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

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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 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 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].

The first non-chloroaluminate room temperature acidic ionic liquid, such as SO3H-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 CH2Cl2. This feature has been exploited for the porphyrin synthesis in a Forbes’ ionic liquid/CH2Cl2 biphasic system [8]. Recently, we have prepared a kind of SO2Cl3-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][HSO4]), which could be prepared by ion exchange between [BMIm][Cl] and H2SO4 or NaHSO4, has been used in esterification [11] and alkylation [12]. Furthermore, some inorganic or organic acids, such as HCl, HBF4 and CF3COOH, 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 few 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
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

CHCl₃, Et₂O and CH₂Cl₂ were dried by standard procedure before use. In a typical preparation procedure, 2-methylpyridine (0.3 mol) and 30 ml CHCl₃ were charged in a three-necked flask, which was equipped with a magnetic stirring and condenser. Then trifluoroacetanilide (0.3 mol) was added slowly over a period of 60 min while stirring and cooling to maintain the temperature at 0–5 °C. After the solvent was removed by distillation under reduced pressure, the product was dried under vacuum at 80 °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.

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Tmp (°C)</th>
<th>Tfp (°C)</th>
<th>Observed supercooling (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpyridinium trifluoroacetate</td>
<td>72</td>
<td>32</td>
<td>40</td>
</tr>
<tr>
<td>2-Methylpyridinium trifluoromethanesulfonate</td>
<td>99</td>
<td>40</td>
<td>58</td>
</tr>
</tbody>
</table>

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 (CF₃COOH, CF₃SO₃H and CH₃SO₃H) 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][CH₃SO₃] 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 HNTf₂ (NTf₂ = N(CF₃SO₂)₂) in [BMIm][NTf₂] ionic liquid from the determination of the Hammett acidity functions using UV–vis spectroscopy (Hammett 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 charged indicator bases (named I) in a solution, in terms of the measurable ratio [I]/[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 340 nm in CH₂Cl₂ (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 CH₂Cl₂ solution, spectrum a), we could determine the [I]/[IH⁺] ratio from the measured absorbances after addition of [2-MPyH]OTf, and then the Hammett function (H₀) is calculated (see Table 2). No absorbance decrease could be observed when [2-MPyH][CH₃SO₃] 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][CH₃SO₃] and [2-MPyH][Tfa]. Further-
more, to make the relative acid strength of [2-MPyH][CH3SO3] 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][CH3SO3] 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][CH3SO3] > [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 SO3H-functionalized ionic liquid and [OMIm]BF4/H3PO4 (entries 10 and 11). [2-MPyH][CH3SO3] 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][CH3SO3] favors the formation of 2-TBP rather than 2,4-DTBP. These observations imply that the ionic liquid [2-MPyH][CH3SO3] is a moderately effective catalyst for the tert-butylation of phenol. Attempts to

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Indicator</th>
<th>Amax</th>
<th>[I] (%)</th>
<th>[IH+] (%)</th>
<th>H0</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>4-Nitroaniline</td>
<td>2.75</td>
<td>100</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>[2-MPyH]OTf</td>
<td>4-Nitroaniline</td>
<td>2.14</td>
<td>77.7</td>
<td>22.3</td>
<td>1.53</td>
</tr>
<tr>
<td>–</td>
<td>Methyl yellow</td>
<td>2.98</td>
<td>100</td>
<td>0</td>
<td>3.13</td>
</tr>
<tr>
<td>[2-MPyH][CH3SO3]</td>
<td>Methyl yellow</td>
<td>1.20</td>
<td>40.4</td>
<td>59.6</td>
<td>–</td>
</tr>
<tr>
<td>[2-MPyH]Tfa</td>
<td>4-Nitroaniline</td>
<td>––</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[2-MPyH]Tfa</td>
<td>Methyl yellow</td>
<td>––</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

H0 = pK(I)aq + log([I]s/[IH+]s).

a Indicator: 4-nitroaniline (pK(I)aq = 0.99).
b Indicator: methyl yellow (pK(I)aq = 3.3).
c No protonation of the indicator.

3.3. Catalytic test over protic 2-methylpyridinium ionic liquids

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Table 4

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ionic liquids</th>
<th>Cyclic olefins</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Conversion a (%)</th>
<th>Selectivity c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[2-MPyH]OTf</td>
<td>Dicyclopentadiene</td>
<td>90</td>
<td>3</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>[2-MPyH]OTf</td>
<td>Norbornene</td>
<td>90</td>
<td>3</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>[2-MPyH][CH₃SO₃]</td>
<td>Dicyclopentadiene</td>
<td>90</td>
<td>3</td>
<td>22</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>[2-MPyH][CH₃SO₃]</td>
<td>Norbornene</td>
<td>90</td>
<td>3</td>
<td>31</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>[2-MPyH]Tfa</td>
<td>Dicyclopentadiene</td>
<td>120</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>[2-MPyH]Tfa</td>
<td>Norbornene</td>
<td>120</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>SO₃H-modified ionic liquid [35]</td>
<td>Dicyclopentadiene</td>
<td>120</td>
<td>4</td>
<td>100 e</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>SO₃H-modified ionic liquid [35]</td>
<td>Norbornene</td>
<td>120</td>
<td>4</td>
<td>100 f</td>
<td>100</td>
</tr>
</tbody>
</table>

a Reaction conditions: cyclic olefins/acetic acid/ionic liquid = 10:20:1 mol/mol/mol.
b Conversion of cyclic olefins.
c Selectivity to the corresponding esters.
d Reaction conditions: cyclic olefins/acetic acid/ionic liquid = 45:15:10 mol/mol/mol.
e 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][CH₃SO₃] 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][CH₃SO₃] 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][CH₃SO₃] > [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 studies, on acidity–activity relationship between diverse non-chloroaluminate acidic ionic liquids and traditional liquid acids are in progress in our group.

Acknowledgements

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References


