

# Protic pyridinium ionic liquids: Synthesis, acidity determination and their performances for acid catalysis

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Received 30 November 2005; received in revised form 19 January 2006; accepted 19 January 2006

Available online 3 March 2006

## Abstract

Three new protic ionic liquids based on 2-methylpyridinium were prepared and characterized. Their catalytic activities for the *tert*-butylation of phenol and the esterification of cyclic olefins with acetic acid were examined and satisfactory results were obtained over 2-methylpyridinium trifluoromethanesulfonate ([2-MPyH]OTf). Hammett method was used to determine the acidity order of these ionic liquids and the results are consistent with the catalytic activities observed in the acid-catalyzed probe reactions.

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**Keywords:** Protic ionic liquids; 2-Methylpyridinium; Hammett acidity; Brønsted acidity; Acid catalysis

## 1. Introduction

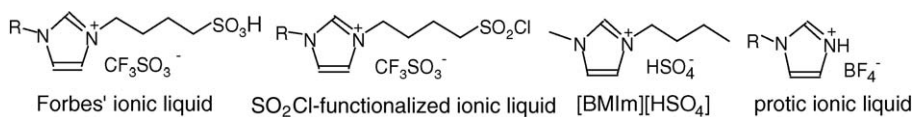
The application of ionic liquids as reaction media for a wide variety of synthetic processes is an area of intense research. Ionic liquids provide a vapourless, thermally stable and reusable 'green' solvent for chemical reactions [1]. Acid catalysis based on ionic liquids has been considered to be very important because of the widespread use of acid catalysis in synthetic and industrial chemistry [2,3]. Over the past decade, chloroaluminate ionic liquids have gained increasing attention in replacement of the conventional mineral and solid acid catalysts because of their negligible vapour pressure, outstanding acidity and tunable solubility for some organic species [4]. Nevertheless, chloroaluminate ionic liquids are very sensitive to hydrolysis [5,6]. Trace amount of water can change the composition of the salt and the concentration of the protons. As a result, it is difficult to accurately control the acidity of these ionic liquids. Therefore, the development of water- and air-stable and more efficient non-chloroaluminate acidic ionic liquids is highly desirable.

The first non-chloroaluminate room temperature acidic ionic liquid, such as SO<sub>3</sub>H-functionalized ionic liquid, was prepared by Forbes and co-workers [7] (Scheme 1). It is flexible, non-volatile, and immiscible with many organic solvents, especially

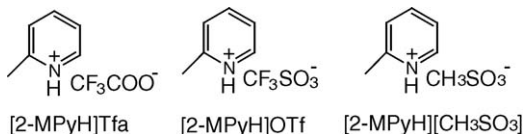
with CH<sub>2</sub>Cl<sub>2</sub>. This feature has been exploited for the porphyrin synthesis in a Forbes' ionic liquid/CH<sub>2</sub>Cl<sub>2</sub> biphasic system [8]. Recently, we have prepared a kind of SO<sub>2</sub>Cl-functionalized ionic liquid starting from Forbes' ionic liquid aimed at Beckmann rearrangement [9,10]. Another acidic ionic liquid, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIm][HSO<sub>4</sub>]), which could be prepared by ion exchange between [BMIm]Cl and H<sub>2</sub>SO<sub>4</sub> or NaHSO<sub>4</sub>, has been used in esterification [11] and alkylation [12]. Furthermore, some inorganic or organic acids, such as HCl, HBF<sub>4</sub> and CF<sub>3</sub>COOH, could react directly with *N*-alkylimidazoles to form a new class of protic ionic liquids, which bear an acidic proton on nitrogen 3 of the imidazolium ring. It is noted that on the basis of protic ionic liquids, BASF has commercialized a process under the name BASIL [1]. Recently, the protic ionic liquids have been used as acidic catalysts for the esterification [13], protection reaction of aldehyde carbonyls [14], Mannich reaction [15], Biginelli condensation [16] and Friedlander annulation [17].

We are especially interested in the applications of functionalized acidic ionic liquids in catalytic and organic reactions. The reactions investigated previously in our research group were esterification [18], acetalization [19] and cyclization of 1-dodecene [20]. During our investigations, we have noted that the synthesis and applications of pyridinium-based acidic ionic liquids [21,22] is much fewer as compared to that of imidazolium. Therefore, we chose to evolve a new class of functionalized acidic ionic liquids based on pyridinium (Scheme 2). Catalytic

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Scheme 1. The structures of the representative non-chloroaluminate acidic ionic liquids.



Scheme 2. Protic pyridinium ionic liquids were synthesized in this paper.

activities of these new ionic liquids in probe acid catalytic reactions were also examined. In order to gain an understanding of the acidity–activity relationship, the Hammett method was introduced to evaluate the acidity of the ionic liquids.

## 2. Experimental

### 2.1. Preparation of protic ionic liquids

$\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  were dried by standard procedure before use. In a typical preparation procedure, 2-methylpyridine (0.3 mol) and 30 ml  $\text{CHCl}_3$  were charged in a three-necked flask, which was equipped with a magnetic stirring and condenser. Then trifluoromethanesulfonic acid (0.3 mol) was added slowly over a period of 60 min while stirring and cooling to maintain the temperature at  $0\text{--}5\text{ }^\circ\text{C}$ . Then, the reaction mixture was stirred for an additional period of 4 h at  $50\text{ }^\circ\text{C}$ . After the solvent was removed by distillation under reduced pressure, the product was dried under vacuum at  $80\text{ }^\circ\text{C}$  for 2 h. Synthesis and purification of the other two ionic liquids (Table 1) were analogous to the above procedure.

### 2.2. Characterization of protic ionic liquids

#### 2.2.1. Identification of ionic liquids

The obtained organic salts were identified by NMR, IR and elements analysis, and the obtained data are listed below.

**2-Methylpyridinium trifluoroacetate** ([2-MPyH]Tfa). Colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 2.87 (s, 3H), 7.80–7.84 (m, 2H), 8.40 (t,  $J_1 = 8.4\text{ Hz}$ ,  $J_2 = 7.2\text{ Hz}$ , 1H), 8.73 (d,  $J = 5.2\text{ Hz}$ , 1H), 16.83 (brs, 1H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 160.8, 153.9, 145.4, 140.9, 127.6, 124.1, 115.8, 19.2; IR

(KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3071, 2361, 1670, 1194, 1138, 768, 720. Analysis:  $\text{C}_8\text{H}_8\text{NF}_3\text{O}_2$ , calcd (%): C 46.39, H 3.89, N 6.76; found: C 46.33, H 3.96, N, 6.74.

**2-Methylpyridinium trifluoromethanesulfonate** ([2-MPyH]OTf). White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 2.89 (s, 3H), 7.28–7.89 (m, 2H), 8.41–8.45 (m, 1H), 8.70 (d,  $J = 6.0\text{ Hz}$ , 1H), 15.01 (brs, 1H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 154.1, 146.3, 141.2, 128.0, 124.7, 120.2, 19.7; IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3275, 2972, 1640, 1294, 1252, 1164, 1029, 777, 640. Analysis:  $\text{C}_7\text{H}_8\text{NF}_3\text{SO}_3$ , calcd (%): C 34.57, H 3.32, N 5.76, S 13.18; found: C 34.52, H 3.41, N 5.74, S 13.23.

**2-Methylpyridinium methanesulfonate** ([2-MPyH][ $\text{CH}_3\text{SO}_3$ ]). White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 2.91 (s, 3H), 7.29–7.79 (m, 2H), 8.33–8.35 (m, 1H), 8.90 (d,  $J = 5.6\text{ Hz}$ , 1H), 17.08 (brs, 1H); IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 2924, 1617, 1192, 1050, 772, 582. Analysis:  $\text{C}_7\text{H}_{11}\text{NSO}_3$ , calcd (%): C 44.43, H 5.86, N 7.40, S 16.95; found: C 44.39, H 5.95, N 7.41, S 16.99.

#### 2.2.2. DSC characterization of ionic liquids

Differential scanning calorimetry (DSC) data were obtained in sealed aluminium pans with a cooling and heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  on a Mettler DSC822<sup>e</sup> using the STAR analysis software. Temperatures reported from DSC data are curve peaks, freezing points being exothermic upon cooling and melting points being endothermic upon heating.

#### 2.2.3. UV–vis acidity evaluation

Dichloromethane solutions of the ionic liquids were prepared from dried  $\text{CH}_2\text{Cl}_2$  and the ionic liquids (dried under vacuum at  $80\text{ }^\circ\text{C}$  for 2 h). All spectra were obtained with an Agilent B453 spectrophotometer.

#### 2.2.4. Catalytic tests

All *tert*-butylation of phenol reactions were conducted in a 90 ml autoclave with a glass tube inside, equipped with magnetic stirring. In each reaction, 2 mmol ionic liquid, 20 mmol *tert*-butyl alcohol (TBA) and 10 mmol phenol were successively introduced and allowed to react at  $100\text{ }^\circ\text{C}$  for 6 h. After the reaction, the autoclave was cooled to room temperature and the product recovery was conducted through  $\text{Et}_2\text{O}$  (5 ml  $\times$  2) extraction, the upper organic phase containing the product was simply separated from the ionic liquid by filtration and decantation. The extract was combined, followed by GC analysis. Quantitative analysis was conducted with an Agilent 1790 GC (FID detector) using benzene as an internal standard with a 30 m  $\times$  0.25 mm  $\times$  0.33  $\mu\text{m}$  capillary column (SE-54). Qualitative analyses were conducted with a HP 6890/5973 GC–MS with a 30 m  $\times$  0.25 mm  $\times$  0.33  $\mu\text{m}$  capillary column with chemstation containing a NIST Mass Spectral Database. The ionic

Table 1  
2-Methylpyridinium ionic liquids melting and freezing points as determined from DSC data

Ionic liquids	$T_{\text{mp}}^{\text{a}}$ ( $^\circ\text{C}$ )	$T_{\text{fp}}^{\text{a}}$ ( $^\circ\text{C}$ )	Observed supercooling ( $\Delta T$ )
[2-MPyH]OTf	72	32	40
[2-MPyH][ $\text{CH}_3\text{SO}_3$ ]	99	40	58
[2-MPyH]Tfa	<sup>b</sup>	<sup>b</sup>	–

<sup>a</sup> The temperature peak associated with a  $1\text{ }^\circ\text{C}$  phase transition observed upon cooling ( $T_{\text{fp}}$ , exotherm) and warming ( $T_{\text{mp}}$ , endotherm).

<sup>b</sup> Only a glass transition at  $-80\text{ }^\circ\text{C}$  was observed.

liquid could be reused in the next run through purification under vacuum (8 mmHg) at 80 °C for 2 h.

In the esterification of cyclic olefins with acetic acid reaction, 1 mmol ionic liquid, 20 mmol acetic acid and 10 mmol cyclic olefins were successively introduced and allowed to react at 90 °C for 3 h. The other details are analogous to the above procedure.

### 3. Results and discussion

#### 3.1. Preparations and characterizations of ionic liquids

Three 2-methylpyridinium salts were prepared from 2-methylpyridine and organic acids ( $\text{CF}_3\text{COOH}$ ,  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{CH}_3\text{SO}_3\text{H}$ ) through an analogous procedure. 2-Methylpyridine was chosen because of its asymmetric property, easy availability as well as low cost. The obtained organic salts were characterized by NMR, IR, and elemental analysis and the results are in good agreement with that of the expected structures. Calorimetric data were obtained by heating and cooling the sample in a DSC apparatus. We typically observed substantial supercooling as the freezing points of the samples are significantly lower than the melting points (Fig. 1 and Table 1), probably due to the presence of the methyl group in two-position in the pyridine ring that enhances the asymmetry of the cation [23]. Of the three prepared organic salts, only [2-MPyH]Tfa was liquid at room temperature (25 °C) and has a glass transition around  $-80$  °C. Melting points for [2-MPyH]OTf and [2-MPyH][ $\text{CH}_3\text{SO}_3$ ] are 72 and 99 °C, respectively.

#### 3.2. Determination of the ionic liquid acidity

The acidity determination of room temperature ionic liquids is a relatively new subject, so the development of the acidity–activity relationship based on the acidic ionic liquids is much rare. Yang and Kou [24] have determined the Lewis acidity of several chloroaluminate ionic liquids by means of an IR spectroscopic probe method. Recently, Zingg et al. [25], King et al. [26] and Thomazeau et al. [27] have described a procedure to evaluate the Brønsted superacidity of HCl in a liquid chloroaluminate or the Brønsted acidity of HNTf<sub>2</sub> ( $\text{NTf}_2 = \text{N}(\text{CF}_3\text{SO}_2)_2$ ) in [BMIm][NTf<sub>2</sub>] ionic liquid from the determination of the Hammett acidity functions using UV–vis spectroscopy (Ham-

mett method), wherein a basic indicator was used to trap the dissociative proton. These research works implied that the spectrophotometric indicator method maybe a possible way to evaluate the Brønsted acidity of non-chloroaluminate ionic liquids. In the present case, this method consists of evaluating the protonation extent of uncharged indicator bases (named I) in a solution, in terms of the measurable ratio  $[\text{I}]/[\text{IH}^+]$ . However, the acidity determination of a pure acidic ionic liquid without solvent should be impossible because the initial absorbance of the total unprotonated form of the indicator (blank value) cannot be obtained. For comparison purpose, the acidity of 2-methylpyridinium-based protic ionic liquids have been examined using 4-nitroaniline as indicator in dichloromethane and the results are shown in Fig. 2. In this experiment, dichloromethane was chosen as solvent because it is an aprotic polar solvent, stable under acidic conditions and has considerable solubility for all tested ionic liquids. The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 349 nm in  $\text{CH}_2\text{Cl}_2$  (Fig. 2(top)). As the acid concentration of [2-MPyH]OTf increases, the absorbance of the unprotonated form of the indicator observed at 349 nm decreases. By taking as the initial reference the total unprotonated form of the indicator (when no acid is added to the  $\text{CH}_2\text{Cl}_2$  solution, spectrum a), we could determine the  $[\text{I}]/[\text{IH}^+]$  ratio from the measured absorbances after addition of [2-MPyH]OTf, and then the Hammett function ( $H_0$ ) is calculated (see Table 2). No absorbance decrease could be observed when [2-MPyH][ $\text{CH}_3\text{SO}_3$ ] or [2-MPyH]Tfa was added. These results clearly show the stronger acidity of [2-MPyH]OTf in dichloromethane solution as compared to that of [2-MPyH][ $\text{CH}_3\text{SO}_3$ ] and [2-MPyH]Tfa. Further-

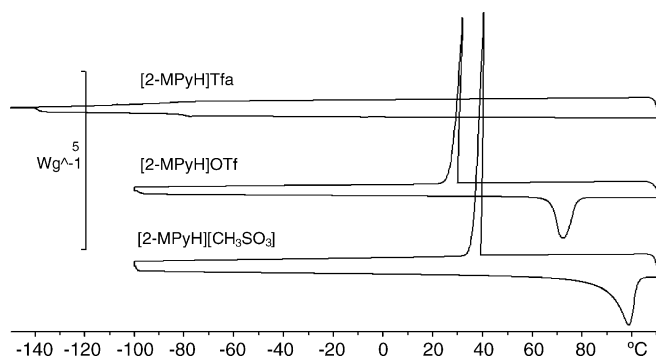


Fig. 1. Differential scanning calorimetry results for protic ionic liquids.

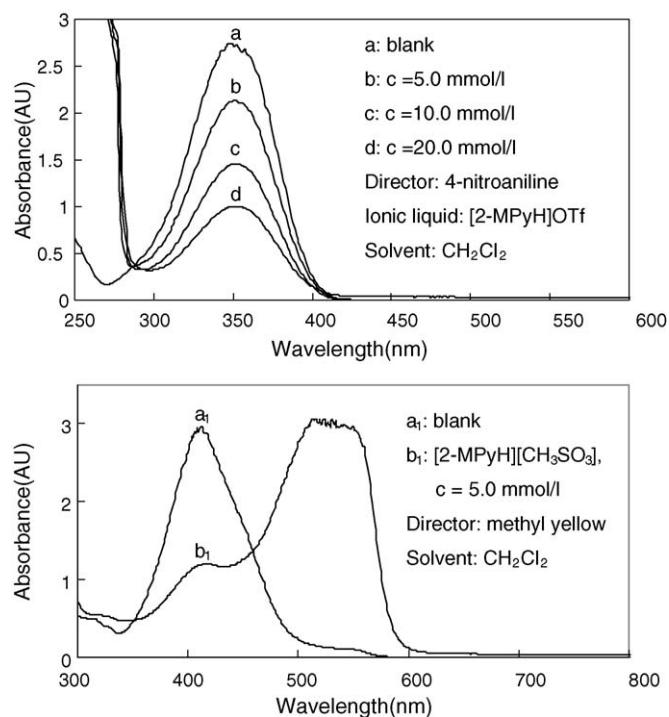


Fig. 2. (Top) Absorption spectra of 4-nitroaniline for various concentrations of [2-MPyH]OTf in  $\text{CH}_2\text{Cl}_2$ . (Bottom) Absorption spectra of methyl yellow for [2-MPyH][ $\text{CH}_3\text{SO}_3$ ] in  $\text{CH}_2\text{Cl}_2$ .

Table 2  
Calculation and comparison of Hammett functions of different protic ionic liquids (5.0 mmol l<sup>-1</sup>) in dichloromethane (20 °C)

Ionic liquids	Indicator	A <sub>max</sub>	[I] (%)	[IH <sup>+</sup> ] (%)	H <sub>0</sub>
–	4-Nitroaniline <sup>a</sup>	2.75	100	0	–
[2-MPyH]OTf	4-Nitroaniline	2.14	77.7	22.3	1.53
–	Methyl yellow <sup>b</sup>	2.98	100	0	–
[2-MPyH][CH <sub>3</sub> SO <sub>3</sub> ]	Methyl yellow	1.20	40.4	59.6	3.13
[2-MPyH]Tfa	4-Nitroaniline	<sup>c</sup>	–	–	–
[2-MPyH]Tfa	Methyl yellow	<sup>c</sup>	–	–	–

H<sub>0</sub> = pK(I)<sub>aq</sub> + log([I]<sub>s</sub>/[IH<sup>+</sup>]<sub>s</sub>).

<sup>a</sup> Indicator: 4-nitroaniline (pK(I)<sub>aq</sub> = 0.99).

<sup>b</sup> Indicator: methyl yellow (pK(I)<sub>aq</sub> = 3.3).

<sup>c</sup> No protonation of the indicator.

more, to make the relative acid strength of [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] to [2-MPyH]Tfa clear, the stronger base methyl yellow was chosen as Hammett indicator (Hammett constant 3.3) and the results were recorded in Fig. 2(bottom). Methyl yellow responded to the addition of [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] but not to [2-MPyH]Tfa (no absorbance decrease was observed). In light of the above discussion, the acidity order could be established under our experimental conditions (Table 2): [2-MPyH]OTf > [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] > [2-MPyH]Tfa.

### 3.3. Catalytic test over protic 2-methylpyridinium ionic liquids

One of the main aims of the present work was to study the possibility of using 2-methylpyridinium-based protic ionic liquids as acidic catalysts for different types of reactions and to elucidate the effect of the acidity on activity. The alkylation of phenol with *tert*-butyl alcohol (TBA) is a typical acid-catalyzed reaction and has been investigated over many acidic catalysts [28,29]. The reaction generally gives a wide product distribution of substituted phenols depending on the acidity of the catalyst. Thanks to the studies of several research groups [30,31], it is now well known that medium acids are advantageous for the formation of 4-*tert*-butylphenol (4-TBP), and that strong acids

give a product distribution in favor of 2,4-di-*tert*-butylphenol (2,4-DTBP), while weak acids are effective in producing 2-*tert*-butylphenol (2-TBP). Because of this unique and important feature, *tert*-butylation of phenol was used as the probe reaction to test the catalytic activities of the present three protic ionic liquids.

Table 3 shows the results of the experiments carried out under the same conditions (which have been optimized in advance, entries 1–4, phenol/TBA/ionic liquid = 10/20/2, 100 °C, 6 h) for comparing the catalytic performances of the ionic liquids. The results of two studies recently reported in the literature [32,33] are presented for comparison. In our hands, [2-MPyH]OTf proved to be very active (entry 3), leading to 94% conversion of phenol with a major selectivity in favor of 2,4-DTBP (83%). This result is even better than that of SO<sub>3</sub>H-functionalized ionic liquid and [OMIm]BF<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (entries 10 and 11). [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] is also capable of catalyzing the *tert*-butylation of phenol. However, the reaction was sluggish with this ionic liquid (entries 5 and 6), and a phenol conversion of less than 50% was achieved, even after 20 h. It is noteworthy that the use of the ionic liquid [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] favors the formation of 2-TBP rather than 2,4-DTBP. These observations imply that the ionic liquid [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] is a moderately effective catalyst for the *tert*-butylation of phenol. Attempts to

Table 3  
*tert*-Butylation of phenol over different protic ionic liquids<sup>a</sup>

Entry	Catalysts	Temperature (°C)	Time (h)	Conversion <sup>b</sup> (%)	Selectivity (%)			
					2-TBP	4-TBP	2,4-DTBP	2,6-DTBP
1	[2-MPyH]OTf	100	4	92	5	14	77	4
2	[2-MPyH]OTf	80	6	83	11	33	52	4
3	[2-MPyH]OTf	100	6	94	2	11	83	4
4	[2-MPyH]OTf	120	6	95	1	10	82	7
5	[2-MPyH][CH <sub>3</sub> SO <sub>3</sub> ]	100	6	35	57	29	13	1
6	[2-MPyH][CH <sub>3</sub> SO <sub>3</sub> ]	100	20	42	50	33	16	1
7	[2-MPyH]Tfa	100	20	0	–	–	–	–
8	–	100	20	0	–	–	–	–
9	[2-MPyH]OTf <sup>c</sup>	100	6	92	3	11	82	4
10	[OMIm]BF <sub>4</sub> /H <sub>3</sub> PO <sub>4</sub> (1:1, v/v) [32]	60	4	77	20	15	65	–
11	SO <sub>3</sub> H-modified ionic liquid <sup>d</sup> [33]	70	8	80	26	9	60	5

<sup>a</sup> Reaction conditions: phenol/TBA/ILs = 10:20:2 mol/mol/mol.

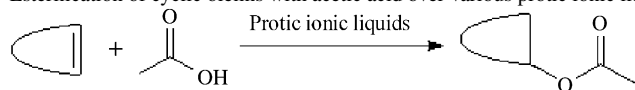
<sup>b</sup> Conversion of phenol.

<sup>c</sup> Four times reused.

<sup>d</sup> Reaction conditions: phenol/TBA/ILs = 10:20:15 mol/mol/mol.



Table 4

Esterification of cyclic olefins with acetic acid over various protic ionic liquids<sup>a</sup>

Entry	Ionic liquids	Cyclic olefins	Temperature (°C)	Time (h)	Conversion <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)
1	[2-MPyH]OTf	Dicyclopentadiene	90	3	98	99
2	[2-MPyH]OTf	Norbornene	90	3	100	99
3	[2-MPyH][CH <sub>3</sub> SO <sub>3</sub> ]	Dicyclopentadiene	90	3	22	99
4	[2-MPyH][CH <sub>3</sub> SO <sub>3</sub> ]	Norbornene	90	3	31	99
5	[2-MPyH]Tfa	Dicyclopentadiene	120	6	0	0
6	[2-MPyH]Tfa	Norbornene	120	6	0	0
7	SO <sub>3</sub> H-modified ionic liquid <sup>d</sup> [35]	Dicyclopentadiene	120	4	100 <sup>e</sup>	100
8	SO <sub>3</sub> H-modified ionic liquid <sup>d</sup> [35]	Norbornene	120	4	100 <sup>e</sup>	100

<sup>a</sup> Reaction conditions: cyclic olefins/acetic acid/ionic liquid = 10:20:1 mol/mol/mol.<sup>b</sup> Conversion of cyclic olefins.<sup>c</sup> Selectivity to the corresponding esters.<sup>d</sup> Reaction conditions: cyclic olefins/acetic acid/ionic liquid = 45:15:10 mol/mol/mol.<sup>e</sup> Conversion of acetic acid.

perform the reaction with [2-MPyH]Tfa led only to the recovery of the unreacted starting materials (entry 7). Similarly, no reaction was observed in the absence of ionic liquid (entry 8). It is also to be noted that the ionic liquid [2-MPyH]OTf can indeed be reused several times without visible loss of activity in the *tert*-butylation of phenol (entry 9).

In view of the foregoing, as a new catalyst for the *tert*-butylation of phenol, [2-MPyH]OTf is far superior to [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] in terms of the phenol conversion. The acidity order determined by Hammett method is consistent with the order of catalytic activities observed in the *tert*-butylation of phenol.

To further substantiate the results of the Hammett experiments, the esterification of cyclic olefins with acetic acid was examined over our protic 2-methylpyridinium ionic liquids, and the results are listed in Table 4. This designated probe reaction is considered to be irreversible and has been proved to be Brønsted acid sensitive in our previously works [34,35]. Under the experimental conditions, dicyclopentadiene and norbornene could be completely consumed after 3 h reaction despite the fact that the ionic liquid [2-MPyH]OTf only represented 0.1 M equiv. with respect to the cyclic olefins (entries 1 and 2). It is also worthy to note that in this case the selectivity proved to be quite high reaching nearly 100%. The catalytic efficiencies of [2-MPyH]OTf in this esterification reaction were comparable or even better than previously published data [35] (entries 7 and 8). [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] is less active than [2-MPyH]OTf under the same reaction conditions, since the conversions of dicyclopentadiene and norbornene were only 22% and 31%, respectively (entries 3 and 4). No reaction was observed in the ionic liquid [2-MPyH]Tfa (entries 5 and 6), even at elevated temperature (120 °C) and prolonged reaction time (6 h). We also find the catalytic activities decrease as follows: [2-MPyH]OTf > [2-MPyH][CH<sub>3</sub>SO<sub>3</sub>] > [2-MPyH]Tfa, which is in good agreement with the acidity order determined by the Hammett method.

#### 4. Conclusions

In summary, three new protic ionic liquids based on 2-methylpyridinium were synthesized and characterized. Their catalytic activities in the *tert*-butylation of phenol and the esterification of cyclic olefins with acetic acid were examined and satisfactory results were obtained over [2-MPyH]OTf. Further investigations revealed that the ionic liquids acidity plays a key role in the acid-catalyzed probe reactions. Based on the Hammett method, studies on acidity–activity relationship between diverse non-chloroaluminate acidic ionic liquids and traditional liquid acids are in progress in our group.

#### Acknowledgements

This work was financially supported by National Natural Science Foundation of China (nos. 20225309 and 20533080).

#### References

- [1] R.D. Rogers, K.R. Seddon, *Science* 302 (2003) 792.
- [2] J. Dupont, R.F. de Souza, P.A.Z. Suarez, *Chem. Rev.* 102 (2002) 3667.
- [3] T. Welton, *Coord. Chem. Rev.* 248 (2004) 2459.
- [4] C. Gordon, *Appl. Catal. A: Gen.* 222 (2001) 101.
- [5] H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A: Chem.* 182–183 (2002) 419.
- [6] K.R. Sheldon, *Chem. Commun.* (2001) 2399.
- [7] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weave, D.C. Forbes, J.H. Davis, *J. Am. Chem. Soc.* 124 (2002) 5962.
- [8] S. Kitaoka, K. Nobuoka, Y. Ishikawa, *Chem. Commun.* (2004) 1902.
- [9] J. Gui, Y. Deng, Z. Hua, Z. Sun, *Tetrahedron Lett.* 45 (2004) 2681.
- [10] K. Qiao, Y. Deng, C. Yokoyama, H. Sato, M. Yamashina, *Chem. Lett.* 33 (2004) 1350.
- [11] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, *Catal. Commun.* 3 (2002) 185.
- [12] P. Wasserscheid, M. Sesing, W. Korth, *Green Chem.* 4 (2002) 134.
- [13] H.P. Zhu, F. Yang, J. Tang, M.Y. He, *Green Chem.* 5 (2003) 38.
- [14] H.H. Wu, F. Yang, P. Cui, J. Tang, M.Y. He, *Tetrahedron Lett.* 45 (2004) 4963.

- [15] G. Zhao, T. Jiang, H. Gao, B. Han, J. Huang, D. Sun, *Green Chem.* 6 (2004) 75.
- [16] A.R. Gholap, K. Venkatesan, T. Daniel, R.J. Lahoti, K.V. Srinivasan, *Green Chem.* 6 (2004) 147.
- [17] S.S. Palimkar, S.A. Siddiqui, T. Daniel, R.J. Lahoti, K.V. Srinivasan, *J. Org. Chem.* 68 (2003) 9371.
- [18] Y. Deng, F. Shi, J. Peng, K. Qiao, *J. Mol. Catal. A: Chem.* 165 (2001) 33.
- [19] D. Li, F. Shi, J. Peng, S. Guo, Y. Deng, *J. Org. Chem.* 69 (2004) 3582.
- [20] K. Qiao, Y. Deng, *Tetrahedron Lett.* 44 (2003) 2191.
- [21] A. Arfan, J.P. Bazureau, *Org. Process. Res. Dev.* 9 (2005) 743.
- [22] H. Xing, T. Wang, Z. Zhou, Y. Dai, *Ind. Eng. Chem. Res.* 44 (2005) 4147.
- [23] H.L. Ngo, K. LeCompte, L. Hargens, A.B. McEwen, *Thermochim. Acta* 357–358 (2000) 97.
- [24] Y. Yang, Y. Kou, *Chem. Commun.* (2004) 226.
- [25] G.P. Smith, A.S. Dworkin, R.M. Pagni, S.P. Zingg, *J. Am. Chem. Soc.* 111 (1989) 525.
- [26] D. King, R. Mantz, R. Osteryoung, *J. Am. Chem. Soc.* 118 (1996) 11933.
- [27] C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts, B. Gilbert, *J. Am. Chem. Soc.* 125 (2003) 5264.
- [28] H. Shen, Z.M.A. Judeh, C. Ching, *Tetrahedron Lett.* 44 (2003) 981.
- [29] K. Zhang, H. Zhang, G. Xua, S. Xiang, D. Xu, S. Liu, H. Li, *Appl. Catal. A: Gen.* 207 (2001) 183.
- [30] B.M. Devassy, S.B. Halligudi, S.P. Elangovan, S. Ernst, M. Hartmann, F. Lefebvre, *J. Mol. Catal. A: Chem.* 221 (2004) 113.
- [31] G.D. Yadav, N.S. Doshi, *Appl. Catal. A: Gen.* 236 (2002) 129.
- [32] H.Y. Shen, Z.M.A. Judeh, C.B. Ching, Q.H. Xia, *J. Mol. Catal. A: Chem.* 212 (2004) 301.
- [33] J. Gui, H. Ban, X. Cong, X. Zhang, Z. Hu, Z. Sun, *J. Mol. Catal. A: Chem.* 225 (2005) 27.
- [34] Y. Gu, F. Shi, Y. Deng, *Catal. Commun.* 4 (2003) 597.
- [35] Y. Gu, F. Shi, Y. Deng, *J. Mol. Catal. A: Chem.* 212 (2004) 71.