



Research Article

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## Synthesis and characterization of 1-Isopropyl Imidazolium based Brønsted room temperature ionic liquids

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### ABSTRACT

Six examples of 1-isopropyl imidazolium cation based Brønsted acid ionic liquids with counter anions such as  $OTf^-$ ,  $CH_3SO_3^-$ ,  $C_6H_5SO_3^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $NO_3^-$  have been synthesized by acid-base neutralization reaction and anion exchange metathesis reaction methods. The structure of the reported ionic liquids has been confirmed by  $H^1$  NMR and mass spectrometry.

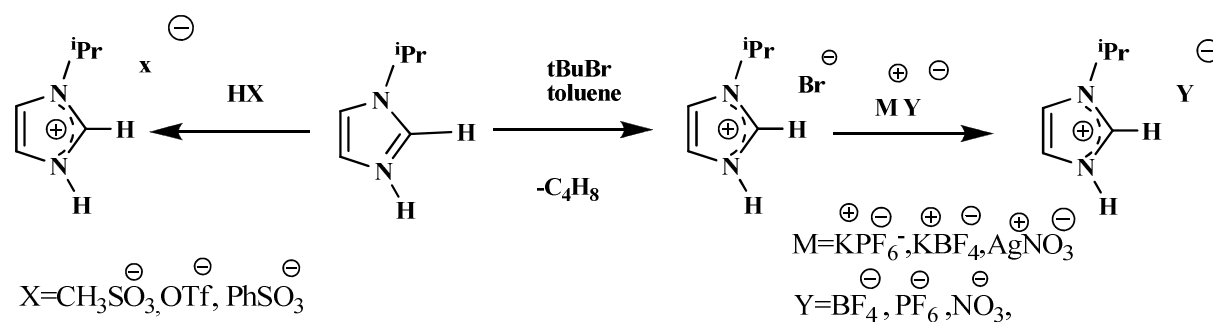
**Keywords:** Brønsted acidic ionic liquids, designer solvent, imidazolium ionic liquids, green solvent and catalyst.

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### INTRODUCTION

Replacement of volatile organic solvents in organic reactions by the more eco-friendly green solvents has been an impressive development in chemical industries to avoid pollution and other hazards [1]. The toxic hazardous properties of many synthesized solvents, chlorinated hydrocarbons are combined with serious environmental issues [2-4] such as atmospheric emissions and contamination of aqueous effluent making their use prohibitive. The current emphasis on novel media is also motivated by need for an efficient method for recycling and reusable [5] homogenous catalysts. Ionic liquids serve as neoteric solvents [6] like supercritical  $CO_2$  [7-9] in green technology [10-13].

The recent literature reports have prompted the researchers to synthesis new classes of ionic liquids since it has very good physico-chemical properties such as low melting point, high polarity, non flammability, non-volatility, high viscosity, negligible vapor pressure, high conductivity [14] reasonable thermal stability.[15]. Ionic liquids have been referred as designer solvents [16].The literature survey suggests that the use of imidazolium based ionic liquid as solvent results in the greatest improvement towards greener process in many fields like chemical and pharmaceutical industries. The physical and chemical properties of imidazolium based ionic liquids are easily tunable [17] by means of changing substitution on nitrogen in the ring and also using different anions. The choice of synthesis of imidazolium based ionic liquids is that numerous examples of ionic liquids can be synthesized by changing the substituent of N- centre of the imidazolium cation and changing the counter anions.



Scheme 1: Synthesis of 1-Isopropyl imidazolium based ionic liquids

There are three methods to synthesize ionic liquids a) Acid-base neutralization b) Quaternisation c) Anion exchange by metathesis. a) Imidazolium based Brønsted acidic ionic liquid can be easily synthesized by neutralization method. This is the simplest method to synthesize ionic liquid due to the basic nature of imidazole and acid nature of strong protic acids [18]. They can easily form salts. b) Imidazole combined with tertiary butyl bromide [19] to form ionic liquid on heating the reaction mixture HBr acid and Isobutene released from tertiary butyl bromide. The released HBr gas will be abstracted by 1-isopropyl imidazole followed by conversion into desired ionic liquid. c) Different 1-alkyl imidazolium based Brønsted acidic ionic liquid [20] can be prepared by using different alkali metal salts like  $\text{KBF}_4$ ,  $\text{KPF}_6$ ,  $\text{AgNO}_3$  and  $\text{AgBr}$  etc.

## EXPERIMENTAL SECTION

Toluene, hexane, dichloromethane and methanol were freshly distilled prior to use. Glassware was dried in oven at 120 °C overnight. Chemicals such as isopropyl bromide, tert-butyl bromide, imidazole, acetic acid, glyoxal, paraformaldehyde, Ammonium carbonate were purchased from SD fine chemicals, India and used as received. Ammonium tetrafluoroborate, potassium hexafluorophosphate, silver nitrate were purchased from Aldrich chemicals and used as received. 1-isopropyl imidazole was prepared by using reported procedures[21].  $^1\text{H}$  NMR spectra were recorded in 400 mhz. Mass spectrometry was performed on a Q-ToF premier [waters corporation] mass spectrometer operating in positive ion electro spray mode and methanol was used as a mobile phase The capillary and cone voltages were set at 2.5kv and 39.0kv. The desolvation temperature was set to 350°C and the source temperature was set to 100°C. the cone gas was set was set to a flow rate of 30.0L/hr and the desolvation gas flow was maintained at 626.0L/hr

### Synthesis of 1-Isopropyl imidazolium based Brønsted acidic ionic liquids.

#### Acid base neutralisation method

In a two neck flask, trifluoromethanesulfonic acid or methanesulphonic acid or benzenesulfonic acid (10 mmol) was added to a toluene (10 mL) solution of 1-isopropylimidazole (10 mmol). The resulting mixture was heated to 80°C and stirred for 16 hr. The immiscible layers were separated by decanting the toluene and the sticky product was washed with hexane and dried over vacuum.

(a) 1-isopropylimidazolium triflate (ImiPrHTA); Pale yellow color liquid, yield 83 %,  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz): 9.16 (s, 1H, 2-CH), 7.89 (d, 1H, 4CH), 7.69 (d, 1H, 5CH), 4.62 (m, 1H, CH(CH $_3$ ) $_2$ ), 1.47 (d, 6H, CH(CH $_3$ ) $_2$ ). ES-MS  $m/z$ : 111.1 [M-CF $_3$ SO $_3$ ] $^+$ .

(b) 1-isopropylimidazolium methanesulphonate (ImiPrHMS); Pale yellow color liquid, yield 88 %,  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz): 9.17 (s, 1H, 2-CH), 7.89 (d, 1H, 4CH), 7.69 (d, 1H, 5CH), 4.61 (m, 1H, CH(CH $_3$ ) $_2$ ), 2.32 (s, 3H, CH $_3$ SO $_3$ ), 1.47 (d, 6H, CH(CH $_3$ ) $_2$ ). ES-MS  $m/z$ : 111.0 [M-CH $_3$ SO $_3$ ] $^+$ .

(c) 1-isopropylimidazolium phenylsulfonate (ImiPrHPS); Pale yellow color liquid, yield 90 %,  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz): 9.12 (s, 1H, 2-CH), 7.87 (d, 1H, 4CH), 7.67 (d, 1H, 5CH), 7.58 (2H, C $_6$ H $_5$ SO $_3$ ), 7.28 (3H, C $_6$ H $_5$ SO $_3$ ), 4.61 (m, 1H, CH(CH $_3$ ) $_2$ ), 1.48 (d, 6H, CH(CH $_3$ ) $_2$ ). ES-MS  $m/z$ : 111.0 [M-C $_6$ H $_5$ SO $_3$ ] $^+$ .

**Metathesis Method**

In a two neck flask, tertiary butyl bromide was added to a toluene (10 mL) solution of 1-isopropylimidazole (10 mmol). The resulting mixture was heated to 80°C and stirred for 16 h. The immiscible layers were separated by decanting the toluene and the ionic liquids are repeatedly washed with hexane and dried over vacuum.

Isopropylimidazolium bromide (ImiPrHBr); Pale brown color liquid, yield 78% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 9.35 (s, 1H, 2-CH), 7.92 (d, 1H, 4CH), 7.75(d, 1H, 5CH), 4.65(m, 1H, CH (CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, 6H, CH (CH<sub>3</sub>)<sub>2</sub>). ES-MS *m/z*: 111.08 [M-Br]<sup>+</sup>

**Metathesis followed by anion exchange method**

10mmol of ammonium tetrafluoroborate or potassium hexafluorophosphate or silver nitrate was added to a solution of 10mmol of 1-isopropylimidazolium bromide in (10 mL) CH<sub>2</sub>Cl<sub>2</sub> / CH<sub>3</sub>OH (4:1). The resulting mixture stirred for 3 hours at room temperature. The solution was filtered and the solvents were removed by vacuum.

(a) 1-isopropylimidazolium tetrafluoroborate (ImiPrHTFB); Pale yellow color liquid, yield 86% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 9.24 (s, 1H, 2-CH), 7.92 (d, 1H, 4CH), 7.72 (d, 1H, 5CH), 4.63 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). ES-MS *m/z*: 111.1 [M-BF<sub>4</sub>]<sup>+</sup>

(b) 1-isopropylimidazolium hexafluorophosphate (ImiPrHHFP); Pale yellow color liquid, yield 87% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 9.18 (s, 1H, 2-CH), 7.89 (d, 1H, 4CH), 7.70 (d, 1H, 5CH), 4.63 (m, 1H, CH (CH<sub>3</sub>)<sub>2</sub>), 1.48 (d, 6H, CH (CH<sub>3</sub>)<sub>2</sub>). ES-MS *m/z*: 111.1 [M-PF<sub>6</sub>]<sup>+</sup>

(c) 1-isopropylimidazolium nitrate (ImiPrHN); Pale yellow color liquid, yield 80% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 9.13 (s, 1H, 2-CH), 7.88 (d, 1H, 4CH), 7.68 (d, 1H, 5CH), 4.62 (m, 1H, CH (CH<sub>3</sub>)<sub>2</sub>), 1.47 (d, 6H, CH (CH<sub>3</sub>)<sub>2</sub>). ES-MS *m/z*: 111.1 [M-NO<sub>3</sub>]<sup>+</sup>

**RESULTS AND DISCUSSION**

Six examples of 1- isopropyl imidazolium based ionic liquids (ILs) by changing the counter anions were synthesized. The following reported procedures have been adapted to synthesize the ILs. a) An equivalent of 1-Isopropyl imidazolium bromide was treated with one equivalent of potassium tetrafluoroborate or hexafluorophosphate or silver nitrate, the resulting mixture was stirred for 16 hours at 80°C. b) Treating one equivalent of 1-isopropyl imidazole with one equivalent of corresponding protic acids at 80°C results the ILs. The indication of the completion of course of reaction was the formation of two distinct layers in the flask. The immiscible layers were separated by decanting the toluene and the ionic liquids are repeatedly washed with hexane and dried over vacuum. The brønsted acidic ionic liquids are soluble in polar protic solvent such as water, methanol, ethanol, dichloromethane, chloroform, dimethyl sulfoxide, dimethyl formamide and immiscible with non polar solvents like hydrocarbon solvents [22]. All the synthesised 1-isopropyl imidazolium salts are liquids. All the ionic liquids were characterized by <sup>1</sup>H NMR and mass spectroscopy.

**Table 1: Spectral values of 1-isopropyl imidazolium based brønsted acidic ionic liquids**

Ionic liquids	<sup>1</sup> H-NMR Value (ppm)			ESI-MASS (M/Z)
	2-CH	4-CH	5-CH	
ImiPrHTA	9.16	7.89	7.69	111.108
ImiPrHMS	9.17	7.89	7.69	111.109
ImiPrHPS	9.12	7.87	7.67	111.109
ImiPrHTFB	9.24	7.92	7.72	111.109
ImiPrHHFP	9.18	7.89	7.70	111.108
ImiPrHN	9.13	7.88	7.68	111.109

The proton NMR spectra of reported ionic liquids suggest that 2-CH, 4-CH and 5-CH proton falls in the range of 9.12-9.24 ppm, 7.87-7.92 ppm, and 7.67-7.72 ppm respectively. The chemical shift value of 1-isopropyl imidazolium tetrafluoroborate is higher than other anions of 1-isopropyl imidazolium ionic liquids. The value of sulfonium ion is just below that of the tetrafluoroborate. The 4-CH and 5-CH proton value of 1-isopropyl imidazolium tetrafluoroborate is higher 7.92, 7.72 ppm and 1- isopropyl benzene sulphonate value is lower 7.87, 7.67 ppm. Moreover the positive ion gave the corresponding cationic peak in the ESI mass spectrometry ([M-X]<sup>+</sup>) and it falls in the range of 111.1 (m/z)

Based on the observed chemical shifts for 2-CH proton of imidazolium moiety the acidity of ionic liquids has been written in the following increasing order.

1-isopropyl imidazolium tetrafluoroborate > 1-isopropyl imidazolium hexafluorophosphate > 1-isopropyl imidazolium methanesulphonate > 1-isopropylimidazoliumtriflate > 1-isopropylimidazoliumnitrate > 1-isopropylimidazolium benzene sulphonate

### CONCLUSION

Six examples of 1-isopropyl imidazolium based bronsted acid ionic liquids has been synthesized and characterized by  $H^1$ NMR and mass spectroscopy by changing the counter anions.

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