Journal of Molecular Catalysis A: Chemical 376 (2013) 90–97

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

A simple, eco-friendly, and recyclable bi-functional acidic ionic liquid catalysts for Beckmann rearrangement

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ARTICLE INFO

Article history:
Received 10 November 2012
Received in revised form 9 April 2013
Accepted 10 April 2013
Available online xxx

Keywords:
Ionic liquids
Bi-functional acid catalysts
Beckmann rearrangements
Lewis acidity
Brönsted acidity

ABSTRACT

A library of ionic liquids was prepared by varying the cations and anions. Bi-functional acidic ionic liquids were prepared by the direct combination of ionic liquids and $ZnCl_2$. Ionic liquids were investigated in the Beckmann rearrangements. A simple, eco-friendly, and recyclable bi-functional acidic ionic liquid based protocol for Beckmann rearrangement is developed, which is based on the fine tuning of the Brönsted and the Lewis acidity of ionic liquids.

1. Introduction

Beckmann rearrangement is one of the classical and most popular reactions in the organic chemistry, in which amides are formed by the acid catalyzed rearrangement of oximes [1,2]. Co-production of large amount of undesired by-product and corrosive phenomenon associated with conventional acid (H_2SO_4 and $SOCl_2$) based liquid phase protocol provided a challenging task for chemists to develop alternate methods for this reaction [3]. A variety of organic acids and inorganic solid acids based alternative routes were developed [4–12]. However, low selectivity, low reactant to catalyst ratio, corrosive and large volume of solvents, high operating temperature, and rapid catalyst deactivation are of serious concern. A green chemical method based on supercritical water was developed for Beckmann rearrangement, but low conversion and high temperature condition (646 K) provide its limited scope [13]. Rising demand of caprolactum production and environmental concern of the existed industrial process have provided ample opportunity for the researchers to find eco-friendly and economical procedure for Beckmann rearrangement.

Ionic liquid attracted significant attention to researchers due to their favorable physico-chemical properties [14–19]. Ionic liquids (ILs) have been widely investigated in the inter-disciplinary research areas [14–19]. Our research is focused on the synthesis of a library of ILs and on finding their applications in catalysis and materials synthesis [20–28]. Several ILs based catalysts have been reported for Beckman rearrangement [29–32]. However, few of them have suffered from the separation of the desired product from the reaction mixture. State of the art for the Beckmann rearrangement suggests that this reaction can be catalyzed by using Brönsted or Lewis acidic catalysts [29–33]. However, it is not precisely known whether Brönsted acid or Lewis acid or a combination of Brönsted and Lewis acid is good for this reaction. To understand this phenomenon, varieties of ILs were prepared and their performance was evaluated in the Beckmann rearrangement. In this study, a comprehensive and systematic study was made to develop a simple, economical, eco-friendly, and recyclable catalytic protocol for Beckmann rearrangement.

2. Experimental

2.1. Synthesis of ILs

[Bmim][Cl] is commercially available and [Hmim][Cl] was prepared by following the reported procedure (Scheme 1) [25,26]. [HPyr][Cl] was prepared by the similar procedure that was adopted for the synthesis of [Hmim][Cl]. We have already reported the synthesis of various $—SO_3H$ functionalized ILs used in this work (Scheme 1) [25,26]. However, we did not report the synthesis of metal anion (especially Zn) containing ILs, which is described as follows: In a typical synthesis, [C_3SO_3Hmim][Cl] was reacted with various amounts of $ZnCl_2$ under neat condition at 353 K for 12 h to

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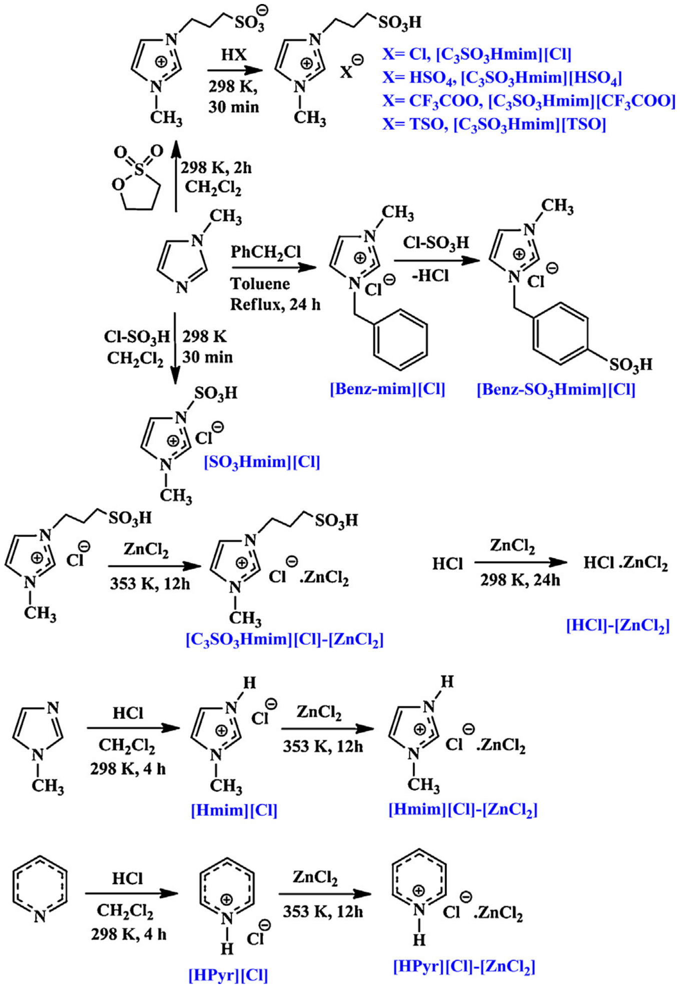
http://dx.doi.org/10.1016/j.molcata.2013.04.021



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

get $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ as a viscous liquid. With an increase of the $ZnCl_2$ mass in the reaction, the viscosity of the ionic liquid ($[C_3SO_3Hmim][Cl]–[ZnCl_2]$) also increased.

$[Hmim][Cl]–[ZnCl_2]$, $[HPyr][Cl]–[ZnCl_2]$, and $[HCl]–[ZnCl_2]$ were synthesized according to the similar procedure that was adopted for the synthesis of $[C_3SO_3Hmim][Cl]–[ZnCl_2]$. In a typical synthesis, $ZnCl_2$ was reacted with equivalent amount of ([Hmim][Cl]/[HPyr][Cl]/[HCl]) to obtain $[Hmim][Cl]–[ZnCl_2]/[HPyr][Cl]–[ZnCl_2]/[HCl][ZnCl_2]$.

[HPyr][Cl]: IR (KBr, υ, cm^{-1}) = 615, 679, 752, 926, 1000, 1053, 1163, 1198, 1249, 1332, 1385, 1485, 1537, 1611, 1634, 2621, 2947, 3060, 3400. ^1H NMR (400 MHz, D_2O): δ (ppm) = 8.8 (d, 2H), 8.7 (t, 1H), 8.1 (t, 2H). ^{13}C NMR (400 MHz, D_2O): δ (ppm) = 145, 143, 128. Elemental analysis for C_5H_6NCl: Theoretical (%): C 51.97, H 5.23, N 12.12; Experimental (%): C 51.23, H 5.74, N 12.5.

$[C_3SO_3Hmim][Cl]–[ZnCl_2]$: IR (KBr, υ, cm^{-1}) = 655, 745, 1033, 1169, 1215, 1367, 1443, 1532, 1739, 2321, 2970, 3022, 3108, 3151, 3443. ^1H NMR (400 MHz, D_2O): δ (ppm) = 8.6 (s, 1H), 7.2 (s, 2H), 4.1 (t, 2H), 3.6 (s, 3H), 2.7 (t, 2H), 2.1 (m, 2H). ^{13}C NMR (400 MHz, D_2O): δ (ppm) = 134, 121, 120, 46, 44, 33, 24. MS (ESI) for $[ZnCl_3]^-$ m/z 171, $[Zn_2Cl_5]^-$ m/z 306.6, and $[Zn_3Cl_7]^-$ m/z 443.

2.2. Characterization details

Fourier transform infrared (FT-IR) spectra were recorded on Bruker Tensor-27 spectrometer in the range of 600–4000 cm^{-1} (spectral resolution = 4 cm^{-1}; number of scans = 100). UV–vis spectra were recorded on Analytikjena Specord 250 PLUS spectrophotometer. Nuclear magnetic resonance (NMR) (^1H and ^{13}C) spectra were recorded on Bruker AM, 400 MHz NMR. Electrospray ionization-mass spectrometry (ESI-MS) was performed by a Waters Q-ToF Micro equipped with ESI Source with capillary voltage of 3000 V and cone voltage 30 V. Analysis was performed in negative ion mode. Acid values of the BAILs were determined by titration with alkali solution using phenolphthalein as the indicator.

2.3. Catalytic reaction

In a typical procedure, the oxime (1.0 mmol), catalyst1 + catalyst2 (catalyst1 = ILs, 0.0–0.1 mmol); catalyst2 = metal chlorides (0.0–0.125 mmol), where metal = Al, Mn, Fe, Co, Ni, Cu, Zn, Sn, and Ce) and 4 mL acetonitrile were charged into a 25 mL round-bottom flask equipped with a magnetic stirrer and condenser. The reactions were allowed to proceed for 0.5–4 h at 298–373 K. 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 (Hewlett-Packard; 30 m long, 0.25 mm i.d., with a 0.25-μm-thick capillary HP5column) and authentic samples obtained from Aldrich.

For the recovery of the ILs after the reaction, reaction mixture was evaporated. Since reactant and products are soluble in diethyl ether, therefore reaction mixture was washed 4–5 times with diethyl ether to remove the reactant and products and leaving behind the catalyst in the reaction flask. Reaction flask containing ILs were subjected to Rota-evaporation, followed by drying in vacuum to remove solvent from the ILs. Reactants were again charged into the reaction flask containing recovered ILs and reaction was performed by the above mentioned method.

2.4. Theoretical study details

The minimum-energy geometries of ILs were determined by performing DFT geometry optimizations at the B3LYP/6-31G level using the Gaussian09 program [34]. A vibrational analysis was performed to ensure the absence of negative frequencies and verify the existence of a true minimum.

3. Results and discussions

3.1. Synthesis and characterization of ILs

A library of ILs was prepared by varying the cations and anions (Scheme 1). Structure of ILs was characterized using various spectroscopic tools such as FT-IR, NMR, and Mass spectrometer. Acidity of Brönsted acidic ILs (BAILs) investigated in this study was measured using UV–visible spectrophotometer with a basic indicator by following the method reported in literature [35,36]. Acidity of BAILs was investigated in water 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 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.

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

Under the same concentration of 4-nitroanline (3 mg/L, $\mathrm{p}K(I)_{\mathrm{aq}} = \mathrm{p}K_a = 0.99$) 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

Table 1
Absorbance spectra of 4-nitroaniline in water after addition of BAILs.

Entry no.	BAILs	A_{max}	[*I*] (%)	[*IH*$^+$] (%)	H_0	Acid value (mg KOH/mol)
1	None	0.95	100	–	–	–
2	[C_3SO_3Hmim][Cl]	0.80	84	16	1.71	18.9
3	[C_3SO_3Hmim][HSO_4]	0.64	67	33	1.30	81.3
4	[C_3SO_3Hmim][CF_3COO]	0.69	73	27	1.42	39.7
5	[C_3SO_3Hmim][TSO]	0.71	75	25	1.46	37.2

Indicator: 4-nitroaline.

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). Acid values of the BAILs were determined by titration with 0.02 M KOH solution using phenolphthalein as the indicator (Table 1).

Acetonitrile (ACN) is a weak base and used as a probe molecule in IR spectroscopy to characterize the Lewis acidity [37]. It is well known that the C≡N group can react with Lewis acid to produce CN–Lewis complex, which shows a new absorption peak at 2200–2400 cm^{-1} in the FT-IR spectra. Upon increasing the strength of Lewis acid, the absorption peak shifts to higher wave number. ACN has two peaks at 2252 and 2294 cm^{-1} due to C≡N group. Significant shift in 2294 cm^{-1} was observed for metal halide/ACN systems. Here, we first compared the ACN-IR of $AlCl_3$, $CoCl_2$, and $ZnCl_2$. $AlCl_3$/ACN, $CoCl_2$/ACN, and $ZnCl_2$/ACN exhibited FT-IR peaks at (2310 and 2331), (2320 and 2331), 2321 cm^{-1}, respectively (Fig. 2a). Peak observed at 2331 cm^{-1} in the case of $AlCl_3$ or $CoCl_2$, clearly shows the high strength of Lewis acidity. ACN FT-IR of various [C_3SO_3Hmim][Cl]–[$ZnCl_2$] samples were investigated (Fig. 2b). No shift in 2294 cm^{-1} peak was observed for [C_3SO_3Hmim][Cl]–[$ZnCl_2$] samples (where [C_3SO_3Hmim][Cl]:$ZnCl_2$ molar ratio were 1:0.25 and 1:0.5). 2294 cm^{-1} peaks of ACN was shifted to 2313 cm^{-1} for [C_3SO_3Hmim][Cl]–[$ZnCl_2$] (where, [C_3SO_3Hmim][Cl]:$ZnCl_2$ molar ratio = 1:075) and 2317 cm^{-1} for [C_3SO_3Hmim][Cl]–[$ZnCl_2$] (where, [C_3SO_3Hmim][Cl]:$ZnCl_2$ molar ratio = 1:1). FT-IR study clearly shows that [C_3SO_3Hmim][Cl]–[$ZnCl_2$] exhibited the highest strength of Lewis acidity, when the complex was formed with 1:1 molar ratio of [C_3SO_3Hmim][Cl] and $ZnCl_2$. ACN FT-IR of various [$ZnCl_2$] containing ILs was investigated. 2294 cm^{-1} peak of ACN was shifted to 2319 cm^{-1}, (2323 and 2340 cm^{-1}), and 2329 cm^{-1} for [HCl]–[$ZnCl_2$], [HPyr][Cl]–[$ZnCl_2$], and [Hmim][Cl]–[$ZnCl_2$], respectively (Fig. 2c).

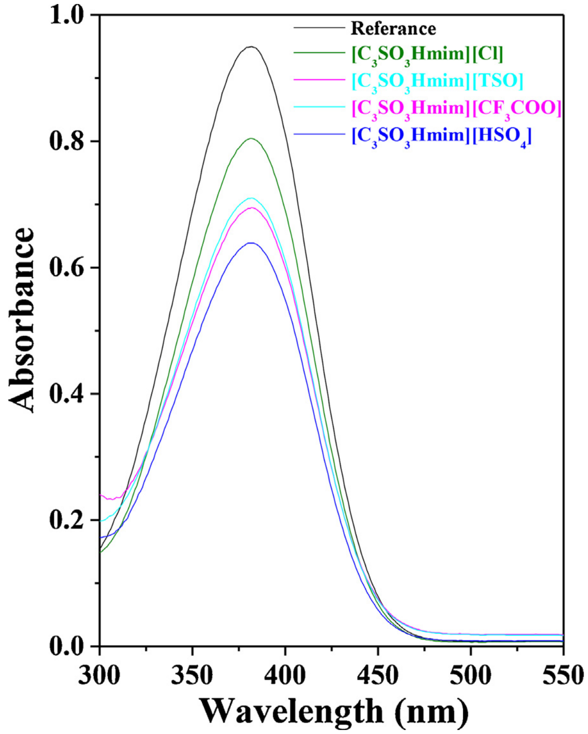


Fig. 1. Absorbance spectra of 4-nitroaniline in water after addition of BAILs.

Pyridine (Pyr) reacts with the Brönsted acid and Lewis acid sites, and produce a cation of [PyrH]$^+$ and a complex of Pyr–Lewis acid, respectively [38]. In general, following are the peak positions of various kinds of Brönsted and Lewis acid sites observed using pyridine IR: Brönsted acid sites = (1540–1550) and (1630–1640) cm^{-1}; strong Lewis acid sites = (1620–1625) and (1450–1455) cm^{-1}; weak Lewis acid sites = (1480–1490) and (1575–1585) cm^{-1}; hydrogen bonded pyridine = (1440–1445) and (1595–1605) cm^{-1}. Fig. 3 represents the Pyr FT-IR spectra of various [$ZnCl_2$] containing BAILs investigated in this study, which confirm the presence of both, Brönsted and Lewis acid sites based on the peaks observed (described above) in their Pyr-IR spectra.

3.2. Catalytic investigations

First Beckmann rearrangement was investigated using catalytic amount of [C_3SO_3Hmim][Cl] and acetophenone oxime as a model substrate. [C_3SO_3Hmim][Cl] was found to be inactive in the Beckmann rearrangement (Table 2, entry 2). It is known in the literature that the Beckmann rearrangement takes place, when PTSA is used along with $ZnCl_2$ [32]. This gave us an indication to use $ZnCl_2$ along

Table 2
Catalytic activity of ILs in the Beckmann rearrangement.

Entry no.	IL	Acetophenone oxime conversion (%)	N-phenylacetamide selectivity (%)
1	–	0	–
2	[C_3SO_3Hmim][Cl]^a	0	–
3	[C_3SO_3Hmim][Cl]^b	2	92
4	[C_3SO_3Hmim][Cl]^c	8	97
5	[C_3SO_3Hmim][Cl]^d	21	95
6	[C_3SO_3Hmim][Cl]^e	48	94
7	[C_3SO_3Hmim][Cl]	46	97
8	[C_3SO_3Hmim][HSO_4]	6	84
9	[C_3SO_3Hmim][TFA]	31	98
10	[C_3SO_3Hmim][TSO]	100	25
11	[SO_3Hmim][Cl]	25	90
12	[Benz-SO_3Hmim][Cl]	16	97
13	[Bmim][Cl]	0	–
14	[Benz-mim][Cl]	0	–
15	[Hmim][Cl]	100	93
16	[HPyr][Cl]	73	86
17	HCl^a	16	0
18	HCl	98	85

Reaction and conditions: IL (0.10 mmol), $ZnCl_2$ (0.10 mmol), acetophenone oxime (1.0 mmol), CH_3CN (4 mL), reaction temperature (353 K), and reaction time (4 h).

[a] $ZnCl_2$ = 0.

[b] $ZnCl_2$ = 0.025 mmol.

[c] $ZnCl_2$ = 0.050 mmol.

[d] $ZnCl_2$ = 0.075 mmol.

[e] $ZnCl_2$ = 0.125 mmol.

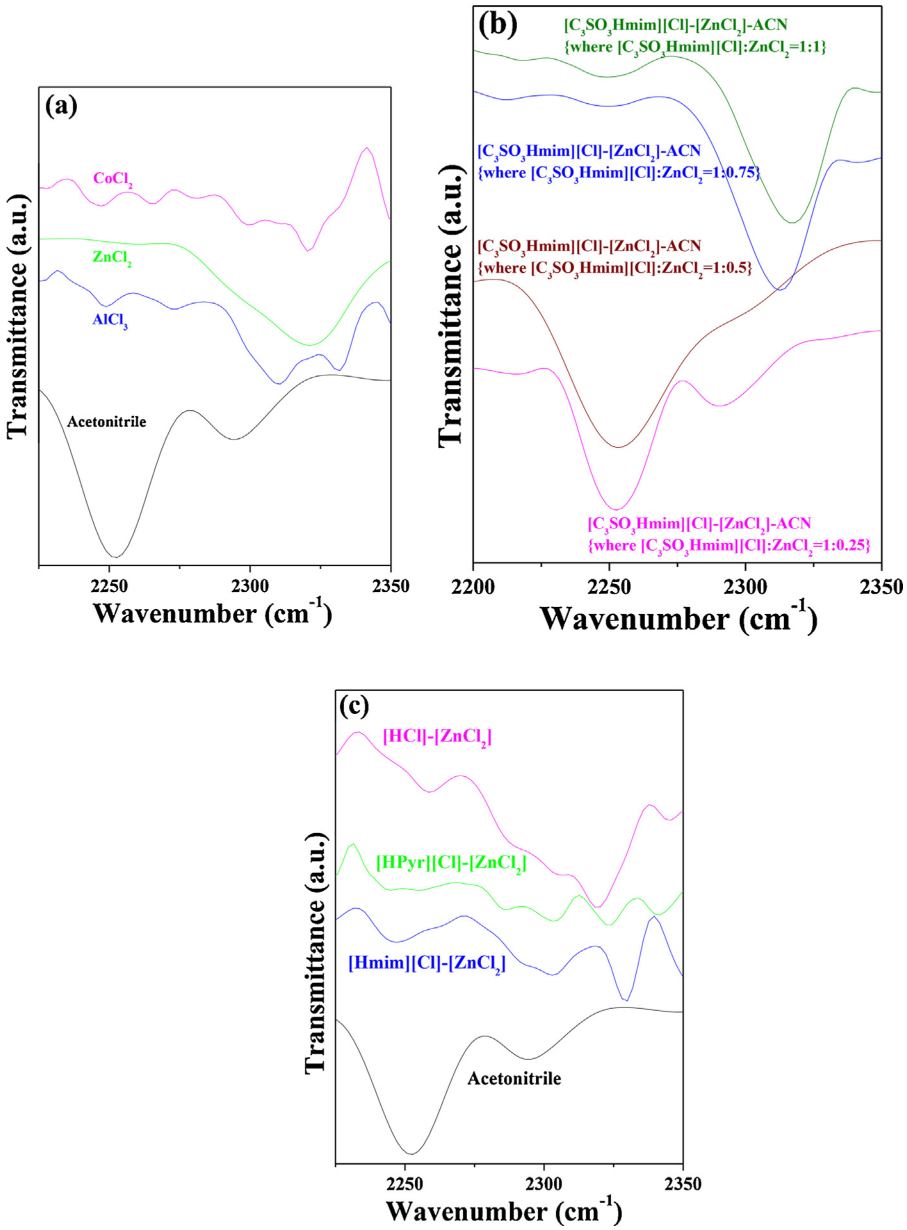


Fig. 2. ACN-FT-IR spectra of (a) metal halides (metal halide:ACN = 2:1); (b) [C_3SO_3Hmim][Cl]–[$ZnCl_2$] samples with different $ZnCl_2$ contents ([C_3SO_3Hmim][Cl]–[$ZnCl_2$]:ACN = 2:1); (c) $ZnCl_2$ containing ILs (ILs:ACN = 2:1).

with [C_3SO_3Hmim][Cl]. $ZnCl_2$ alone was found to be inactive under our reaction condition (Table 2). Reaction was found to be occurring when both [C_3SO_3Hmim][Cl] and $ZnCl_2$ were used together in the reaction. It was found that by increasing the amount of $ZnCl_2$ (with respect to [C_3SO_3Hmim][Cl]), the activity of the catalytic system increased (Table 2). Based on the catalytic data obtained, one can conclude that 1:1 molar ratio of [C_3SO_3Hmim][Cl]:$ZnCl_2$ was found to be optimum for this reaction.

Next, the influence of anions and location of —SO_3H in the structure of BAILs were investigated. To study the influence of anion, [C_3SO_3Hmim] cation based BAILs were investigated. Catalytic activity data confirmed that among the anions investigated; [Cl] was found to be the best anion (Table 2). At one instance, if we assume that this reaction is an acid catalyzed reaction, then with increase in the acidity, the catalytic activity should increase. Hammett acidity and acid value for [C_3SO_3Hmim][HSO_4] was found to be the maximum (Table 1), therefore, its activity should found to be maximum among this series of BAILs investigated. However, catalytic activity data is just reverse of the acidity trends observed using Hammett acidity and acid value (Table 2). Based on these observations, it can be said that the Beckmann rearrangement does not depend solely on the acidity of BAILs. It may be noted that $ZnCl_2$ alone and BAILs alone are inactive, therefore the catalytic species are generated in situ by the reaction of BAILs and $ZnCl_2$. Based on the catalytic activity data of [C_3SO_3Hmim] cation and various anions (Entries 7–10, Table 2), it can be concluded that the catalytic active species formed by the reaction of [C_3SO_3Hmim][Cl] and [$ZnCl_2$] is more active than [C_3SO_3Hmim][HSO_4]/[C_3SO_3Hmim][CF_3COO]/[C_3SO_3Hmim][TSO] and [$ZnCl_2$]. It is known that $ZnCl_2$ reacts with [C_3SO_3Hmim][Cl] and form [C_3SO_3Hmim][Cl]–[$ZnCl_2$] or similar species [19], which is the active species for the Beckmann rearrangement investigated in this study. Based on this observation, it can be concluded that [C_3SO_3Hmim][Cl]–[$ZnCl_2$] is the most active species for the Beckmann rearrangement compared to other [BAILs]–[$ZnCl_2$] species. In order to validate this observation, several control experiments

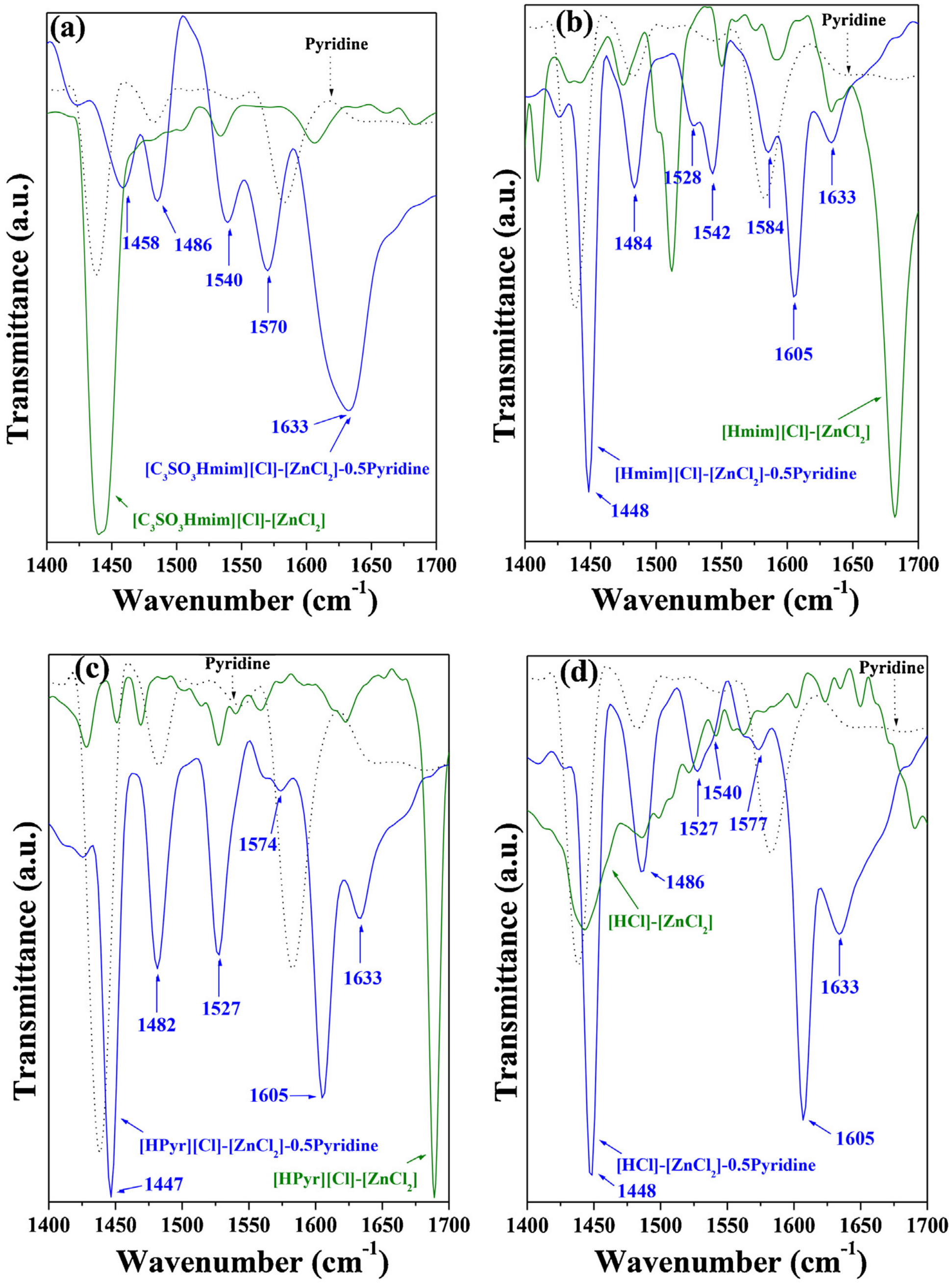


Fig. 3. Pyridine FT-IR spectra of (a) $[C_3SO_3Hmim][Cl]–[ZnCl_2]$, (b) $[Hmim][Cl]–[ZnCl_2]$, (c) $[HPyr][Cl]–[ZnCl_2]$, (d) $[HCl]–[ZnCl_2]$. In these studies ILs and Pyr were taken in 2:1.

were performed. When only HCl was used as catalyst under the optimized reaction condition, it did not form any desired product (acetophenone oxime conversion = 16%, product selectivity (%) = N-phenylacetamide: acetophenone = 0: 100). It may further be noted that in the presence of only $[C_3SO_3Hmim][Cl]$ (Entry no. 2, Table 2) or PTSA [31], no reaction took place, which confirms that only Brönsted acidic catalyst (HCl or $[C_3SO_3Hmim][Cl]$ or PTSA) is not suitable for Beckman rearrangement. Based on our experiment, we can conclude that HCl is not the catalytic active species for the Beckman rearrangement (in case, if it is formed in situ by the reaction of IL and $ZnCl_2$). HCl and a variety of [Cl] containing ILs along with $ZnCl_2$ were investigated (Table 2). Catalytic investigation and FT-IR investigations reveals that Brönsted as well as Lewis acidity provided by the $ZnCl_2$ based ILs are important for this reaction. Though a good activity was observed for catalyst system ($[Hpyr][Cl] + [ZnCl_2]$) but the highest activity was observed for ($[Hmim][Cl] + [ZnCl_2]$) catalytic system (Table 2).

Having found [Cl] as the best anion, the influence of the location of $-SO_3H$ in the structure of BAILs [direct $N-SO_3H$ and N-spacer $-SO_3H$ (where spacer = propyl or benzyl)] was also investigated (Scheme 1). Catalytic activity data shows that among the $-SO_3H$ containing BAILs investigated, $[C_3SO_3Hmim]$ was found to be the best cation investigated in this study (Table 2). Above section shows that the catalytic species are generated in situ by the reaction of [Cl] containing BAILs and $[ZnCl_2]$. Since in these cases, only [Cl] anion is present, then, in-principle the activity should be similar. This is possible at only one condition, when availability of [Cl] in BAILs to make complex with $ZnCl_2$ is the same. If all the [Cl] is not available to make complex then its activity will be less. Based on the catalytic data, one can say that availability of [Cl] to form active species is

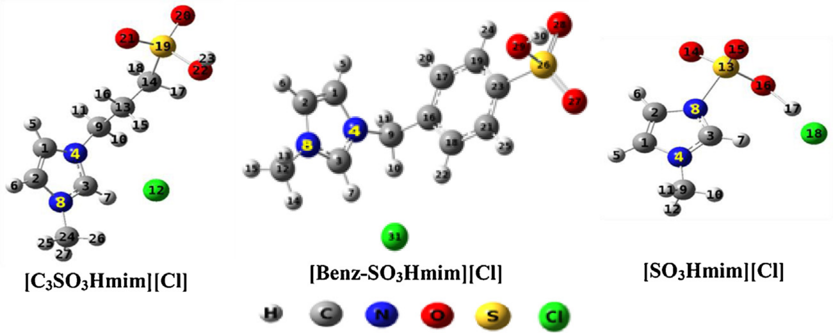


Fig. 4. Optimized structure of BAILs calculated at B3LYP/6-31G.

Table 3
The geometry parameters of BAILs calculated at B3LYP/6-31G.

Observed parameters	$[C_3SO_3Hmim][Cl]$	$[Benz\text{-}SO_3Hmim][Cl]$	$[SO_3Hmim][Cl]$
H—O bond distance of sulfonic acid (Å)	$H_{23}—O_{22} = 0.988$	$H_{30}—O_{29} = 0.989$	$H_{17}—O_{16} = 1.542$
$(N)_2C—H$	$C_3—H_7 = 1.088$	$C_3—H_7 = 1.112$	$C_3—H_7 = 1.077$
Other hydrogen bonds in BAILs (Å)	$H_7\cdots Cl_{12} = 2.520$ $H_{15}\cdots Cl_{12} = 2.674$	$H_7\cdots Cl_{31} = 2.067$ $H_{10}\cdots Cl_{31} = 2.559$ $H_{22}\cdots Cl_{31} = 2.604$	$H_{17}\cdots Cl_{18} = 1.005$ $H_7\cdots Cl_{18} = 2.596$

different for different BAILs investigated in this study. To confirm our hypothesis, structure of $—SO_3H$ containing BAILs were geometrically optimized using B3LYP/6-31G (Fig. 4). In order to confirm the availability of [Cl] to make complex with $ZnCl_2$, the bonding of Cl with its neighboring groups were analyzed. Since the bond length of $(N)_2C—H\cdots Cl$ in $[C_3SO_3Hmim][Cl]$ was found to be maximum (Table 3), hence it is most easily available to make complex with $ZnCl_2$, therefore its activity was found to be the maximum in this series.

After identifying the best BAILs and BAILs:$ZnCl_2$ ratio, the next aim was to find the best metal halide for this reaction. A series of commercially available metal halides along with $[C_3SO_3Hmim][Cl]$ were investigated in the Beckmann rearrangement under the optimized condition and the results were analyzed (Fig. 5). Based on the catalytic activity data, one can conclude that $ZnCl_2$ was found to be the best among the metal halides investigated (based on the selectivity). Based on the catalytic activity and ACN FT-IR, it can be concluded that for the Beckmann rearrangement, moderate Lewis acidity would be more appropriate for high selectivity of amide product.

It is described above that the Beckmann rearrangement occurs efficiently, when along with ILs having [Cl] anion, $ZnCl_2$ is also added in the equimolar ratio (with respect to ILs) in the reaction. It is well known that a catalytic process can be efficient, if the catalyst can be recycled with negligible loss in catalytic activity. Since the above mentioned protocol involves the use of combination of ILs and $ZnCl_2$, separation of these two catalysts from the reaction mixture after the reaction is very difficult. Hence, it was thought that if a catalyst is designed in which both ILs and $ZnCl_2$ were present concomitantly in the same structure then it would be one catalyst system and its separation and reusability would become an easy affair. Keeping that in mind, using direct combination of ILs with $ZnCl_2$, four bi-functional catalysts $[C_3SO_3Hmim][Cl]–[ZnCl_2]$, $[Hmim][Cl]–[ZnCl_2]$, $[HPyr][Cl]–[ZnCl_2]$, and $[HCl]–[ZnCl_2]$ were prepared (Scheme 1) and investigated in the Beckmann rearrangement (Table 4). Influence of the amount of $ZnCl_2$ in the bi-functional ionic liquid was investigated using $[C_3SO_3Hmim][Cl]–[ZnCl_2]$. Based on the catalytic activity data, one can conclude that with an increase in the amount of $ZnCl_2$ in the bi-functional ionic liquid, catalytic activity increases, and it levels off with highest catalytic activity at equimolar ratio of $[C_3SO_3Hmim][Cl]$ and $ZnCl_2$ (Table 4). ACN-IR also confirmed that the Lewis acid strength is found to be the highest for $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ (where $[C_3SO_3Hmim][Cl]:ZnCl_2 = 1:1$) (Fig. 2c). The catalytic activity of $[Hpyr][Cl]–[ZnCl_2]$ was found to be better than the $[Hmim][Cl]–[ZnCl_2]$. Though the complete conversion of acetophenone oxime was observed using $[Hpyr][Cl]–[ZnCl_2]$, but the product selectivity was less (82%). High product selectivity (98%) with good reactant conversion (72%) was

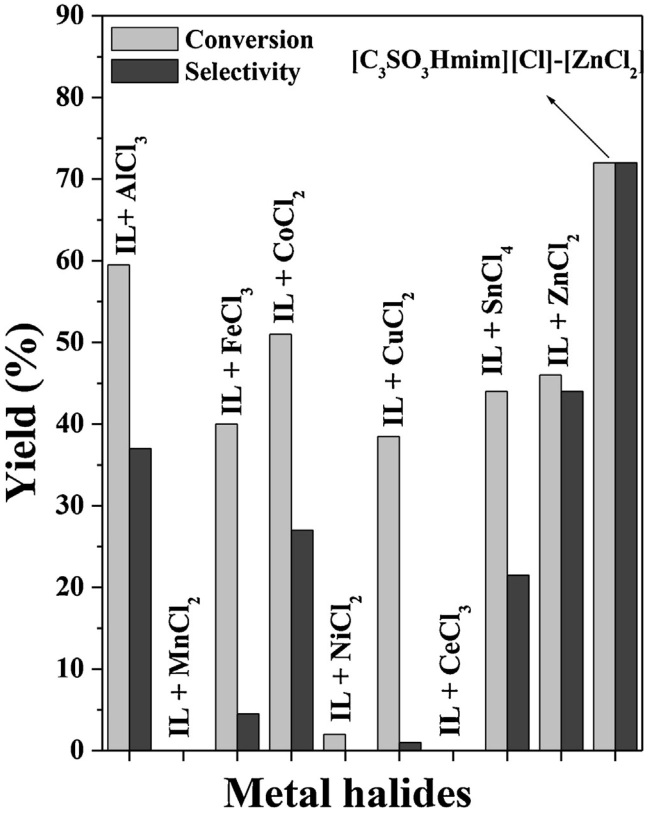


Fig. 5. The Beckmann rearrangement of acetophenone oxime catalyzed by (IL+ metal halides; where IL = $[C_3SO_3Hmim][Cl]$).

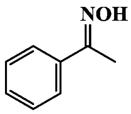
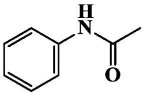
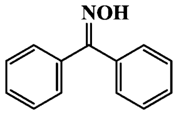
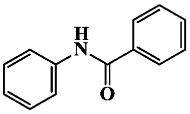
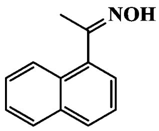
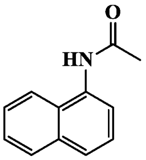
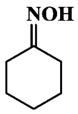
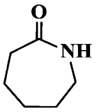
Table 4
Catalytic activity of $[ZnCl_2]$ containing ILs in the Beckmann rearrangement.

Entry No.	Catalyst	Acetophenone oxime conversion (%)	N-phenylacetamide selectivity (%)
1	$[C_3SO_3Hmim][Cl]–[ZnCl_2]$[a]	3	100
2	$[C_3SO_3Hmim][Cl]–[ZnCl_2]$[b]	12	99
3	$[C_3SO_3Hmim][Cl]–[ZnCl_2]$[c]	37	99
4	$[C_3SO_3Hmim][Cl]–[ZnCl_2]$[d]	72 (66)[e]	98 (95)[e]
5	$[C_3SO_3Hmim][Cl]–[ZnCl_2]$[f]	14	0
6	$[Hmim][Cl]–[ZnCl_2]$[d]	70 (65)[e]	90 (85)[e]
7	$[HPyr][Cl]–[ZnCl_2]$[d]	100 (92)[e]	82 (74)[e]
8	$[HCl]–[ZnCl_2]$[d]	95 (0)[e]	89 (0)[e]

Reaction conditions: ILs (0.10 mmol), acetophenone oxime (1.0 mmol), CH_3CN (4 mL), reaction temperature (353 K), and reaction time (4 h).

[a] 0.25 equiv. of $ZnCl_2$ in ILs.
[b] 0.5 equiv. of $ZnCl_2$ in ILs.
[c] 0.75 equiv. of $ZnCl_2$ in ILs.
[d] 1.0 equiv. of $ZnCl_2$ in ILs.
[e] Catalytic activity data after third recycle.
[f] Reaction was performed in the absence of any solvent and using 1.0 equiv. of $ZnCl_2$ in ILs.

Table 5
Catalytic activity of $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ in the Beckmann rearrangement.

Entry no.	Reactant	Product	Conversion (%)	Selectivity (%)
1			72	98
2			69	98
3			65	94
4			35	91

Reaction and conditions: $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ (0.1 mmol), oxime (1.0 mmol), CH_3CN (4 mL), reaction temperature (353 K), and reaction time (4 h).

obtained using $[C_3SO_3Hmim][Cl]–[ZnCl_2]$. Pyridine IR confirms the presence of Brönsted and Lewis acidity and ACN-IR confirms the presence of Lewis acidity in $[C_3SO_3Hmim][Cl]–[ZnCl_2]$, $[Hmim][Cl]–[ZnCl_2]$, $[HPyr][Cl]–[ZnCl_2]$, and $[HCl]–[ZnCl_2]$. Brönsted/Lewis acid ratio for $[C_3SO_3Hmim][Cl]–[ZnCl_2]$, $[Hmim][Cl]–[ZnCl_2]$, $[HPyr][Cl]–[ZnCl_2]$, and $[HCl]–[ZnCl_2]$ were found to be 1.48, 0.54, 0.85, and 0.87, respectively. Therefore, based on FT-IR and catalytic activity data, it can be concluded that an optimum Brönsted and Lewis acidity is required for the catalyst to exhibit the highest activity and selectivity. Such a fine tuned optimum Brönsted and Lewis acidity is provided by $[C_3SO_3Hmim][Cl]–[ZnCl_2]$.

$[ZnCl_2]$ containing BAILs were subjected to reusability up to 3 times (Table 4). $[HCl]–[ZnCl_2]$ was found to be soluble in the reaction medium and other extracting solvents and therefore it is not possible to reuse (Table 4). Catalysts were recovered by evaporating solvent and washing the reaction mixture with diethyl ether. Among other three catalysts investigated for reusability, $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ exhibited excellent reusability profile compared to other two catalysts investigated for the reusability (Table 4). The result suggests that a marginal decrease in the activity was observed using $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ after third recycles. Having found the optimized reaction condition, applicability of $[C_3SO_3Hmim][Cl]–[ZnCl_2]$ was investigated in the wide variety of commercially available oximes. Beckmann rearrangement proceeded well, delivering good product yields, and accommodated a wide range of oximes (Table 5). Both aromatic and aliphatic oximes could be converted to amides under the given conditions.

4. Conclusion

A highly efficient, simple, eco-friendly, economical, and recyclable bi-functional acidic ionic liquids were developed for the Beckmann rearrangement for wide variety of ketoximes. It was possible to find a highly active and selective catalyst by fine tuning the Brönsted and the Lewis acidity of ionic liquids by systematic variation of cations and anions. Structure activity relationship was established by using theoretical studies and acidity measurements.

Acknowledgements

Authors are grateful to Department of Science and Technology (SR/S1/PC/31/2009) and Director IIT Ropar for financial assistance. RK thank CSIR, New Delhi for fellowship.

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