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Influence of $-SO_3H$ functionalization (N-SO₃H or N-R-SO₃H, where R = alkyl/benzyl) on the activity of Brönsted acidic ionic liquids in the hydration reaction

Rajkumar Kore, Rajendra Srivastava*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India

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ABSTRACT

Sulfonic acid group functionalized imidazole based Brönsted acidic ionic liquids (BAILs) were synthesized and their activities were investigated in the hydration reaction of alkynes. The Hammett acidity order determined from UV–visible spectroscopy of BAILs is consistent with their activity order observed in hydration reactions. Theoretical studies further help to establish the structure–activity relationship. Recycling experiments suggest that these novel BAILs can be reused without significant loss in activity. Applicability of BAILs in hydration reaction opens a non-toxic, economical, and eco-friendly route to synthesize alkyl ketones from alkynes.

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Ionic liquids have been initially introduced as green reaction media due to their negligible volatility, excellent thermal stability, and the variety of available structures.^{1–3} Ionic liquids are being widely used in the place of classical organic solvents. They offer a new and environmentally benign approach toward modern synthetic chemistry.^{4,5} Ionic liquids find applications in many areas of interdisciplinary research. However, our interest is to use ionic liquids as catalysts and structure directing agents for material synthesis.⁶⁻⁹ Last decade is the witness for the development of Brönsted acidic and Lewis acidic ionic liquids as environmentalfriendly acid catalysts.^{10,11} Very recently, we have reported the assessment of the catalytic activity of mono-sulfonic and multisulfonic acid group functionalized imidazole/benzimidazole based Brönsted acidic ionic liquids in a variety of chemical reactions.^{8,9} Although various studies have been made for Brönsted acidic ionic liquids, to the best of our knowledge, there is no report in the literature which studies the influence of direct -SO₃H functionalization (N-SO₃H) or functionalization through spacer (N-R-SO₃H where R = alkyl/benzyl) on their activity. In this study, a variety of -SO₃H functionalized Brönsted acidic ionic liquids (BAILs) were prepared (Scheme 1) and their activity was investigated in the hydration reaction of alkynes (Scheme 2). The hydration reaction of alkynes involves the simple addition of a water molecule with 100% atom efficiency and is regarded as a convenient and efficient

method for the production of ketones and has been revealed as a useful tool in total synthesis.¹²

Traditionally Hg(II) catalysts are used for the hydration reaction of terminal alkynes to form methyl ketones.^{13,14} Much research has been devoted to find catalysts based on less toxic metals or Noble metal free hydration of alkynes.^{15–21} Very recently, H₂SO₄ (0.5– 8 mol equiv to substrate) catalyzed hydration reaction of alkynes to ketones in excess amount of ionic liquid has been reported.²² The objective of this study is to develop, non-toxic and economical route for the hydration reaction of alkynes using task-specific ionic liquids. Another objective of this study is to understand the influence of $-SO_3H$ functionalization (N-SO₃H and N-R-SO₃H, where R = alkyl/benzyl) on the acidity and activity of resultant BAILs.

BAILs were synthesized by one-step or multi-step synthesis route (Scheme 1).^{23,24} BAILs were characterized by using FT-IR, NMR, elemental, and thermo gravimetric analyses. Acidity of BAILs was measured using Analytikjena Specord 250 PLUS, UV–visible spectrophotometer with 4-nitroaniline as a basic indicator by following the concept reported in literature.^{25,26} With the increase of acidity of the BAILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas the protonated form of the indicator could not be observed because of its small molar absorptivity and its location, so the [I]/[IH⁺] (I represents indicator) ratio can be determined from the differences of measured absorbance after the addition of BAILs and Hammett function, H_0 , can be calculated using Eq. 1. This value can be regarded as the relative acidity of the BAILs.





^{*} Corresponding author. Tel.: +91 1881 242175; fax: +91 1881 223395. *E-mail address:* rajendra@iitrpr.ac.in (R. Srivastava).

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Scheme 1. Schematic representation for the synthesis of BAILs investigated in this study.



Scheme 2. Hydration reaction of alkynes using BAILs.

$$H_0 = pK(I)_{aa} + \log[(I)/(IH^+)]$$

$$\tag{1}$$

Under the same concentration of 4-nitroanline (10 mg/L, $pK(I)_{aq} = pK_a = 0.99$) and BAILs (50 mmol/L) in ethanol, H_0 values of all BAILs were determined. The maximal absorbance of the unprotonated form of the indicator was observed at 373 nm in ethanol. When the BAIL was added, the absorbance of the unprotonated form of the basic indicator decreased (Fig. 1 and Table 1). Hammett acidity (H_0) of these BAILs was calculated using Eq. 1. As shown in Figure 1, the absorbance of the unprotonated form of the indicator on addition of BAILs decreased as follows: [Hmim][Cl] > [C_3SO_3Hmim][Cl] > [(SO_3H)_2im][Cl] > [C_3SO_3Hmim][HSO_4] > [(SO_3H)_2im][Cl] > [SO_3Hmim][Cl] > [C_3SO_3Hmim][Cl] > [SO_3Hmim][Cl] > [C_3SO_3Hmim][Cl] > [C_3SO_3Hmim][Cl] > [SO_3Hmim][Cl] > [SO_3Hmim][Cl] > [C_3SO_3Hmim][Cl] > [SO_3Hmim][Cl] > [SO_3Hmim][Cl] > [C_3SO_3Hmim][Cl] > [SO_3Hmim][Cl] > [SO_3Hmim][

Activities of BAILs were assessed by hydration reaction of alkynes in the absence of H_2SO_4 /Noble metal catalysts. No product was obtained in the absence of BAILs. In the initial investigation, phenyl acetylene was chosen as a model substrate for hydration reaction. Influence of temperature, amount of BAILs, solvents, and reaction time were investigated. Highest yield of the product was obtained when the reaction was performed in the neat condition. After evaluating several reaction parameters, an optimum condition (Reaction temp. = 333 K, BAILs = 1 equiv with respect to



Figure 1. Absorbance spectra of 4-nitroaniline in ethanol after addition of BAILs.

Table 1Calculation and comparison of H_0 values of different BAILs in ethanol at 298 K

A _{max}	I(%)	$IH^{+}(\%)$	H_0
2.71	100	_	
2.70	99.6	0.4	3.39
2.65	97.8	2.2	2.64
2.35	86.7	13.3	1.8
2.65	97.8	2.2	2.64
2.45	90.4	9.6	1.96
2.25	82.1	17.9	1.65
	A _{max} 2.71 2.70 2.65 2.35 2.65 2.45 2.25	Amax I(%) 2.71 100 2.70 99.6 2.65 97.8 2.35 86.7 2.65 97.8 2.45 90.4 2.25 82.1 <td>$\begin{array}{c c c c c c c c c c c c c c c c c c c$</td>	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Indicator: 4-nitroaniline.

Table 2

Activity of BAILs in the hydration reaction of phenyl acetylene

Entry	BAILs	Yield (%)
1	[Hmim][Cl]	6
2	[C ₃ SO ₃ Hmim][HSO ₄]	30
3	[C ₃ SO ₃ Hmim][Cl]	39
4	[Benz-SO ₃ Hmim][Cl]	41
5	[SO ₃ Hmim][Cl]	65
6	[(SO ₃ H) ₂ im][Cl]	82

Reaction condition: Phenyl acetylene (1.0 mmol), de-ionized water (3.0 mmol), BAILs (1 mmol), temperature (333 K), reaction time (10 h). Experimental errors = ± 2.5.

Table 3 The geometry parameters of BAILs calculated using B3LYP/6-31++G(d,p)

Observed Parameters	[C ₃ SO ₃ Hmim][Cl]	[C ₃ SO ₃ Hmim][HSO ₄]
H–O bond distance of –SO ₃ H (Å)	H ₂₃ -O ₂₂ = 0.975	$H_{22}-O_{21} = 1.024$ $H_{32}-O_{31} = 0.974$
(N) ₂ C-H	$C_3 - H_7 = 1.08$	$C_3 - H_7 = 1.082$
$N)_2C-H\cdots X$	$H_7 \cdot \cdot \cdot Cl_{12} = 2.38$	$H_7 \cdot \cdot \cdot O_{28} = 2.25$
Other hydrogen bonds in BAILs	-	$H_{10} \cdot \cdot \cdot O_{28} = 2.63$
(Å)		$H_{22} \cdots O_{29} = 1.546$
Energy (a.u.)	-1468.2	-1707.6
Dipole Moment (Debye)	19.15	26.01

alkynes, and solvent = none, reaction time = 10 h) was obtained to investigate the influence of a variety of BAILs for this reaction. All BAILs investigated in this study were found to be active. The activity of BAILs follows the order: $[(SO_3H)_2im][Cl] > [SO_3Hmim][Cl] >$

 $[Benz-SO_3Hmim][Cl] > [C_3SO_3Hmim][Cl] > [C_3SO_3Hmim][HSO_4] >$ [Hmim][Cl] (Table 2), which is consistent with the acidity order obtained from UV-visible spectroscopy, except for [C₃SO₃Hmim][H-SO₄]. Acidity of BAILs is due to the presence of acidic [(N₂)C-H] proton and $-SO_3H$ group. However, the pKa of $[(N_2)C-H]$ is expected to be significantly higher than the -SO₃H group.²⁷ The apparent changes in the activity of BAILs may also be due to the thermodynamic and kinetic parameters, geometrical and/or solubility aspects of BAILs. Cl⁻ is a small and coordinating anion and forms interionic hydrogen bonds in imidazolium chloride ILs.^{28,29} However, these interactions are very weak compared to hydrogen bonding between HSO_4^- and $-SO_3H$ group in BAILs containing $HSO_4^$ and -SO₃H groups. In our previous study, we found that the activity of -SO₃H functionalized BAILs having HSO₄⁻ anion is greatly influenced by the hydrogen bonding between -SO₃H group and HSO₄ anion.⁹ To confirm these observations, catalytic activities of [C₃SO₃Hmim][Cl] and [C₃SO₃Hmim][HSO₄⁻] were compared. Catalytic activity data clearly demonstrate that the activity is reduced due to the presence of HSO_4^- . It was found that HSO_4^- strongly influences the -SO₃H group, which is explained in the following section by using theoretical calculations. One of the objectives of this study to understand the influence of -SO₃H functionalization, hence Cl⁻ was chosen as anion, which seems to be having negligible influence on -SO₃H group (because of inability to form hydrogen bonding). N-SO₃H functionalized BAIL ([SO₃Hmim][Cl]) was found to be more active than the N-R-SO₃H functionalized BAILs.

It is known that the water content appreciably changes the structure of the ILs through the participation of water in C(sp²)-H mediated hydrogen bonds.³⁰ Hence, theoretical studies have been performed by considering H₂O molecules and polarization effect in the calculation. The minimum-energy geometries of BAILs were determined by performing DFT geometry optimizations at the B3LYP/6-31++G(d,p) level using the Gaussian 09 program.³¹ A vibrational analysis was performed to ensure the absence of negative frequencies and verify the existence of a true minimum. For comparison, studies were also performed without considering H₂O molecules and the polarization effect (Supplementary data). To confirm, why the activity of [C₃SO₃Hmim][HSO₄] is less compared to the activity of [C₃SO₃Hmim][Cl], theoretical studies were performed. The optimized structure and related parameters of [C₃SO₃Hmim][HSO₄] and [C₃SO₃Hmim][Cl] are provided in this manuscript; whereas the optimized structures and related parameters of other BAILs investigated in this study are provided in the



Figure 2. Optimized molecular structure of BAILs using B3LYP/6-31++G (d,p).



Figure 3. Activity of [SO₃Hmim][Cl] in recycling experiments.

Supplementary data. Optimized structure and related parameters clearly show that a significant interaction exists between HSO_4^- and $-SO_3H$, whereas such interaction is absent in Cl^- and $-SO_3H$ (Table 3 and Fig. 2). H_{23} of $-SO_3H$ group in $[C_3SO_3Hmim][Cl]$ has

Table 4Hydration reaction of alkynes using [SO3Hmim][Cl]

no interaction, whereas H_{22} of $-SO_3H$ group in $[C_3SO_3Hmim][HSO_4]$ interacts with O_{29} of HSO_4^- ($H_{22} \cdots O_{29} = 1.546$) and inhibits the accessibility of H₂₂ to the reactant molecules for the hydration reaction and hence [C₃SO₃Hmim][HSO₄] activity was found to be less compared to the activity of [C₃SO₃Hmim][Cl]. N-Me substitution provides some electron density to the imidazole ring due the electron donating nature of -CH₃ group, whereas in [(SO₃H)₂im][Cl], imidazole ring will become more electropositive because of the two electron withdrawing –SO₃H functionalizations. Due to this reason, the O-H bond length in -SO₃H group of these two BAILs was found to be different (Table 1, Supplementary data). O-H bond length in [SO₃Hmim][Cl] was found to be 1.721 Å, whereas O-H bond lengths in [(SO₃H)₂im][Cl] were found to be 1.031 Å and 1.038 Å, which makes –SO₃H group in [[(SO₃H)₂im][Cl] less active and hence [[(SO₃H)₂im][Cl] activity is not as significantly high as it should be expected because of the presence of two -SO₃H functionalizations.

To demonstrate the robustness and durability of BAILs, $[SO_3H-mim][Cl]$ was recycled 5 times. At the end of each cycle, the reaction product was extracted and yield was determination by using gas chromatography.³² Throughout all the recycling, comparable yields (on average 60%) were observed (Fig. 3). The results strongly suggest that the BAILs are a robust and recyclable system that can constantly promote the transformation of phenyl acetylene to acetophenone without losing its activity. Hydration reaction proceeded well, delivered good product yields, and accommodated



Reaction condition: Alkyne (1.0 mmol), de-ionized water (3.0 mmol), $[SO_3Hmim][CI]$ (1 mmol), temperature (333 K), reaction time (10 h).

^a Parenthesis represent the yield obtained after 24 h of reaction.

a wide range of alkynes (Table 4). Both aromatic and aliphatic alkynes could be converted to ketones under the given conditions. Compared to aromatic terminal alkynes, aliphatic terminal alkynes are less reactive. Internal alkynes are less reactive than terminal alkynes. To demonstrate the practicability of this synthesis protocol, hydration reaction of phenyl acetylene was performed on a large scale (100 mmol) to afford the isolated yield of 95% of acetophenone after 24 h of the reaction.

In conclusion, efficient, non-toxic, Noble metal free, and Brönsted acidic ionic liquid based economical route was developed for the hydration reaction of alkynes. N-SO₃H functionalized BAIL ([SO₃Hmim][CI]) was found to be more active than the N-R-SO₃H (R = alkyl/benzyl) functionalized BAILs. These reactions are easy to perform and the purification protocol is simple. Apart from the experimental simplicity, the advantage of this methodology is to use mild and efficient BAILs for hydration reaction which makes them interesting candidates for commercial use. Based on the results, one can conclude that to establish a structure–activity relationship, theoretical studies along with UV–visible study were very helpful.

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Supplementary data

Supplementary data (¹H, ¹³C NMR spectra, and TGA of [Benz-SO₃Hmim][Cl]; optimized structures (Fig. 1 and related parameters (Table 1) of BAILs calculated using B3LYP/6-31++ G(d,p); observed parameters of BAILs calculated using B3LYP/6-31G (Tables 2)) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.04.066.

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- 23. Synthesis of BA/Ls-[Hmim][C1],⁴ [SO₃Hmim][C1],⁵ [(SO₃H)2im][C1],⁵ [C₃SO₃Hmim][C1]²⁴ and [C₃SO₃Hmim][HSO4]²⁴ were synthesized by following the reported procedure.^{4,5,24} For the synthesis of [Benz-SO₃Hmim][C1], first 1-benzyl-3-methylimidazolium chloride was prepared by following the reported procedure.⁹ It was then sulfonated using stoichiometric amount of chlorosulfonic acid in CH₂Cl₂ to obtain [Benz-SO₃Hmim][C1] (Yield = 81%).

[Benz-SO₃Hmim][Cl]: IR (KBr, v, cm⁻¹) = 3415, 3150, 2960, 1655, 1455, 1255, 1060, 880, 775, 665. ¹H NMR (400 MHz, D2O): δ (ppm) 8.56 (s, 1H), 7.35–7.22 (m, 6H), 5.22 (s, 2H), 3.71 (s, 3H); ¹³C NMR (D₂O): δ (ppm) 135.99, 133.49, 129.22, 129.17, 128.47, 123.66, 122.15, 52.69, 35.56. Elemental analysis for C₁₁H₁₃N₂SO₃Cl: Theoretical (%): C 45.75, H 4.51, N 9.71; Experimental (%): C 45.32, H 4.62, N 9.46.

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- 32. Hydration Reaction-In a typical procedure, a solution of phenyl acetylene (1.0 mmol) was mixed with water (3.0 mmol) and BAILS (1.0 mmol). The reaction mixture was stirred for 10 h at 333 K. The reaction mixture was then diluted with H₂O and extracted with chloroform and dried over anhydrous Na₂SO₄. The reaction mixture was analyzed using gas chromatography (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 µm). The products were identified by GC-MS (Shimadzu QP-5000; 30 m long, 0.25 mm i.d., with a 0.25-µm-thick capillary column, DB-1) and authentic samples obtained from Aldrich.

Aqueous portion of the reaction mixture was evaporated to remove the water. Residue was washed three-four times with diethyl ether to remove any organic impurity. Finally, ionic liquid portion was dried under vacuum at 353 K for 4 h. The recovered ionic liquid was used in the recycling experiments.