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Hydration of alkynes using Brönsted acidic ionic liquids in the absence of Nobel metal catalyst/H_2SO_4

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ABSTRACT

In this study, a variety of imidazole based sulfonic acid group functionalized Brönsted acidic ionic liquids (BAILs) were synthesized. BAILs have been successfully developed as task specific ionic liquids for hydration of alkynes under mild conditions to give high yields of ketones as a selective product. Acidity of BAILs was determined using volumetric titration and UV–visible spectroscopic methods. The Hammett acidity order and acid value of BAILs correlate well with the activity order observed for most of the BAILs in the hydration reaction of phenylacetylene. Theoretical studies demonstrate that hydrogen bonding plays a key role in tuning the acidity of BAILs. Density function theory calculations are also able to explain the difference in activity observed in these BAILs. The activity of ionic liquids was theoretically studied by computing the activation energy for the hydration reaction. Recycling experiments suggest that these novel BAILs can be reused without significant loss in activity. BAILs are simple and easy to prepare and exhibit excellent activity toward the hydration of a variety of alkynes to ketones. Moreover, the reaction involving BAILs does not involve heavy metal catalysts or H_2SO_4. Novel BAILs offer several attractive features such as sustainable synthetic route, low cost, moisture stability, high yields, and recyclability.

1. Introduction

Low volatility, chemical and thermal stability, reusability and eco-friendliness are the key properties to develop green and sustainable chemical processes. Ionic liquids (ILs) have been developed as green reaction media and structure directing agents due to their negligible volatility and excellent thermal stability [1,2]. The low vapor pressure of ILs makes them potential substituent for highly volatile organic solvents thus reducing the amount of pollution caused by solvent evaporation. Recently, ILs have been successfully employed as dual nature (solvents as well as catalysts) for a variety of reactions, but their use as catalyst under solvent-free condition needs to be given more attention [3]. Most of the common ILs are based on the nitrogen-containing heterocyclic cations such as imidazolium, benzimidazolium and pyridinium [1–6]. Functionalization ability of these heterocyclic cation forms new families and generations of ILs with more specific and targeted properties. Recently, the synthesis of “task-specific” ILs with special functions according to the requirement of a specific reaction has become an attractive field [7–10]. All these studies allow us to investigate the possibility of suitable ionic liquid catalysts for the appointed reaction. In recent years, Brönsted acidic ionic liquids, as environmental-friendly catalysts, have received great attention of researchers, and many organic reactions, such as esterification, polymerization, alkylation, carbonylation, and Beckmann rearrangement were reported with excellent selectivity [11–16].

The addition of water to alkynes is a synthetic method for the preparation of carbonyl compounds [17]. The transformation is classified as a dihydro, oxo-biaddition, but usually is divided into a hydro-hydroxylation of a triple bond, followed by tautomerization of the intermediary alkenol [18]. The hydration of terminal alkynes gives either a methyl ketone (Markovnikov addition) or an aldehyde (anti-Markovnikov addition). Unlike many other syntheses of carbonyl compounds, the hydration reaction of alkynes involves simple addition of a water molecule with 100% atom efficiency. It is regarded as a convenient and efficient method for the production of ketones and aldehydes, and has been revealed as a useful tool in total synthesis [19]. Traditionally Hg(II) catalysts are used for the hydration reaction of terminal alkynes to form methyl ketones [20,21]. Although this process offers very good yields, but it is not an environmentally benign and sustainable approach. The pollution problems associated with the handling and disposal of toxic mercury compounds discourage its industrial application.

Much research has been devoted to find catalysts based on less toxic metals, the most promising being gold(I), gold(III), platinum(II), and palladium(II) [22–25]. Catalytic anti-Markovnikov

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hydration of terminal alkynes to aldehydes has been realized in an efficient manner using ruthenium(II) complex catalysts [26]. However, the use of expensive metal-transition catalysts limits the process and open up a thrust area to find an economical solution. Therefore, a metal-free hydration of alkynes has been developed under acidic conditions including concentrated sulfuric acid, formic acid, *p*-toluenesulfonic acid (PTSA), trifluoromethanesulfonic acid or trifluoromethanesulfonimide [27,28]. While these catalysts are suitable in the case of robust substrates, many of them require harsh conditions (large excess of strong acid, high temperature (>373 K), organic solvent, long reaction times (18–72 h) [27–29]. Very recently, H_2SO_4 (0.5–8 mol equivalent to substrate) catalyzed hydration reaction of alkynes to ketones in excess amount of ILs has been developed, which is again a non eco-friendly route [30].

The objective of this study is to obtain an economical and eco-friendly solution for the hydration reaction of alkynes. In this manuscript, we are reporting for the first time that $-SO_3H$-functionalized imidazole based Brönsted acidic ionic liquids (BAILs) can be used for the hydration reaction. It may be noted that this method is eco-friendly and economical, because it does not involve corrosive H_2SO_4 or any costly noble metal catalysts. The $-SO_3H$ functionalized task specific BAILs catalysts offer product under mild reaction conditions, which is rather difficult to obtain with other acid catalysts reported in the literature. By systematic variation in the anion {HSO_4, Cl, CF_3COO and *p*-toluene sulfonate (TSO)} and cation {1-methyl, 3-H imidazolium (Hmim), 1-methyl, 3-sulfonyl imidazolium (SO_3Hmim), 1-methyl, 3-(3-sulfo-propyl)-imidazolium (C_3SO_3Hmim), 1-methyl 3-(4-sulfo-benzyl)-imidazolium (Benz-SO_3Hmim)}, it was possible to make a library of task specific BAILs for the hydration reaction of alkynes. Structure–activity relationship was established using acidity measurements and density function theory (DFT) calculations.

2. Experimental

2.1. Synthesis of BAILs

Syntheses of some of the ILs used in this work are already reported (Scheme 1) [15,16,31–33]. However, syntheses of several BAILs such as [SO_3Hmim][HSO_4], [SO_3Hmim][CF_3COO], [SO_3Hmim][TSO], [Benz-SO_3Hmim][TSO], and [Benz-SO_3Hmim][CF_3COO] are reported here for the first time.

For the synthesis of [SO_3Hmim][HSO_4]/[SO_3Hmim][CF_3COO]/[SO_3Hmim][TSO], a solution of H_2SO_4/PTSA/CF_3COOH (10 mmol) in CH_2Cl_2 (10 mL) was added drop wise to a solution of [SO_3Hmim][Cl] (10 mmol) in 10 mL CH_2Cl_2, and the reaction mixture was stirred at 273 K for 10 min. The resulting reaction mixture was refluxed for 24 h. After completion of the reaction, solvent was removed by evaporation under reduced pressure. Further, residue was then washed several times (5 times) with ethyl acetate to obtain [SO_3Hmim][HSO_4] (Yield = 91%), [SO_3Hmim][CF_3COO] (Yield = 89%) and [SO_3Hmim][TSO] (Yield = 92%).

For the synthesis of [Benz-SO_3Hmim][TSO]/[Benz-SO_3Hmim][CF_3COO], first 1-benzyl-3-methylimidazolium chloride was prepared by following the reported procedure [16]. It was then reacted with stoichiometric amount of PTSA/CF_3COOH in dichloromethane to obtain [Benz-mim][TSO] (Yield = 94%)/[Benz-mim][CF_3COO] (Yield = 90%) (Scheme 1). It was then sulfonated using stoichiometric amount of chlorosulfonic acid in CH_2Cl_2 to obtain [Benz-SO_3Hmim][TSO] (Yield = 86%)/[Benz-SO_3Hmim][CF_3COO] (Yield = 85%).

[SO_3Hmim][TSO]: IR (KBr, υ, cm^{-1}) = 3150, 2992, 2876, 2813, 1721, 1592, 1449, 1139, 1019, 876, 686. ^1H NMR (400 MHz, D_2O): δ (ppm) 8.55 (s, 1H), 7.62–7.60 (m, 3H), 7.35 (d, 1H), 7.34–7.28 (m, 2H), 3.83 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (D_2O): δ (ppm) 140.33, 135.51, 130.02, 125.95, 123.62, 120.16, 118.10, 115.21, 36.12, 21.13. MS (ESI) for $[SO_3Hmim]^+$ *m/z* 163.03 and for $[TSO]^-$ *m/z* 171.00.

[SO_3Hmim][CF_3COO]: IR (KBr, υ, cm^{-1}) = 3151, 3075, 2982, 2871, 2810, 1772, 1588, 1454, 1148, 1024, 860, 828, 690. ^1H NMR (400 MHz, D_2O): δ (ppm) 8.77 (s, 1H), 7.28–7.20 (m, 2H), 4.10 (s, 3H); ^{13}C NMR (D_2O): δ (ppm) 161.74, 139.26, 128.85, 124.98, 114.19, 35.15. MS (ESI) for $[SO_3Hmim]^+$ *m/z* 163.03 and for $[CF_3COO]^-$ *m/z* 162.95.

[SO_3Hmim][HSO_4]: IR (KBr, υ, cm^{-1}) = 3320, 3160, 2997, 2881, 2813, 1730, 1588, 1366, 1144, 1033, 889, 765, 624. ^1H NMR (400 MHz, D_2O): δ (ppm) 8.37 (s, 1H), 7.16–7.05 (m, 2H), 3.65 (s, 3H); ^{13}C NMR (D_2O): δ (ppm) 135.56, 125.31, 122.40, 34.90. MS (ESI) for $[SO_3Hmim]^+$ *m/z* 163.03 and for $[HSO_4]^-$ *m/z* 96.93.

[Benz-SO_3Hmim][TSO]: IR (KBr, υ, cm^{-1}) = 3094, 2965, 2817, 1708, 1584, 1352, 1152, 894, 686. ^1H NMR (400 MHz, D_2O): δ (ppm) 8.28 (s, 1H), 7.29 (d, 2H), 7.06 (m, 3H), 6.98 (m, 3H), 6.86 (d, 2H), 4.90 (s, 2H), 3.43 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (D_2O): δ (ppm) 141.87, 139.32, 135.59, 133.18, 129.11, 128.99, 128.76, 128.34, 124.91, 123.51, 121.75, 52.49, 35.46, 20.16. MS (ESI) for $[Benz\text{-}SO_3Hmim]^+$ *m/z* 253.08 and for $[TSO]^-$ *m/z* 171.00.

[Benz-SO_3Hmim][CF_3COO]: IR (KBr, υ, cm^{-1}) = 3146, 3089, 3010, 2808, 1771, 1583, 1449, 1153, 1037, 881, 722. ^1H NMR (400 MHz, D_2O): δ (ppm) 8.48 (s, 1H), 7.22–7.18 (m, 6H), 5.11 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (D_2O): δ (ppm) 162.71, 142.12, 135.66, 133.38, 129.14, 128.57, 128.27, 120.16, 115.21, 52.59, 35.58. MS (ESI) for $[Benz\text{-}SO_3Hmim]^+$ *m/z* 253.08 and for $[CF_3COO]^-$ *m/z* 162.95.

2.2. Catalytic reaction

In a typical procedure, phenylacetylene (1.0 mmol) was mixed with water (3.0 mmol) and BAILs (required amount) and the reaction mixture was heated at 333 K. After 10 h, mixture was diluted with H_2O and extracted with chloroform. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. 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.

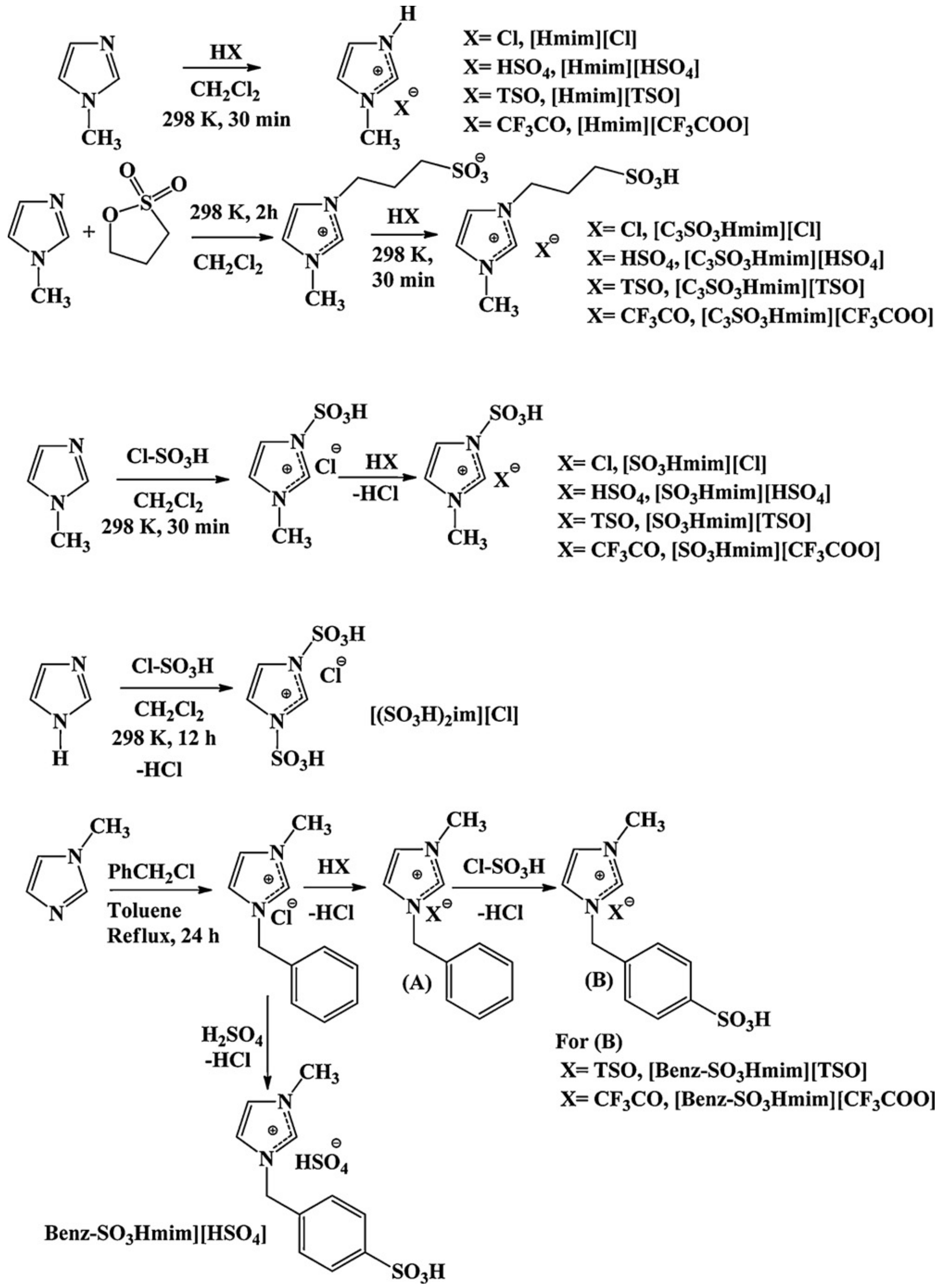
Aqueous portion of the reaction mixture was evaporated to remove the water. Residue was washed three to four times with diethyl ether to remove any organic impurity. Finally, ionic liquid portion was dried under vacuum at 353 K for 4 h. The recovered ionic liquid was used in the recycling experiments.

3. Results and discussion

3.1. Synthesis and characterizations of BAILs

BAILs were synthesized by one step or multi step synthesis route (Scheme 1). Samples were characterized by using FT-IR, NMR, and ESI-MS. The influence of anions and cations of BAILs in the catalytic activity was investigated. For this study, BAILs having CF_3COO^-, HSO_4^-, Cl^-, and $CH_3C_6H_4SO_3^-$ (TSO) anions were prepared. Four sets of BAILs having [Hmim], [SO_3Hmim], [C_3SO_3Hmim], and [Benz-SO_3Hmim] cations were prepared.

Acidity of BAILs was measured using UV–visible spectrophotometer with a basic indicator by following the method reported in the literature [34–36]. Acidity of BAILs was investigated in water medium using 4-nitroanline as indicator. 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



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

and its location. Therefore, 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.

$$H_0 = \mathrm{p}K(\mathrm{I})_{\mathrm{aq}} + \log\left[\frac{(\mathrm{I})}{(\mathrm{IH}^+)}\right] \qquad (1)$$

Under the same concentration of 4-nitroanline (3 mg/L, $\mathrm{p}K(\mathrm{I})_{\mathrm{aq}} = \mathrm{p}K_\mathrm{a} = 0.99$) and BAILs (50 mmol/L) in H_2O, H_0 values of all BAILs were determined. The maximal absorbance of the unprotonated form of the indicator was observed at 380 nm in water. 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). It has been observed that BAILs having HSO_4 anion have more Hammett acidity compared to BAILs having other anions. UV–visible study shows that among the four sets of cations investigated in this study, [SO_3Hmim] exhibited higher Hammett acidity (low H_0 value) when compared with other cations. Acid values of BAILs obtained using volumetric titration method are consistent with the Hammett acidity (obtained using UV–visible spectroscopic) trend for the same series of BAILs (having same cation). BAILs were investigated for the hydration of alkynes for the synthesis of ketones. Activity data can be explained based on the acidity obtained using UV–visible spectroscopy/titration method for several BAILs investigated in this study. Structure activity relationship was also established by performing DFT calculations, which is discussed in the later part of this manuscript.

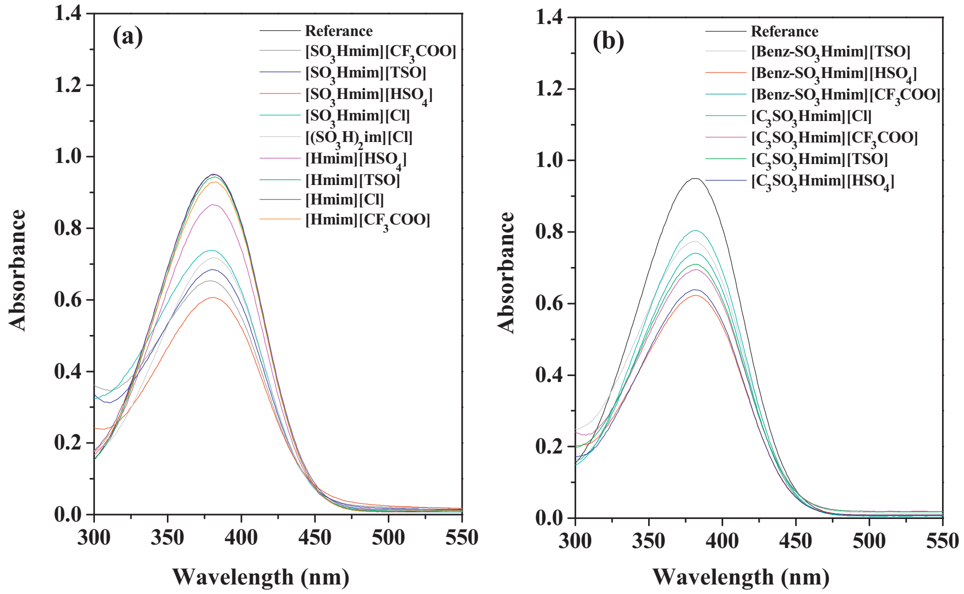


Fig. 1. Absorbance spectra of 4-nitroaniline after addition of (a) Hmim and SO_3Hmim sets of BAILs and (b) C_3SO_3Hmim and Benz-SO_3Hmim sets of BAILs in water.

3.2. BAILs assisted hydration of alkynes

Activities of BAILs were assessed with the help of hydration of alkynes. No product was obtained in the absence of BAILs. Previous work in this direction led us to conclude that [Benz-SO_3Hmim][HSO_4] is the best catalyst among the BAILs investigated [16]. Hence, in this study, preliminary reactions were performed using [Benz-SO_3Hmim][HSO_4] to find the optimized reaction condition. In the initial investigations, phenylacetylene was chosen as a model substrate for alkyne hydration. Influence of temperature, amount of [Benz-SO_3Hmim][HSO_4], solvents and reaction time were investigated. A variety of polar and non-polar solvents such as toluene, dichloromethane (DCM), 1,2-dichloroethane (DCE), methanol (MeOH), acetonitrile (ACN), dimethylformamide (DMF), N-methylpyrrolidone (NMP) were investigated (Table 2). Among the solvent investigated, DCM and DCE afforded the highest yield (Table 2). However, it may be noted that without any solvent, the yield was even higher than that of DCM/DCE (Table 2). Hence, this process follows the green chemical principle in which the reaction was performed in solvent-less medium to afford the high yield of the product. Effect of amount of BAILs in the reaction demonstrates that by increasing the BAILs concentration, yield of the product increased (Table 2). A reasonably good yield of the product was obtained when equivalent amount of BAILs was used. Reaction can be done even at ambient conditions, however the yield was very low (Table 2). With increase in the temperature, product yield increases. A reasonably good yield of the product was obtained at 333 K (Table 2). After evaluating several reaction parameters,

Table 1
H_0 and acidity values of BAILs in water at 298 K and comparison of the reactivity of BAILs for the hydration reaction of phenylacetylene.

Entry no.	BAILs	A_{max}	[I] (%)	[IH$^+$] (%)	H_0	Yield (%)	Acid value (mg KOH/mol)
1	No BAIL	0.95	100	–	–	0	–
2	[Benz-SO_3Hmim][HSO_4]	0.64	67	33	1.30	35	120.89
3	[Benz-SO_3Hmim][CF_3COO]	0.74	78	22	1.54	75	101.3
4	[Benz-SO_3Hmim][TSO]	0.77	81	19	1.62	95.5	96.1
5	[C_3SO_3Hmim][Cl]	0.80	84	16	1.71	39	18.9
6	[C_3SO_3Hmim][HSO_4]	0.64	67	33	1.30	30	81.3
7	[C_3SO_3Hmim][CF_3COO]	0.69	73	27	1.42	79	39.7
8	[C_3SO_3Hmim][TSO]	0.71	75	25	1.46	86	37.2
9	[SO_3Hmim][Cl]	0.74	78	22	1.54	65	89.3
10	[SO_3Hmim][HSO_4]	0.61	64	36	1.24	74	178.5
11	[SO_3Hmim][CF_3COO]	0.65	68	32	1.32	68	130.2
12	[SO_3Hmim][TSO]	0.68	72	28	1.40	79	122.5
13	[$(SO_3H)_2$im][Cl]	0.71	75	25	1.46	82	106.1
14	[HMim][Cl]	0.95	100	–	–	6	48.7
15	[HMim][HSO_4]	0.86	91	9	1.99	8	85.6
16	[HMim][CF_3COO]	0.92	97	3	2.50	11	66.4
17	[HMim][TSO]	0.94	99	1	2.98	14	51.8
18	[Benz-SO_3Hmim][TSO][a]	0.77	81	19	1.62	60.5	96.1
19	[Benz-SO_3Hmim][TSO][b]	0.77	81	19	1.62	21.0	96.1
20	[Benz-SO_3Hmim][TSO][c]	0.77	81	19	1.62	68.9	96.1
21	[Benz-SO_3Hmim][TSO][d]	0.77	81	19	1.62	86.3	96.1

Indicator: 4-nitroanline.
Reaction condition: phenylacetylene (1.0 mmol), deionized water (3.0 mmol), BAIL (1.0 mmol), temperature (333 K), reaction time (10 h).

[a] BAIL (0.5 mmol).

[b] BAIL (0.2 mmol).

[c] BAIL (0.2 mmol), reaction time (24 h).

[d] Catalytic activity data after 5th recycling.

Table 2
Influence of reaction parameters such as solvent, amount of [Benz-SO_3Hmim][HSO_4], and temperature on the hydration of phenylacetylene.

Entry no.	Solvent	Amount of catalyst (mmol)	Temperature (K)	Yield (%)
1	Acetonitrile	1.0	333	3
2	Methanol	1.0	333	7
3	Toluene	1.0	333	1
4	Dimethylformamide	1.0	333	2
5	N-methylpyrrolidone	1.0	333	4
6	Dichloromethane	1.0	333	32
7	1,2-Dichloroethane	1.0	333	28
8	None	1.0	333	35
9	None	0.5	333	19
10	None	2.0	333	64
11	None	1.0	298	2
12	None	1.0	313	10
13	None	1.0	353	76

Reaction condition: phenylacetylene (1.0 mmol), deionized water (3.0 mmol), reaction time (10 h).

an optimum condition (reaction temp. = 333 K, BAILs = 1 equiv. with respect to alkyne, and solvent = none, reaction time = 10 h) was chosen to investigate the influence of a variety of BAILs for this reaction.

The activities of various BAILs were compared in neat condition at 333 K for 10 h (Table 1). Mechanism for the BAILs assisted hydration reaction is illustrated in Scheme 2. The reaction mechanism of acid-catalyzed alkyne hydration proceeds via rate-limiting protonation of the carbon-carbon triple bond by forming a cyclopropenylium ion intermediate (I) (with H^+ of BAILs). Addition of water to the intermediate (I) leads to the formation of an enol (II), which converts to keto form via keto–enol tautomerism (III). H^+ liberated during the addition of the water, reacts with the intermediate (III) to form ketone as a selective product.

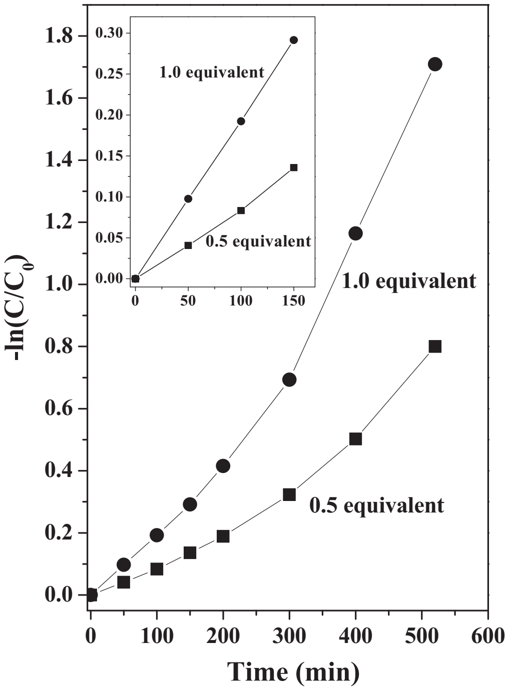


Fig. 2. Kinetics of hydration reaction using 0.5/1.0 equiv. with respect to phenylacetylene over [Benz-SO_3Hmim][TSO].

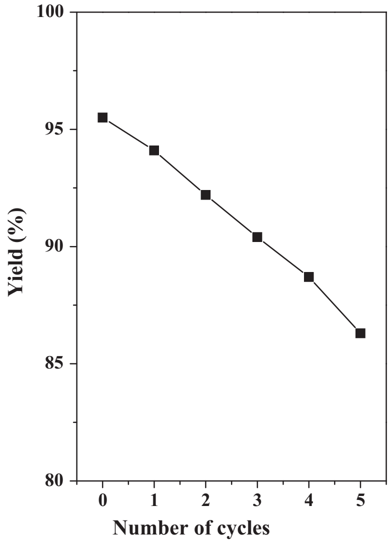
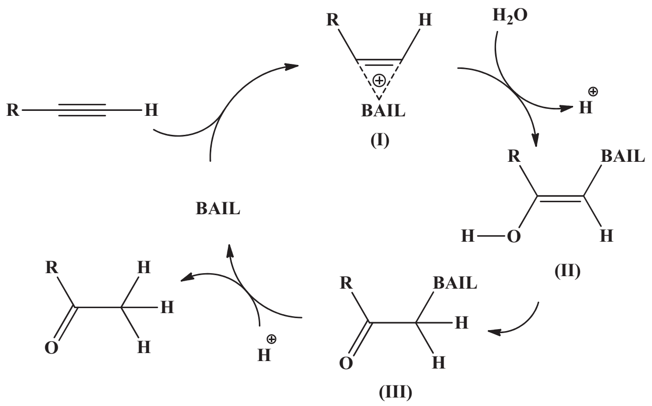
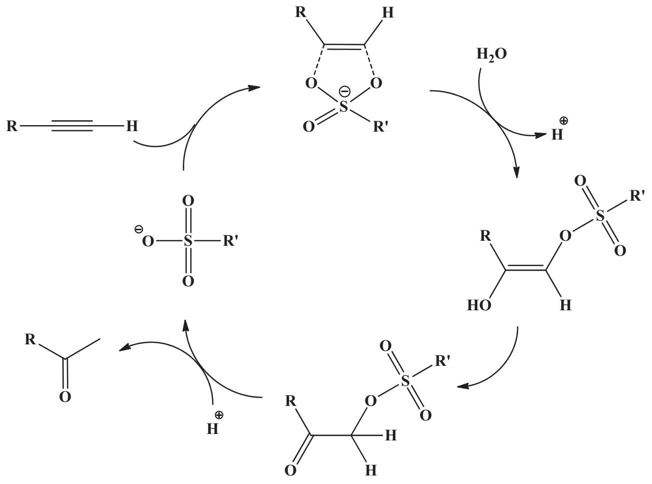


Fig. 3. Recycling study of the [Benz-SO_3Hmim][TSO] for the hydration of phenylacetylene.



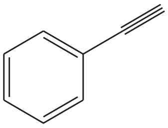
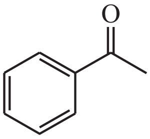
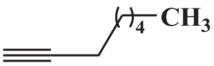
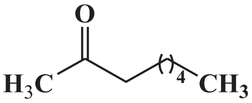
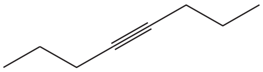
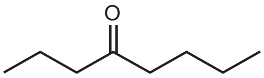
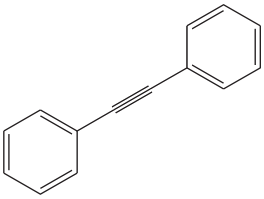
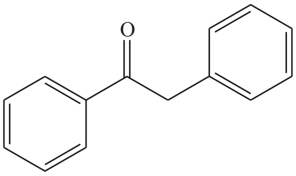
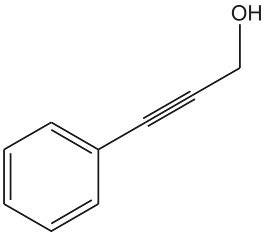
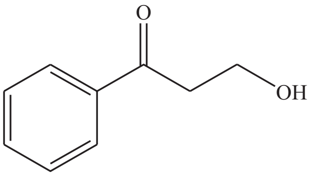
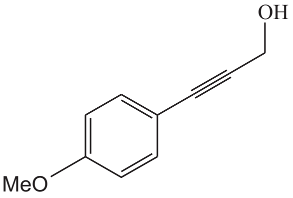
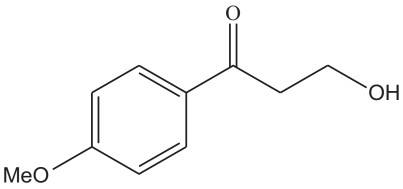
Scheme 2. Mechanism for the acid (BAILs) catalyzed hydration of alkynes.

It is evident from the hydration reaction that the activity of the BAILs are governed by the functionality (—SO_3H) of BAILs. Activity of BAILs having —SO_3H functionalization in cation was found to be more than that of BAILs without —SO_3H functionalization. Results show that Benz-SO_3Hmim cation and TSO anion were found to be the best among the cations and anions investigated in this study. In the case of —SO_3H functionalized BAILs, in addition to the conventional acid catalyzed hydration reaction (Scheme 2), —SO_3H group



Scheme 3. Mechanism for the —SO_3 containing BAILs in the hydration of alkynes.

Table 3
[Benz-SO_3Hmim][TSO] assisted hydration of alkynes.

Entry no.	Alkyne	Product	Yield (%)
1			68.9 (21)[a]
2			40.5 (15.2)[a]
3			34.7 (13.5)[a]
4			21.6 (5)[a]
5			80.5 (25)[a]
6			(100)[a]

Reaction condition: phenylacetylene (1.0 mmol), deionized water (3.0 mmol), BAIL (0.2 mmol), temperature (333 K), reaction time (24 h).

[a] Parenthesis represent the yield obtained after 10 h of reaction.

synergistically facilitate the hydration reaction by following the plausible mechanism shown in Scheme 3. First step of the hydration reaction using —SO_3H functionalized BAILs proceeds through more stable five membered transition state (Scheme 3) compared with three membered transition state in conventional (H^+) acid catalyzed reaction (Scheme 2). Based on the result obtained, one can conclude that the activity of BAILs in hydration reaction is highly dependent on the —SO_3/SO_3H functionalization.

Kinetics of the hydration reaction was monitored using two different amounts of [Benz-SO_3Hmim][TOS] (0.5 and 1.0 equiv. with respect to phenylacetylene) under the optimized reaction condition. From the plot of $-\ln(C/C_0)$ vs time (Fig. 2), it is very clear that the reaction is first order when the kinetics is monitored in the time domain of 0–150 min of the reaction. Fig. 2 (inset) shows that the plot of $-\ln(C/C_0)$ *vs* time is straight line with slope 9×10^{-4} and 1.94×10^{-3} for the reaction conducted with 0.5 and 1.0 equiv. of [Benz-SO_3Hmim][TSO] with respect to phenylacetylene, respectively.

Having found the highest activity of [Benz-SO_3Hmim][TSO] in the hydration reaction under the optimized condition, the influence of the amount of BAIL required for the reaction was investigated (Table 1). It is clear that the catalytic amount of [Benz-SO_3Hmim][TSO] can also be utilized to carry out this reaction but the yield was low under the optimized condition (Table 1). However, the yield of the reaction can be increased by continuing the reaction for longer time (Table 1). To demonstrate the robustness and durability of BAILs, [Benz-SO_3Hmim][TSO] was recycled 5 times. At the end of each cycle, the reaction product was extracted for the determination of yield by gas chromatography. Throughout all the recycling, comparable yields (on average 90%) were observed (Fig. 3). The results strongly suggest that the BAILs are a robust and recyclable system that can constantly promote the transformation of phenylacetylene to acetophenone without losing its reactivity. Hydration reaction proceeded well, delivered good product yields, and accommodated a wide range of alkynes (Table 3). 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. Alkynes having propargyl function provides higher yield, especially when aromatic ring has methoxy substitution at para position. This is due to the fact that alkynes having a propargylic function could provide a four membered cyclic

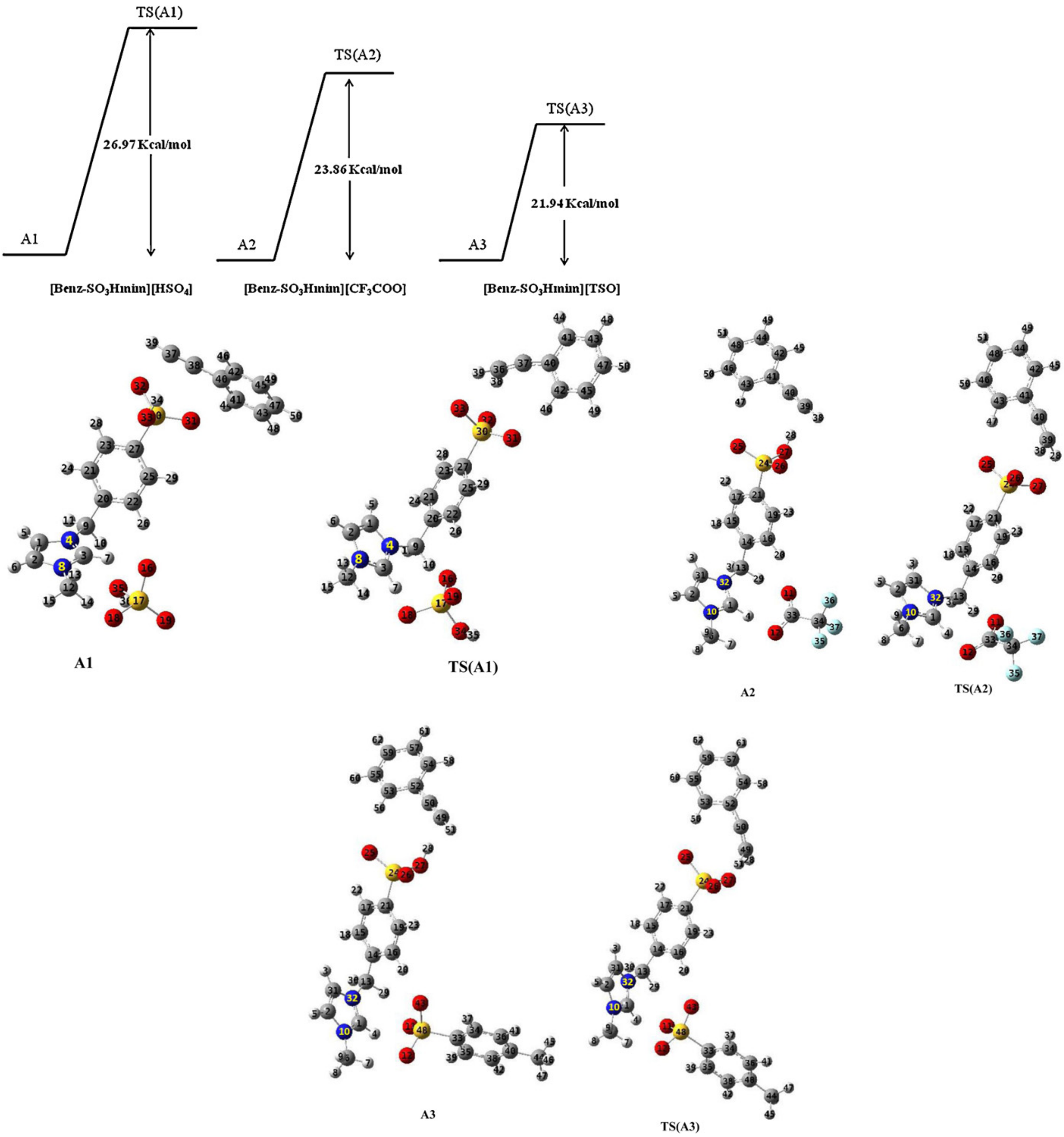


Fig. 4. H C N O S F Activation energy for the protonation step in the hydration reaction using Benz-SO$_3$Hmim set of BAILs. A1 is the adduct of phenylacetylene and [Benz-SO$_3$Hmim][HSO$_4$], A2 is the adduct of phenylacetylene and [Benz-SO$_3$Hmim][CF$_3$COO] and A3 is the adduct of phenylacetylene and [Benz-SO$_3$Hmim][TSO]. TS(A1), TS(A2) and TS(A3) are the corresponding TS of A1, A2 and A3, respectively.

oxonium intermediate which could result from an intra-molecular oxygen atom-addition (Scheme 4). Further nucleophilic ring opening by water gives the carbonyl compound.

3.3. *The molecular geometries of BAILs*

Since the hydration reaction is performed in water, therefore, theoretical studies have been performed by considering H_2O molecules in the calculation. The minimum-energy geometries of BAILs were determined by performing DFT geometry optimizations at the B3LYP/6-31G using the Gaussian09 program [37]. Geometrical parameters of the optimized structures of BAILs (Figs. S1–S5 of supporting information) are provided in Tables 4–7. In addition to this, atomic charge analysis on the protons of —SO_3H, $(N_2)C$—H and HSO_4^- groups of BAILs has also been performed (Table T1–T2, supporting information), which is consistent with the experimental evidences (Table 1). Theoretical study confirmed that hydrogen bonding exists in the BAILs. Molecular geometry study

Table 4
The geometry parameters of Hmim set of BAILs calculated at B3LYP/6-31G.

Observed parameters	[Hmim][Cl]	[Hmim][HSO_4]	[Hmim][TSO]	[Hmim][CF_3COO]
(N···H) bond distance (Å)	$H_{13}\cdots N_8 = 1.047$	$H_5\cdots N_4 = 1.043$	$H_{31}\cdots N_{14} = 1.056$	$H_{20}\cdots N_4 = 1.061$
$(N)_2C{-}H$	$C_3{-}H_7 = 1.075$	$C_3{-}H_8 = 1.077$	$C_1{-}H_4 = 1.078$	$C_3{-}H_7 = 1.077$
$(N)_2C{-}H\cdots O$	–	$H_8\cdots O_{17} = 2.302$	$H_4\cdots O_{12} = 2.217$	$H_7\cdots O_{13} = 2.350$
Other hydrogen bonds in BAILs (Å)	$H_5\cdots Cl_{14} = 2.057$	$H_5\cdots O_{16} = 1.695$	$H_{31}\cdots O_{11} = 1.626$	$H_{20}\cdots O_{14} = 1.610$

Table 5
The geometry parameters of C_3SO_3Hmim set of BAILs calculated at B3LYP/6-31G.

Observed parameters	[C_3SO_3Hmim] [Cl]	[C_3SO_3Hmim] [HSO_4]	[C_3SO_3Hmim] [TSO]	[C_3SO_3Hmim] [CF_3COO]
H—O bond distance of sulfonic acid (Å)	$H_{23}{-}O_{22} = 0.989$	$H_{22}{-}O_{21} = 1.040$ $H_{32}{-}O_{31} = 0.989$	$H_{22}{-}O_{21} = 1.083$	$H_{22}{-}O_{21} = 1.049$
$(N)_2C{-}H$	$C_3{-}H_7 = 1.086$	$C_3{-}H_7 = 1.081$	$C_3{-}H_7 = 1.084$	$C_3{-}H_7 = 1.088$
$(N)_2C{-}H\cdots O$	$H_7\cdots Cl_{12} = 2.5198$	$H_7\cdots O_{28} = 2.038$	$H_7\cdots O_{27} = 2.027$	$H_7\cdots O_{27} = 1.980$
Other hydrogen bonds in BAILs (Å)	$H_{15}\cdots Cl_{12} = 2.402$	$H_{22}\cdots O_{29} = 1.549$ $H_{16}\cdots O_{28} = 2.591$ $H_{10}\cdots O_{28} = 2.418$	$H_{22}\cdots O_{28} = 1.411$ $H_{16}\cdots O_{27} = 2.270$ $H_{33}\cdots O_{43} = 2.593$	$H_{22}\cdots O_{28} = 1.494$ $H_{14}\cdots O_{28} = 2.517$ $H_{16}\cdots O_{28} = 2.518$

Table 6
The geometry parameters of SO_3Hmim set of BAILs calculated at B3LYP/6-31G.

Observed parameters	[SO_3Hmim] [Cl]	[SO_3Hmim] [HSO_4]	[SO_3Hmim] [TSO]	[SO_3Hmim] [CF_3COO]	[$(SO_3Him)_2$] [Cl]
H—O bond distance of sulfonic acid (Å)	$H_{17}{-}O_{16} = 1.134$	$H_{23}{-}O_{19} = 1.477$ $H_{22}{-}O_{16} = 0.991$	$H_{17}{-}O_{16} = 1.60$	$H_{17}{-}O_{16} = 1.536$	$H_{19}{-}O_{18} = 1.049$ $H_{13}{-}O_{12} = 1.050$
$(N)_2C{-}H$ $(N)_2C{-}H\cdots O$	$C_3{-}H_7 = 1.076$	$C_3{-}H_7 = 1.082$ $H_7\cdots O_{13} = 2.053$	$C_1{-}H_4 = 1.086$ $H_4\cdots O_{12} = 1.949$	$C_3{-}H_7 = 1.079$ $H_7\cdots O_{18} = 2.267$	$C_3{-}H_7 = 1.077$
Other hydrogen bonds in BAILs (Å)	$H_{17}\cdots Cl_{18} = 1.697$	$H_{23}\cdots O_{21} = 1.257$	$H_{17}\cdots O_{30} = 1.228$	$H_{17}\cdots O_{18} = 1.230$	$H_{13}\cdots Cl_{14} = 1.939$ $H_{19}\cdots Cl_{14} = 1.951$

Table 7
The geometry parameters of Benz-SO_3Hmim set of BAILs calculated at B3LYP/6-31G.

Observed parameters	[Benz-SO_3Hmim] [HSO_4]	[Benz-SO_3Hmim] [TSO]	[Benz-SO_3Hmim] [CF_3COO]
H—O bond distance of sulfonic acid (Å)	$H_{32}{-}O_{31} = 0.99$ $H_{16}{-}O_{15} = 0.988$	$H_{28}{-}O_{27} = 0.99$	$H_{28}{-}O_{27} = 0.99$
$(N)_2C{-}H$	$C_1{-}H_4 = 1.087$	$C_1{-}H_4 = 1.088$	$C_1{-}H_4 = 1.095$
$(N)_2C{-}H\cdots O$	$H_4\cdots O_{14} = 1.969$	$H_4\cdots O_{11} = 1.933$	$H_4\cdots O_{12} = 1.887$
Other hydrogen bonds in BAILs (Å)	$H_7\cdots O_{13} = 2.415$ $H_{24}\cdots O_{14} = 2.367$	$H_{20}\cdots O_{43} = 2.356$ $H_7\cdots O_{12} = 2.406$ $H_{37}\cdots O_{43} = 2.66$ $H_{39}\cdots O_{11} = 2.66$	$H_{29}\cdots O_{11} = 2.248$ $H_{20}\cdots O_{11} = 2.429$

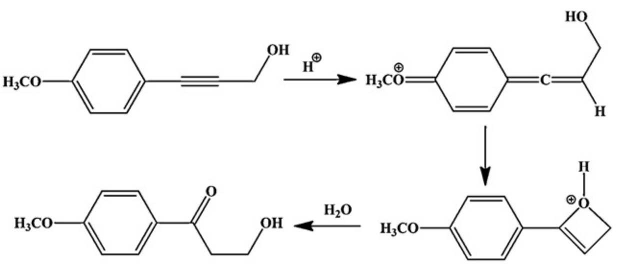
reveals that anions interact with the $-SO_3H$ and imidazole ring through $C{-}H\cdots O$ or $O{-}H\cdots O$ type hydrogen bonding.

Geometrical parameters and hydrogen bonding data of [Hmim] set of BAILs clearly state that [Hmim][Cl] is the least active BAIL in this set (Tables 1 and 4). DFT calculation and H-bonding suggest that [Hmim][CF_3COO] is more active than [Hmim][HSO_4] because the N—H is more labile in case of [Hmim][CF_3COO] (Table 4).

Geometrical parameters and hydrogen bonding data of [C_3SO_3Hmim] set of BAILs correlate well with the activity order obtained from catalytic investigation (Tables 1 and 5). It may be noted that in this case, the activity of [C_3SO_3Hmim][HSO_4] is significantly low compared to [C_3SO_3Hmim][CF_3COO]. A very low activity of [C_3SO_3Hmim][HSO_4] can be explained based on the bond distance of O—H and $(N)_2C{-}H$. The large difference in the

Table 8
Activation energy for the protonation step in the hydration of phenylacetylene over BAILs.

Entry no.	BAILs	Adduct of (BAIL + phenylacetylene) (Hartrees)	TS (Hartrees)	Activation energy (kcal mol^{-1})
1	[Benz-SO_3Hmim][HSO_4]	−2167.603	−2167.560	26.97
2	[Benz-SO_3Hmim][TSO]	−2362.724	−2362.69	21.94
3	[Benz-SO_3Hmim][CF_3COO]	−1994.30	−1994.262	23.86
4	[C_3SO_3Hmim][TSO]	−2210.346	−2210.31	22.59
5	[C_3SO_3Hmim][HSO_4]	−2015.227	−2015.18	29.49
6	[C_3SO_3Hmim][CF_3COO]	−1841.921	−1841.882	24.47
7	[C_3SO_3Hmim][Cl]	−1776.054	−1776.01	27.61
8	[SO_3Hmim][HSO_4]	−1897.32	−1897.281	24.47
9	[SO_3Hmim][CF_3COO]	−1723.98	−1723.939	25.73
10	[SO_3Hmim][TSO]	−2092.375	−2096.34	21.96
11	[Hmim][HSO_4]	−1273.762	−1273.712	31.38



Scheme 4. Proposed mechanism for the BAILs assisted hydration of alkynes having propargyl function.

activity is mainly due to the $(N)_2C—H$ bond distance in these two cases (Table 5). The strong hydrogen bonding $(C_3—H_7 = 1.081)$ in $[C_3SO_3Hmim][HSO_4]$ makes proton less labile compared to other BAILs of this series. 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 5). H_{23} of $—SO_3H$ group in $[C_3SO_3Hmim][Cl]$ has no interaction, whereas H_{22} of $—SO_3H$ group in $[C_3SO_3Hmim][HSO_4]$ significantly interact with O_{29} of HSO_4^- $(H_{22}\cdots O_{29} = 1.549)$ and inhibits the accessibility of H_{22} to the reactant molecules for the hydration reaction and hence $[C_3SO_3Hmim][HSO_4]$ activity was found to be less compared to the activity of $[C_3SO_3Hmim][Cl]$. The highest activity of $(C_3SO_3Hmim][TSO]$ in this set of BAILs is due to the presence of an additional $—SO_3$ group in anion, which enhances the activity by following the mechanism shown in Scheme 3.

Geometrical parameters and hydrogen bonding data of $[SO_3Hmim]$ set of BAILs correlate well with the activity order obtained from catalytic investigation (Tables 1 and 6). Less activity of $[SO_3mim][Cl]$ can be correlated well with the shorter bond distance of $H_{17}\cdots O_{16}$ (Table 6). It may be noted that in this case, opposite trend in the activity was observed $([SO_3Hmim][CF_3COO] < [SO_3Hmim][HSO_4])$. Again this activity order can be very well explained using hydrogen bonding. H_{23} and H_7 are more labile in $[SO_3Hmim][HSO_4]$ due to the weak hydrogen bonding (Table 6). The highest activity of $[SO_3Hmim][TSO]$ in this set of BAILs is due to the presence of an additional $—SO_3$ group in anion, which enhances the activity by following the mechanism shown in Scheme 3.

Geometrical parameters and hydrogen bonding data of $[Benz\text{-}SO_3Hmim]$ set of BAILs correlates well with the activity order obtained from catalytic investigation (Tables 1 and 7). It may be noted that in this case also the activity of $[Benz\text{-}SO_3Hmim][CF_3COO]$ is significantly higher than $[Benz\text{-}SO_3Hmim][HSO_4]$. Low activity of $[Benz\text{-}SO_3Hmim][HSO_4]$ can be explained based on the short $(N)_2C—H$ bond distance $(C_3—H_7 = 1.083)$ compared to other BAILs of this series. The highest activity of $[Benz\text{-}SO_3Hmim][TSO]$ in mainly due to $(N)_2C—H$ bond distance $(C_3—H_7 = 1.087)$ and the presence of an additional $—SO_3$ group in the anion, which enhance the activity by following the mechanism shown in Scheme 3.

The reaction mechanism of acid-catalyzed alkyne hydration proceeds via the rate-limiting protonation of the carbon-carbon triple bond, followed by rapid addition of water to generate an enol, which gives ketone as the final product via keto–enol tautomerism [38,39]. The activity of $[Benz\text{-}SO_3Hmim]$ set was theoretically studied by computing the activation energy for the protonation rate-limiting step in the hydration reaction. The transition states for the rate-limiting protonation step using $[Benz\text{-}SO_3Hmim]$ set of BAILs were obtained. The vibrational analysis was performed for the minimum and transition state optimized geometries. The vibrational analysis data confirmed the structures from the number of imaginary frequencies. The activation energies for the protonation step of phenylacetylene with $[Benz\text{-}SO_3Hmim]$ set of BAILs were obtained (Table 8, Fig. 4). The activation energy of the $[Benz\text{-}SO_3Hmim][TSO]$ is found to be lowest with a value of 21.94 kcal mol^{-1} of all the BAILs studied. Experimentally, the activity of $[Benz\text{-}SO_3Hmim][TSO]$ is found to be the maximum (ketone yield = 95%). The activation energy of the $[Benz\text{-}SO_3Hmim][HSO_4]$ is found to be the highest with a value of 26.97 kcal mol^{-1} and the yield of the product was only 35%. The activation energy for $[Benz\text{-}SO_3Hmim][CF_3COO]$ is calculated to be 23.86 kcal mol^{-1} with the experimental ketone yield of 75%. The activation energies for the protonation rate-limiting step in the hydration reaction using several other BAILs are provided in Table 8 (Figs. S6–S13, supporting information). Based on these results, one can conclude that acidity measurement along with DFT calculation is needed to establish the structure activity relationship for the hydration reaction using BAILs.

4. Conclusions

In summary, an effective and recyclable protocol using a variety of Brönsted acidic ionic liquids without using costly Nobel metal catalysts or H_2SO_4 for the transformation of alkynes to ketones under mild conditions has been successfully developed. BAILs are easy to prepare and exhibit excellent reactivity and stability over multiple cycles. BAILs having more number of $—SO_3H$ functionalization exhibited comparatively high activity. The activity of ionic liquids in the hydration reaction is well supported by the acidity measurements, geometrically optimized parameters, and the activation energy of the rate determining protonation step using DFT calculations. Based on the results, one can conclude that to understand the activity difference of these ionic liquids catalysts, along with UV–visible/volumetric titration investigations, DFT calculation is very essential.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.04.010.

References

[1] T. Welton, Chem. Rev. 99 (1999) 2071–2084.
[2] R. Kore, B. Satpati, R. Srivastava, Chem. Eur. J. 17 (2011) 14360–14365.
[3] H.O. Bourbigou, L. Magna, D. Morvan, Appl. Catal. A: Gen. 373 (2010) 1–56.
[4] K. Ishihara, A. Hasegama, H. Yamamoto, Angew. Chem. Int. Ed. 40 (2001) 4077–4079.
[5] A. Arfan, J.P. Bazureau, Org. Process Res. Dev. 9 (2005) 743–748.
[6] J.E. Bara, Ind. Eng. Chem. Res. 50 (2011) 13614–13619.
[7] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 926–927.
[8] A.E. Visser, J.D. Holbrey, R.D. Rogers, Chem. Commun. (2001) 2484–2485.
[9] T.L. Merrigan, E.D. Bates, S.C. Dorman, J.H. Davis Jr., Chem. Commun. (2000) 2051–2052.
[10] P. Virtanen, H. Karhu, G. Toth, K. Kordas, J.P. Mikkola, J. Catal. 263 (2009) 209–219.
[11] J.F. Huang, G.A. Baker, H. Luo, K. Hong, Q.F. Li, N.J. Bjerrum, S. Dai, Green Chem. 8 (2006) 599–602.
[12] D. Fang, J. Yang, C. Jiao, ACS Catal. 1 (2011) 42–47.
[13] A.C. Cole, J.L. Jensen, L. Ntai, K. Loan, T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 5962–5963.
[14] Y.J. Kim, R.S Varma, J. Org. Chem. 70 (2005) 7882–7891.

[15] R. Kore, R. Srivastava, Catal. Commun. 12 (2011) 1420–1424.
[16] R. Kore, R. Srivastava, J. Mol. Catal. A: Chem. 345 (2011) 117–126.
[17] L.C. Larock, W.W. Leong, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, Oxford, 1991.
[18] L. Hintermann, A. Labonne, Synthesis 8 (2007) 1121–1150.
[19] B.M. Trost, Science 254 (1991) 1471.
[20] M. Kutscheroff, Chem. Ber. 14 (1881) 1540–1542.
[21] D.A. Ponomarev, S.M. Shevchenko, J. Chem. Educ. 84 (2007) 1725–1726.
[22] E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, Angew. Chem. Int. Ed. 41 (2002) 4563–4565.
[23] M. Nicolas, S.R. Ruben, P.N. Steven, J. Am. Chem. Soc. 131 (2009) 448–449.
[24] W. Baidossi, M. Lahav, J. Blum, J. Org. Chem. 62 (1997) 669–672.
[25] K. Imi, K. Imai, K. Utimoto, Tetrahedron Lett. 28 (1987) 3127–3130.
[26] Y. Sasaki, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1986) 790–791.
[27] T. Tsuchimoto, T. Joya, E. Shirakawa, Y. Kawakami, Synlett (2000) 1777–1778.
[28] N. Olivi, E. Thomas, J.F. Peyrat, M. Alami, J.D. Brion, Synlett (2004) 2175–2179.
[29] A.D. Allen, Y. Chiang, A.J. Kresge, T.T. Tidwell, J. Org. Chem. 47 (1982) 775–779.
[30] W.L. Wong, K.P. Ho, L.Y.S. Lee, K.M. Lam, Z.Y. Zhou, T.H. Chan, K.Y. Wong, ACS Catal. 1 (2011) 116–119.
[31] G. Zhao, T. Jiang, H. Gao, B. Han, J. Huang, D. Sun, Green Chem. 6 (2004) 75–77.
[32] M.A. Zolfigol, A. Khazaei, A.R.M. Zare, A. Zare, V. Khakyzadeh, Appl. Catal. A 400 (2011) 70–81.
[33] L. Zhang, M. Xian, Y. He, L. Li, J. Yang, S. Yu, X. Xu, Bioresour. Technol. 100 (2009) 4368–4373.
[34] C. Thomazeau, H.O. Bourbigou, L. Magna, S. Luts, B. Gilbert, J. Am. Chem. Soc. 125 (2003) 5264–5265.
[35] Y. Gu, J. Zhang, Z. Duan, Y. Deng, Adv. Synth. Catal. 347 (2005) 512–516.
[36] Y. Wang, X. Gong, Z. Wang, L. Dai, J. Mol. Catal. A: Chem. 322 (2010) 7–16.
[37] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.
[38] V. Lucchini, G. Modena, J. Am. Chem. Soc. 112 (1990) 6291–6296.
[39] R.C. Gonzalez, L. Escalante, J.A. Varela, L. Castedo, C. Saa, Org. Lett. 11 (2009) 1531–1533.