

Study of Preparation and Thermal Stability of Cyano-Functionalized Imidazolium Type Ionic Liquids

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Sixteen imidazolium type cyano-functionalized Brønsted acidic ionic liquids with HSO_4^- and H_2PO_4^- anion were prepared adopting two-step method and were characterized by FT-IR, ^1H and ^{13}C NMR. The onset temperatures of thermal decomposition of the ionic liquids were measured using thermogravimetric analysis. It was found that the decomposition onset temperatures of the as-synthesized ionic liquids were in the range of 200–260 °C. Additionally, the decomposition temperatures were highly dependent on the nature of the anions. Thermal stability of these cyano-functionalized ionic liquids decreased in the order of $\text{HSO}_4^- > \text{H}_2\text{PO}_4^-$.

Key Words: Brønsted acid, Ionic liquid, Cyano-functionalized, Thermal stability, Imidazolium.

INTRODUCTION

There are a growing awareness of research in the field of ionic liquids^{1–3} due to their particular properties, such as non-flammability, insignificant vapour pressure and wide electrochemical window, which make them suitable candidates for a wide variety of applications. Ionic liquids based on AlCl_3 appeared the earliest that are unstable and difficult for reutilization. Therefore, non-chloroaluminate ionic liquids, which are air and moisture stable, have been developed and successfully applied to synthesis, extraction, separation, etc. With the development of ionic liquids study, which contain exclusively alkyl functional group cannot meet specific demands. Thus a novel class of task specific ionic liquids (TSILs) containing special functional group with cations or anions have been developed⁴. The specific functional groups include hydroxyl group⁵, carboxyl group⁶, ester group⁷, cyano group⁸, amino group⁹, chiral group¹⁰.

As the application of ionic liquids in high-temperature systems has progressively increased, thermal stability of ionic liquids has become a significant property. The thermal properties of alkyl imidazolium-type ionic liquids are stable up to about 300 °C¹¹. Amarasekara *et al.*¹² studied the thermal stabilities of sulfonic acid group-functionalized ionic liquids and reported that the decomposition temperatures of these ionic liquids are highly dependent on the nature of the anion. Wooster *et al.*¹³ reported the long term thermal stability of ionic liquids

containing cyano group. It has been reported that alkali melt as well as alkali melt oxides, quaternary ammonium alkali, which added more difficulty on result after-treatment¹⁴, play an important role in catalyzing cyanoethylation reaction¹⁵.

As far as we are aware, there is a lack of data concerning cyano-functionalized ionic liquids containing carboxyl, alcohol, long chain alkyl on the cation. In this paper, we report the synthesis of precursor without catalyst in order to obtain cyano-functionalized Brønsted acidic ionic liquids (Fig. 1) and determine the thermal stability of these ionic liquids by thermogravimetric analysis (TGA).

EXPERIMENTAL

All chemicals are commercially available and used without further purification. FT-IR spectra were recorded on a Bruker EQUINOX FT-IR spectrometer using KBr pellets in the range of 5000–4000 cm^{-1} , ^1H and ^{13}C NMR spectra were obtained on a Mercury-400BB spectrometer at 400 MHz in $\text{DMSO}-d_6$ solution. TGA was performed on a thermal analysis system (Seiko Instruments, STA 499C), which were run in alumina pan with a heating rate of 10 °C/min under argon atmosphere and the temperature was programmed from 25–900 °C.

Synthesis of precursor 1-(2-cyanoethyl)imidazole (1):

In a three-necked, 250 mL round-bottomed flask equipped with reflux condenser and magnetic stirrer, 6.808 g (0.1 mol) of imidazole was mixed with 30 mL methanol, then 7.25 mL

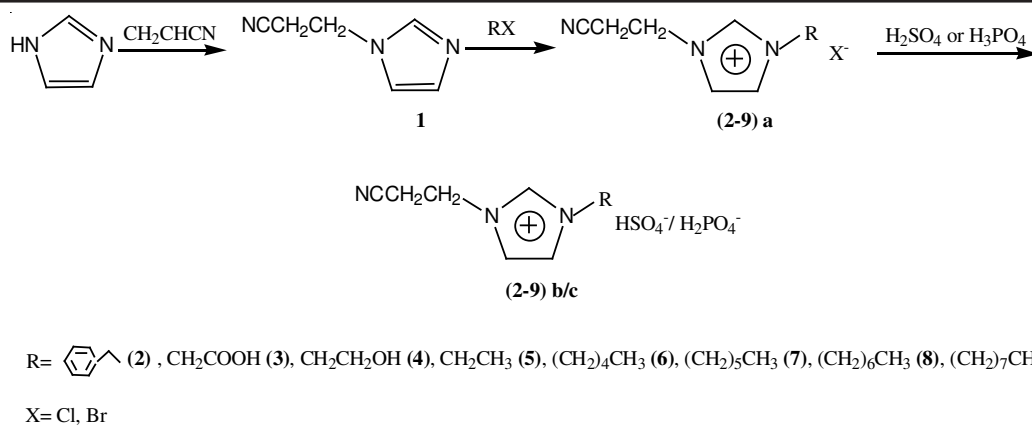


Fig. 1. Synthetic pathway to functional Brønsted acidic ionic liquids

(0.11 mol) of acrylonitrile was dropped into the solution over a period of 0.5 h at 20–30 °C. The solution was heated rapidly to 60 °C under stirring for an additional period of 6 h. Finally, the solvent and residual acrylonitrile was removed under reduced pressure. A pale yellow liquid was obtained with a yield of 97.3 % (11.783 g).

Synthesis of intermediates (2-9)a: The synthesis of 1-(2-cyanoethyl)-3-benzylimidazolium chloride ([cebzim]Cl) (**2a**) was carried out in a 250 mL round-bottomed flask, which was immersed in a recirculating heated oil-bath and fitted with a reflux condenser. 3.635 g (30 mmol) 1-(2-cyanoethyl)-imidazole was dissolved in 20 mL of acetonitrile. Then 3.5 mL (33 mmol) of freshly distilled benzyl chloride was added with constant stirring at 40 °C and refluxed for 6 h. Finally, the reaction mixture was distilled to remove the solvent. The molten salt was repeatedly washed with absolute ether and distilled at 50 °C to yield objective product as a yellowish oil liquid. And the pure product was obtained by column chromatography (petroleum ether:ethyl acetate = 6:1) as a light yellow liquid. The product was dried under vacuum for 24 h (6.986 g, 94 %).

Chloroacetic acid instead of benzyl chloride was used for preparation of 1-(2-cyanoethyl)-3-carboxymethyl imidazolium chloride ([cecmim]Cl) (**3a**), 1-(2-cyanoethyl)-3-hydroxyethylimidazolium chloride ([ceheim]Cl) (**4a**) as a viscous liquid at 50 °C under N_2 atmosphere.

1-(2-Cyanoethyl)-3-alkylimidazolium bromides (**5a-9a**) were prepared as Gong and coworkers described¹⁶.

Synthesis of objective ionic liquids (2-9b/c): 1-(2-Cyanoethyl)-3-benzylimidazolium hydrogen sulphate ([cebzim]HSO₄) (**2b**) was synthesized as following: 1-(2-Cyanoethyl)-3-benzylimidazolium chloride (30 mmol) was dissolved in 30 mL of absolute alcohol. Equal molar of sulfuric acid (98 %) was added dropwise with stirring in ice bath, which was warmed to 80 °C with sufficient reflux for 2 h. The produced ionic liquid was washed repeatedly with diethyl ether and dried in a vacuum to afford [cebzim]HSO₄ (**2b**) as highly viscous and pale-yellow oily liquid (9.093 g, 98 %).

[cebzim]H₂PO₄ (**2c**) was a viscous liquid and also prepared with a similar procedure by using phosphoric acid (85 %) instead of sulfuric acid (98 %). The other 14 kinds of ionic liquids (**3-9b/c**) were synthesized as [cebzim]HSO₄ and [cebzim]H₂PO₄ and obtained as yellowish oily liquid (Table-1).

TABLE-1
SPECIFIC TEMPERATURES, REACTION TIMES
AND YIELDS FOR COMPOUNDS (2-9)b/c

Comp.	R	Anion	Temp. (°C)	Reaction time (h)	Yield (%)
2b	bzl	HSO ₄ ⁻	80	2	98
3b	Carboxymethyl			4	93
4b	Hydroxyethyl			4	87
5b	Et			6	93
6b	Pen			6	97
7b	Hex			8	99
8b	Hep	H ₂ PO ₄ ⁻	80	10	95
9b	Oct			10	99
2c	Benzyl			2	97
3c	Carboxymethyl			4	94
4c	Hydroxyethyl			4	90
5c	Ethyl			6	89
6c	Pentyl			8	96
7c	Hexyl			8	92
8c	Heptyl			10	99
9c	Octyl			10	98

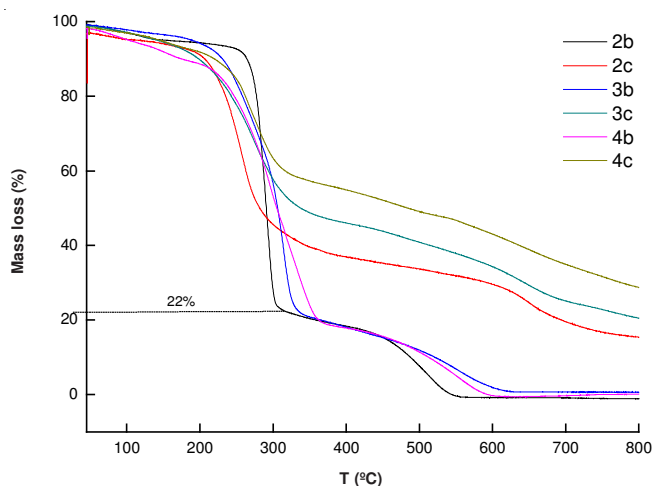
RESULTS AND DISCUSSION

The decomposition onset temperature data of the prepared cyano-functionalized Brønsted acidic ionic liquids are summarized in Table-2. They are thermally stable up to 200–260 °C. It is evident that all of the HSO₄⁻ based ionic liquids present higher thermal stability than that of H₂PO₄⁻ based ionic liquids, except for **9b** which shows a distinct weight loss at 45 °C and exhibits three peaks in the DTG curves different from the other ionic liquids that show one to two peaks. Therefore, it is suggested that their decompositions are highly dependent upon the anion associated with the ionic liquids. Meanwhile, all of the cyano-functionalized imidazolium hydrogen sulphates with the unsaturated side chains (bzl, carboxymethyl) are thermally more stable than the corresponding ionic liquids with saturated side chains.

TABLE-2
DECOMPOSITION ONSET TEMPERATURE
(°C) OF COMPOUNDS **2b-9c**

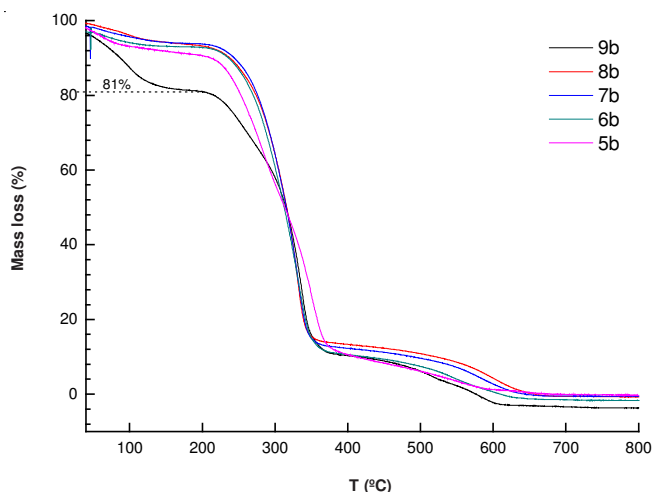
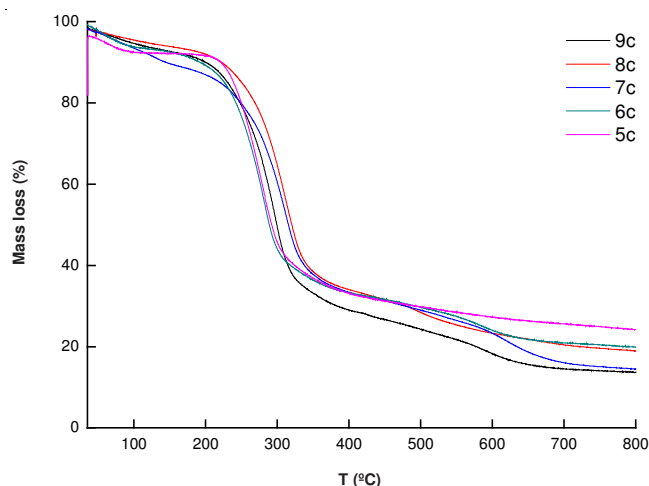
	2	3	4	5	6	7	8	9
b	260	220	218	219	212	218	217	45
c	200	202	203	210	205	202	204	203

The order of thermal stability of ionic liquids **2b-4c** was found to be **2b** > **3b** > **4b** > **2c** ≈ **3c** ≈ **4c**, as illustrated in Fig. 2.

Fig. 2. Thermal gravimetric analysis of **2b-4c**

Obviously, the thermal stability of these compounds are highly dependent on the anion and decrease in the order $\text{HSO}_4^- > \text{H}_2\text{PO}_4^-$. Meanwhile, all of these ionic liquids present similar two-step decomposition behaviours. Herein, we make the explanation for the decomposable process of **2b** as an example. $[\text{Cebzim}]\text{H}_2\text{PO}_4$ begins to decompose at 257 °C and its mass loss is 78 % when the temperature rises to 310 °C. Ultimately, decomposition is almost complete at 550 °C and come to a plateau. In addition, for the samples of **2b**, **3b** and **4b**, which have a thorough decomposition at nearly 615 °C, whereas the samples of **2c**, **3c** and **4c** are not completely decomposed.

The TGA curves for alkylimidazolium type ionic liquids series with HSO_4^- and H_2PO_4^- anion ($\text{R} = \text{alkyl}$) are shown in Figs. 3 and 4, respectively. However, the length of the alkyl chain has not a strong influence on decomposition onset temperature. It can be seen from Fig. 3 that decomposition onset temperatures for the samples of **5b**, **6b**, **7b** and **8b** are similar. The TGA measurement of **9b** shows a distinct mass-loss of ca. 19 % at ca. 200 °C. The decomposition temperature decreases in the order of **8b** $\approx$ **7b** $\approx$ **6b** $\approx$ **5b** $>$ **9b**. Interestingly, a somewhat close thermal stability is found in the alkylimidazolium type ionic liquids with H_2PO_4^- anion, all of which are stable up to ca. 200 °C, as represented in Fig. 4.

Fig. 3. Thermal gravimetric analysis (TGA) of **(5-9)b**Fig. 4. Thermal gravimetric analysis of **(5-9)c**

Most of the cyano-functionalized ionic liquids are stable at or above 200 °C, which is low compared to alkylimidazolium based-ionic liquids (general $T_d > 300\text{ °C}^{11}$). The reason for it could be relative to lower symmetry of the functionalized imidazolium. In addition, cation size increases with the increasing of alkyl chain length, which leads to the weakening of gravity between cation and anion with the distance widening. Hence, ionic liquids decompose more easily in the process of heating, resulting in onset decomposition temperature drop¹⁷. Moreover, the thermal decomposition depends on the nature of anions. Further thermal decomposition also decreases with increasing hydrophilicity of anions¹⁸. The decomposition step was noticed to be steeper for an ionic liquid containing HSO_4^- rather than H_2PO_4^- and all ionic liquids (**2-9**)b/c show two-stage decomposition process in the TG curves, which may be due to the fact that their decomposition mechanisms are highly dependent on the nature of the anion.

Conclusion

Cyano-functionalized Brønsted acidic ionic liquids were successfully synthesized from the precursor of 1-(2-cyanoethyl)-imidazole, which was prepared by cyanoethylation without catalyst. The decomposition onset temperatures of ionic liquids are in the range of 200-260 °C in this study. The main factors that influence the thermal stability of these ionic liquids are attributed to the structure of the corresponding anions and the thermal stability decreases in the order $\text{HSO}_4^- > \text{H}_2\text{PO}_4^-$. The onset temperatures of ionic liquids are affected slightly by the size of the alkyl chain of the cation. Most of the salts studied exhibit apparently two-stage mass loss. In addition, all hydrogen sulphates containing the unsaturated side chains ($\text{R} = \text{bzl}$, carboxymethyl) are thermally more stable compared to the corresponding ionic liquids with the saturated side chains. Herein, it is expected that the present work may provide the basic guidance for designing novel ionic liquids catalysts for acid catalytic reaction.

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