Ring-opening of cyclic anhydrides using ionic liquids

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Four novel Brønsted acidic ionic liquids with two different acid sites on the imidazolium cations were synthesised and employed as catalysts and solvents for the ring-opening of cyclic anhydrides to synthesise half-esters. The results showed that these novel Brønsted acidic ionic liquids were efficient and recyclable. Good yields, short reaction times and mild reaction conditions were achieved.

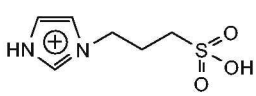
Keywords: ionic liquid, ring-opening, half-ester, cyclic anhydride

Half-esters are versatile intermediates for the synthesis of various natural products. General methods for the synthesis of half-esters or acid-esters involve the esterification or transesterification with alcohols and the hydrolysis of diesters with $Ba(OH)_2$ or pig liver esterase. The ring-opening of cyclic anhydrides with alkoxides is also a popular method for the synthesis of half-esters. Recently, Sabitha *et al.* used the Lewis acid BF_3 as a catalyst in the synthesis of half-esters from cyclic anhydrides. This catalyst was efficient, but also suffered from some drawbacks.[1] BF_3 is unstable to air and moisture, making its recovery a significant challenge. When using BF_3 as catalyst, alcohols were used as both reactants and solvents, so a large amount of alcohol was used, which was wasteful.

The development of environmentally friendly catalysts and media for organic chemistry is an area of great importance. Ionic liquids (ILs) which are known as environmentally benign and reusable reagents have attracted growing attention, due to their particular properties, such as large electrochemical window, high thermal stability and reusability.[2-4] The potential of ILs as green "designer catalysts and media" has become a practical target for reducing waste and hazards by eliminating traditional volatile organic media and corrosive catalysts.[5-7] Brønsted acidic ILs such as 1-hydro-3-methyl-imidazolium hydrogensulfate ([Hmim]HSO_4), 1-hydro-3-methyl-imidazolium tetrafluoroborate ([Hmim]BF_4), 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate ([HSO_3–pmim]HSO_4) and 1-methyl-3-(3-sulfopropyl)-imidazolium tetrafluoroborate ([HSO_3–pmim]BF_4) have been used as satisfactory catalysts and solvents in many organic reactions.[8-10] Traditionally, the acidic IL had only one acid site on the imidazolium cation, the acid sites on the imidazolium cations of [Hmim]HSO_4 and [Hmim]BF_4 were N-H, while the acid sites on the imidazolium cations of [HSO_3-pmim]HSO_4 and [HSO_3–pmim]BF_4 were -SO_3H. Here, four novel Brønsted acidic ILs with these two different acid sites on the imidazolium cations (Scheme 1) were synthesised and used as catalysts and solvents for the ring-opening of cyclic anhydrides to form half-esters (Scheme 2). The results of experiments showed that these ILs were efficient and recyclable. Good yields, short reaction times and mild reaction conditions were achieved.

Experimental

Imidazole (99%), 1, 3-propane sultone (99%) and other chemicals (AR) were commercially available and used without any further purification.



Scheme 1 Cationic structure of novel Brønsted acidic ILs.

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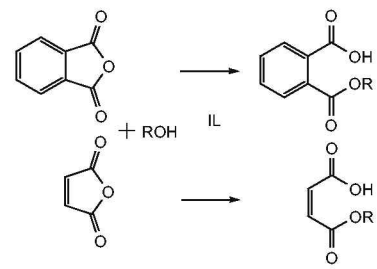


Scheme 2 Ring-opening of cyclic anhydrides to synthesise half-esters in ILs.

NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer and tetramethylsilane (TMS) was used as an internal reference. IR measurements were performed on a Nicolet Nexus 670 FT-IR absorption spectrometer. Elemental analyses were carried out on an Elementar Varioel III apparatus. The melting point was determined on a Büchi B-540 instrument.

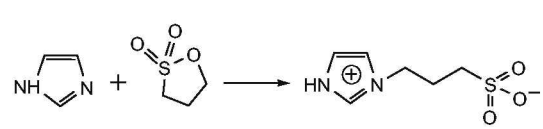
Synthesis of 3-(1-hydro-imidazolium-3-yl)-propane-1-sulfonate (Him-pS) (Scheme 3)

Under vigorous stirring, imidazole (20 mmol) was dissolved in acetonitrile (15 mL) and 1, 3-propane sulfone (20 mmol) was added slowly at room temperature. After 12 h, the reaction mixture was filtered to recover the white precipitate. The precipitate was washed with acetone (10 mL) three times and dried under reduced pressure (0.01 torr) at 60 °C for 1 h, giving Him–pS as a white powder (yield 82%).

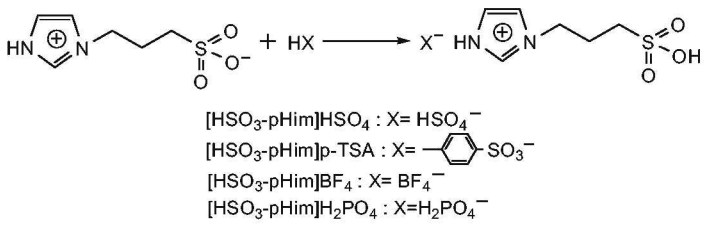
Him-pS: M.p. 191–192 °C. ^{1}H NMR (500 MHz, D_2O):δ 2.21–2.25 (m, 2H, $NCH_2CH_2CH_2$), 2.83 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 4.29 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 7.35 (s, 1H, NCHCHN), 7.45 (s, 1H, NCHCHN), 8.65 (s, 1H, NCHN). ^{13}C NMR (125 MHz, D_2O): δ 25.1 ($NCH_2CH_2CH_2$), 47.4 ($NCH_2CH_2CH_2$), 47.9 ($NCH_2CH_2CH_2$), 120.3 (NCHCHN), 122.6 (NCHCHN), 135.3 (NCHN). IR (KBr disc):ν 3435 (O–H), 3180 (N–H), 3114 (C–H), 1654 (C=C), 1580 (C=N), 1191 (S=O), 1036 (S=O), 631 (S–O), 523 (C–S). Anal. Calcd for $C_6H_{10}N_2O_3S$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.82; H, 5.39; N, 14.82%.

Synthesis of 1-hydro-3-(3-sulfopropyl)-imidazolium hydrogensulfate ([HSO_3-pHim]HSO_4) and 1-hydro-3-(3-sulfopropyl)-imidazolium 4-methyl-benzenesulfonate ([HSO_3-pHim]p-TSA) (Scheme 4)

Under vigorous stirring, Him-pS (20 mmol) was dissolved in water (30 mL) and conc. sulfuric acid (20 mmol) or toluene-*p*-sulfonic acid (20 mmol) was added slowly at room temperature. Then the system was slowly heated up to 80 °C for 2 h, the water was removed under reduced pressure (0.01 torr) at 80 °C for 6 h, giving [HSO_3–pHim]HSO_4 or [HSO_3–pHim]p-TSA as a viscous liquid (yield 98%).



Scheme 3 Synthesis of Him-pS.



Scheme 4 Synthesis of $[HSO_3–pHim]HSO_4$, $[HSO_3–pHim]$p-TSA, $[HSO_3–pHim]BF_4$ and $[HSO_3–pHim]H_2PO_4$.

$[HSO_3$-pHim$]HSO_4$: ^{1}H NMR (500 MHz, D_2O):δ 1.93–1.96 (m, 2H, $NCH_2CH_2CH_2$), 2.55 (t, J = 6 Hz, 2H, $NCH_2CH_2CH_2$), 4.01 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 7.10 (s, 1H, NCHCHN), 7.18 (s, 1H, NCHCHN), 8.39 (s, 1H, NCHN). ^{13}C NMR (125 MHz, D_2O):δ 24.8 ($NCH_2CH_2CH_2$), 47.1 ($NCH_2CH_2CH_2$), 47.7 ($NCH_2CH_2CH_2$), 119.7 (NCHCHN), 122.4 (NCHCHN), 135.5 (NCHN). IR (liquid film):ν 3432 (O–H), 3150 (N–H), 2982 (O–H), 1666 (C=C), 1582 (C=N), 1231 (S=O), 1031 (S=O), 853 (S–O), 580 (C–S). Anal. Calcd for $C_6H_{12}N_2O_7S_2$: C, 25.00; H, 4.20; N, 9.72. Found: C, 25.12; H, 4.26; N, 9.76%.

$[HSO_3$-pHim$]$p-TSA: ^{1}H NMR (500 MHz, D_2O):δ 2.00–2.05 (m, 2H, $NCH_2CH_2CH_2$), 2.06 (s, 3H, CH_3), 2.66 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 4.06 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 7.02 (d, J = 8 Hz, 2H, $CHC(CH_3)CH$), 7.15 (s, 1H, NCHCHN), 7.23 (s, 1H, NCHCHN), 7.40 (d, J = 8 Hz, 2H, $CHC(SO_3H)CH$), 8.44 (s, 1H, NCHN). ^{13}C NMR (125 MHz, D_2O):δ 20.5 ($NCH_2CH_2CH_2$), 25.1 (CH_3), 47.3 ($NCH_2CH_2CH_2$), 47.9 ($NCH_2CH_2CH_2$), 119.4 (NCHCHN), 122.2 (NCHCHN), 125.3 ($CHC(SO_3H)CH$), 129.4 ($CHC(CH_3)CH$), 135.0 (NCHN), 139.7 ($CHC(SO_3H)CH$), 142.3 ($CHC(CH_3)CH$). IR (liquid film):ν 3435 (O–H), 3146 (N–H), 2965 (O–H), 1677 (C=C), 1551 (C=N), 1225 (S=O), 1034 (S=O), 820 (S–O), 568 (C–S). Anal. Calcd for $C_{13}H_{18}N_2O_6S_2$: C, 43.07; H, 5.02; N, 7.73. Found: C, 42.88; H, 5.16; N, 7.68%.

Synthesis of 1-hydro-3-(3-sulfopropyl)-imidazolium tetrafluoroborate ($[HSO_3$-pHim$]BF_4$) and 1-hydro-3-(3-sulfopropyl)-imidazolium dihydrogen phosphate ($[HSO_3$-pHim$]H_2PO_4$) (Scheme 4)

Under vigorous stirring, Him-pS (20 mmol) was dissolved in water (30 mL) and fluoboric acid (20 mmol) or phosphoric acid (20 mmol) was added slowly at room temperature. The system was stirred for 12 h at room temperature, then the water was removed under reduced pressure (0.01 torr) at 80 °C for 6 h, giving $[HSO_3–pHim]BF_4$ or $[HSO_3–pHim]H_2PO_4$ as a viscous liquid (yield 99%).

$[HSO_3$-pHim$]BF_4$: ^{1}H NMR (500 MHz, D_2O):δ 2.13–2.16 (m, 2H, $NCH_2CH_2CH_2$), 2.75 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 4.20 (t, J = 7 Hz, 2H, $NCH_2CH_2CH_2$), 7.30 (s, 1H, NCHCHN), 7.37 (s, 1H, NCHCHN), 8.57 (s, 1H, NCHN). ^{13}C NMR (125 MHz, D_2O):δ 25.0 ($NCH_2CH_2CH_2$), 47.0 ($NCH_2CH_2CH_2$), 47.8 ($NCH_2CH_2CH_2$), 119.9 (NCHCHN), 122.6 (NCHCHN), 135.6 (NCHN). IR (liquid film): ν 3436 (O–H), 3161 (N–H), 2991 (O–H), 1665 (C=C), 1583 (C=N), 1221 (S=O), 1128 (B–F), 1043 (S=O), 844 (S–O), 592 (C–S). Anal. Calcd for $C_6H_{11}N_2O_3F_4SB$: C, 25.92; H, 3.99; N, 10.08. Found: C, 25.80; H, 4.06; N, 10.01%.

$[HSO_3$-pHim$]H_2PO_4$: ^{1}H NMR (500 MHz, D_2O):δ 1.97–2.01 (m, 2H, $NCH_2CH_2CH_2$), 2.60 (t, J = 8 Hz, 2H, $NCH_2CH_2CH_2$), 4.06 (t, J = 6 Hz, 2H, $NCH_2CH_2CH_2$), 7.14 (s, 1H, NCHCHN), 7.22 (s, 1H, NCHCHN), 8.42 (s, 1H, NCHN). ^{13}C NMR (125 MHz, D_2O):δ 24.9 ($NCH_2CH_2CH_2$), 47.2 ($NCH_2CH_2CH_2$), 47.7 ($NCH_2CH_2CH_2$), 119.8 (NCHCHN), 122.5 (NCHCHN), 135.5 (NCHN). IR (liquid film): ν 3430 (O–H), 3151 (N–H), 2972 (O–H), 1656 (C=C), 1583 (C=N), 1225 (S=O), 1169 (P=O), 1040 (S=O), 853 (S–O), 592 (C–S). Anal. Calcd for $C_6H_{13}N_2O_7SP$: C, 25.00; H, 4.55; N, 9.72. Found: C, 25.06; H, 4.50; N, 9.82%.

General procedure for the ring-opening of cyclic anhydrides to synthesise half-esters

The alcohol (30 mmol), cyclic anhydride (10 mmol) and IL (10 mmol) were added into a flask and stirred at 60 °C. After the cyclic anhydride had dissolved in the liquid phase, the reaction mixture was heated for 10 min. Upon completion of the reaction, water (8 mL) was added to the reaction mixture. The reaction mixture was extracted with ether (10 mL) three times. Then the ether was added to a saturated solution of sodium bicarbonate (20 mL) and separated. The solution of sodium bicarbonate was neutralised with conc. HCl (8 mL) at 0 °C and extracted with ether (10 mL) three times, and the ether was dried by anhydrous sodium sulfate (6 g) and concentrated under reduced pressure to give the half-ester. Then the half-ester was characterised by FT-IR and ^{1}H NMR.[11-18] IL was reused after removal of water under reduced pressure (0.01 torr) at 80 °C for 5 h.

Examples:

Methyl hydrogen phthalate:[12] ^{1}H NMR (500 MHz, $CDCl_3$):δ 3.90 (s, 3H, CH_3), 7.38–7.56 (m, 2H, 2CH), 7.65 (d, J = 7 Hz, 1H, CH), 7.90 (d, J = 8 Hz, 1H, CH), 11.97 (s, 1H, OH); IR (KBr disc):ν 3080 (O–H), 2950 (CH_2–H), 1740 (C=O), 1692 (C=O), 1601 (C=C), 1291 (C–O).

Benzyl hydrogen phthalate:[15] ^{1}H NMR (500 MHz, $CDCl_3$):δ 5.32 (s, 2H, CH_2), 7.19–7.30 (m, 5H, CH_2Ph), 7.41–7.56 (m, 2H, 2CH), 7.68 (d, J = 8 Hz, 1H, CH), 7.92 (d, J = 8 Hz, 1H, CH), 11.88 (s, 1H, OH); IR (KBr disc):ν 3046 (O–H), 3013 (C–H), 1726 (C=O), 1695 (C=O), 1605 (C=C), 1288 (C–O).

Methyl hydrogen maleate:[16] ^{1}H NMR (500 MHz, $CDCl_3$):δ 3.86 (s, 3H, CH_3), 6.43 (d, J = 3 Hz, 2H, CH=CH), 12.10 (s, 1H, OH); IR (liquid film):ν 3442 (O–H), 3060 (C–H), 2966 (CH_2–H), 1735 (C=O), 1662 (C=O), 1638 (C=C), 1246 (C–O).

Benzyl hydrogen maleate:[17] ^{1}H NMR (500 MHz, $CDCl_3$):δ 5.27 (s, 2H, CH_2), 6.63 (d, J = 4 Hz, 2H, CH=CH), 7.26–7.39 (m, 5H, CH_2Ph), 11.93 (s, 1H, OH); IR (KBr disc):ν 3415 (O–H), 3040 (C–H), 3016 (C–H), 1732 (C=O), 1690 (C=O), 1632 (C=C), 1262 (C–O).

Results and discussion

Four novel Brønsted acidic ILs were synthesised and identified by ^{1}H NMR, ^{13}C NMR and FT-IR. All of these ILs contained two different acid sites on the imidazolium cations, one acid site was N-H and the other was $–SO_3H$, as shown in Scheme 1. Each had the potential to be used as an acidic catalyst in organic reactions.

The ring-opening of cyclic anhydrides to synthesise half-esters was carried out in these Brønsted acidic ILs $[HSO_3–pHim]HSO_4$, $[HSO_3–pHim]BF_4$, $[HSO_3–pHim]H_2PO_4$ and $[HSO_3–pHim]$p-TSA. The results are listed in Table 1 showing good yields, and confirming that these ILs are efficient catalysts and solvents for the ring-opening of cyclic anhydrides to form half-esters.

From the results in Table 1, it is shown that the yields of half-esters using $[HSO_3–pHim]H_2PO_4$ and $[HSO_3–pHim]$p-TSA as catalysts and solvents were a little higher than those using $[HSO_3–pHim]HSO_4$ and $[HSO_3–pHim]BF_4$. The acidities of ILs containing HSO_4^- and BF_4^- should be stronger than those of ILs containing $H_2PO_4^-$ and p-TSA^-.[19] We supposed that when using the strongly Brønsted acidic ILs $[HSO_3–pHim]HSO_4$ and $[HSO_3–pHim]BF_4$ as catalysts and solvents, the esterification of half-esters with excess alcohols to synthesise diesters was much easier than that using the weaker Brønsted acidic ILs $[HSO_3–pHim]H_2PO_4$ and $[HSO_3–pHim]$p-TSA, thus affording reduced yields of the half-esters.

Compared with the yields of ethyl hydrogen phthalate using Brønsted acidic ILs as catalysts and solvents, the yield obtained in the absence of ILs was very low (entry 6, Table 1) and the solubility of phthalic anhydride in ethyl alcohol was not good at 60 °C without ILs. This revealed that Brønsted acidic ILs were efficient catalysts and solvents for the ring-opening of cyclic anhydrides to form half-esters.

One important advantage of using Brønsted acidic ILs is the possibility of recycling. We examined the synthesis of ethyl hydrogen phthalate in Brønsted acidic IL $[HSO_3–pHim]$p-TSA. The results of the recycling experiments are summarised in Table 2, which revealed that Brønsted acidic ILs used as catalysts and solvents for the ring-opening of cyclic anhydrides to form half-esters were recyclable. The slight decline in the yield should be ascribed to the slight loss of ILs.

Table 1 Results of the ring-opening of cyclic anhydrides to synthesise half-esters in ILs

Entry	Cyclic anhydride	IL	Alcohol	Yield/%
1	Phthalic anhydride	$[HSO_3–pHim]HSO_4$	Methyl alcohol	85
2			Ethyl alcohol	88
3			Isopropyl alcohol	87
4			Butyl alcohol	88
5			Benzyl alcohol	87
6		—	Ethyl alcohol	16
7		$[HSO_3–pHim]BF_4$	Methyl alcohol	87
8			Ethyl alcohol	88
9			Isopropyl alcohol	88
10			Butyl alcohol	89
11			Benzyl alcohol	90
12		$[HSO_3–pHim]H_2PO_4$	Methyl alcohol	89
13			Ethyl alcohol	91
14			Isopropyl alcohol	90
15			Butyl alcohol	93
16			Benzyl alcohol	94
17		[HSO$_3$–pHim]p-TSA	Methyl alcohol	90
18			Ethyl alcohol	93
19			Isopropyl alcohol	92
20			Butyl alcohol	93
21			Benzyl alcohol	95
22	Maleic anhydride	$[HSO_3–pHim]HSO_4$	Methyl alcohol	82
23			Ethyl alcohol	82
24			Isopropyl alcohol	80
25			Butyl alcohol	84
26			Benzyl alcohol	85
27		$[HSO_3–pHim]BF_4$	Methyl alcohol	82
28			Ethyl alcohol	83
29			Isopropyl alcohol	82
30			Butyl alcohol	86
31			Benzyl alcohol	85
32		$[HSO_3–pHim]H_2PO_4$	Methyl alcohol	87
33			Ethyl alcohol	88
34			Isopropyl alcohol	89
35			Butyl alcohol	91
36			Benzyl alcohol	90
37		[HSO$_3$–pHim]p-TSA	Methyl alcohol	85
38			Ethyl alcohol	87
39			Isopropyl alcohol	88
40			Butyl alcohol	90
41			Benzyl alcohol	89

—, No IL added

Table 2 Results of the recycling use of $[HSO_3–pHim]$p-TSA in the synthesis of ethyl hydrogen phthalate

Entry	1	2	3	4	5
Yield/%	93	92	93	91	90

Conclusion

In summary, four novel Brønsted acidic ILs with two different acid sites on the imidazolium cations were synthesised and a procedure for the ring-opening of cyclic anhydrides to form half-esters in these ILs has been developed. The ring-opening of cyclic anhydrides to form half-esters, using ILs $[HSO_3–pHim]HSO_4$, $[HSO_3–pHim]BF_4$, $[HSO_3–pHim]H_2PO_4$ and $[HSO_3–pHim]$p-TSA as catalysts and solvents, has several advantages: (1) ILs as catalysts, show good catalytic activities. (2) Short reaction time and mild reaction conditions are achieved. (3) The amount of alcohols used is greatly reduced. (4) ILs could be directly reused after removal of water under reduced pressure.

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