 is also less acidic (-12.7). The IL formed from $InCl_3$, which was inactive for the toluene carbonylation, showed a $-H_0 = 4.7$ as inferred from the ^{13}C -NMR chemical shift.

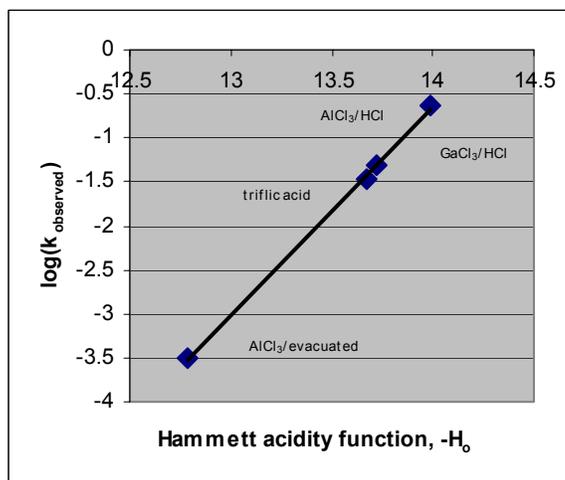


Fig 2 Correlation of Reactivity with Hammett Acidity Function

Conclusions

¹ Sood, D. S., S. C. Sherman, A. V. Iretskii, J. C. Kenvin, D. A. Schiraldi, M. G. White, "Formylation of Toluene in Triflic Acid", *J. Catal.* **199**, 149 (2001).

These data show how the activity of the IL's can be tuned by varying either the HCl partial pressure or the MCl_3 . Moreover, the acidity of the IL's 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.