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Article

Coupling of epoxides and carbon dioxide catalyzed by Brönsted acid ionic liquids

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ABSTRACT

A series of Brönsted acid ionic liquids (BAILs) containing a long chain Brönsted acid site in the cationic part and a Lewis basic site in the anionic part were designed, synthesized, and used as catalyst for the coupling of epoxides and carbon dioxide to cyclic carbonates without a co-catalyst or co-solvent. The effects of catalyst structure and other parameters on the catalytic performance were investigated. The long chain 2-(*N*,*N*-dimethyldodecylammonium) acetic acid bromide ([(CH$_2$COOH)DMDA]Br) showed high catalytic activity and good reusability. This protocol was expanded to various epoxides, which gave the corresponding cyclic carbonates in good yields. The acidity of the catalyst influenced its catalytic activity.

1. Introduction

Carbon dioxide fixation is a very active research area because of the greenhouse effect [1]. An important product of carbon dioxide fixation is a cyclic carbonate, which has broad applications in polycarbonate synthesis, pharmaceutical intermediates, and aprotic solvents [2–4]. Many catalysts for the synthesis of cyclic carbonates have been developed, including salen metal compounds [5–10], metalloporphyrins [11–13], and others [14–17]. However, these catalysts suffer from low catalyst activity or the need for a co-solvent or a metal ion.

In recent years, ionic liquids as catalysts have gained much interest [18–28]. Some literature reports demonstrated that hydrogen bonding can activate an epoxide and allow its coupling reaction [29–37]. These investigations implied that hydrogen bonding between the catalyst and epoxide may be the key factor in the coupling of epoxides and CO$_2$. However, Brönsted acid ionic liquids (BAILs) with imidazolium as the cation are expensive, which hindered their industrial application. Furthermore, the commonly used dialkylimidazolium-based ionic liquids showed negligible biodegradability. Thus, it is necessary to synthesize a less expensive ionic liquid. Meanwhile, the factors such as the structure and acidity of the catalyst have not been studied well. It was reported in our previous reports that the structure of the ionic liquid has an important influence on the catalytic activity [38–40]. Here, several novel long chain BAILs functionalized with a carboxyl group (Scheme 1) were synthesized. A detailed study of the effects of alkyl chain length and nucleophilicity of the anion on the coupling reaction and recycle performance was also conducted. To un-

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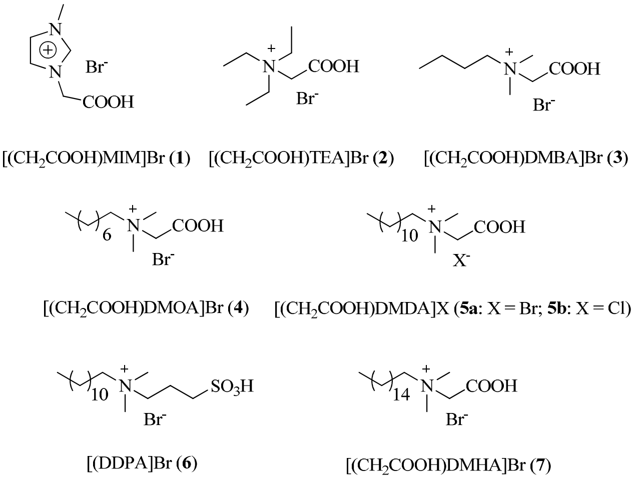

Scheme 1. Structure of the Brönsted acid ionic liquids (BAILs).

derstand the relationship between acidity and activity, the Hammett method was used to evaluate the acidity of the BAILs.

2. Experimental

2.1. Reagents and analysis

1-Methylimidazole (99%), triethylamine, *N,N*-dimethylbutylamine (97%), *N,N*-dimethyloctylamine (95%), *N,N*-dimethyldodecylamine(97%), *N,N*-dimethylhexadecylamine (97%), *p*-toluenesulfonic acid monohydrate, 1,3-propanesultone, methyl chloroacetate, and methyl bromoacetate were obtained from Aladdin Reagent Co. (Shanghai, China). Propylene oxide, epichlorohydrin, styrene oxide, butylene oxide, phenyl glycidyl ether, and epoxy cyclohexane were obtained from Energy Chemicals (Shanghai, China). The other reagents were purchased from Tianjin Kemio Fine Chemical Institute (China) and used without purification. NMR spectra were recorded on a Bruker 500 MHz spectrometer. ESI-MS was performed on an Esquire 6000 mass spectrometer. The Hammett acidity of BAILs was measured using a PerkinElmer Lambda 35 UV/Vis spectrometer with a basic indicator as reported in our previous paper [39]. The melting point was determined on an XT-4 melting point apparatus without calibration.

2.2. Catalyst preparation

The BAILs were prepared according to reported procedures [41]. A typical synthesis route of [(CH$_2$COOH)DMDA]Br (**5a**) is as follows. Under an inert atmosphere of N$_2$, a mixture of *N,N*-dimethyldodecylamine (0.01 mol, 1.27 mL) and methyl bromoacetate (0.01 mol, 0.6 mL) was stirred at room temperature for 12 h, during which time the reaction mixture turned into a solid. A mixture of the solid and HCl (37% H$_2$O solution, 0.012 mol) was refluxed for 1 h. The solvent was removed under vacuum, and the remaining solid was washed three times with cold diethyl ether to give the product as a white powder.

[(CH$_2$COOH)TEA]Br (**2**). mp 188–190 °C, yield 86%, a white solid; ^{1}H NMR (500 M, D$_2$O): δ = 1.12 (dd, *J* = 7.5 Hz, 9H, $\mathit{CH_3}$CH$_2$–), 3.36–3.40 (m, 6H, $\mathit{CH_2}$N), 3.89 (s, 2H, N$\mathit{CH_2}$COOH); ^{1}C NMR (125 M, D$_2$O): δ = 7.02, 54.20, 55.37, 167.34; ESI-MS: calcd for C$_8$H$_{18}$NO$_2$Br *m/z* [M]$^+$ = 160.2, found 160.3.

[(CH$_2$COOH)DMBA]Br (**3**). mp 156–158 °C, yield 90%, a white solid; ^{1}H NMR (500 M, D$_2$O): δ = 0.76 (dd, *J* = 7.5 Hz, 3H, $\mathit{CH_3}$CH$_2$–), 1.16–1.23 (m, 2H, CH$_3\mathit{CH_2}$CH$_2$CH$_2$N), 1.53–1.69 (m, 2H, CH$_3$CH$_2\mathit{CH_2}$CH$_2$N), 3.07 (s, 6H, N$\mathit{CH_3}$), 3.86 (dd, *J* = 8.5 Hz, 2H, CH$_2\mathit{CH_2}$N), 3.97 (s, 2H, N$\mathit{CH_2}$COOH); ^{1}C NMR (125 M, D$_2$O): δ = 12.91, 19.11, 24.13, 51.57, 65.41, 167.50; ESI-MS: calcd for C$_8$H$_{18}$NO$_2$Br *m/z* [M]$^+$ = 160.2, found 160.3.

[(CH$_2$COOH)DMOA]Br (**4**). mp 134–135 °C, yield 92%, a white solid; ^{1}H NMR (500 M, D$_2$O): δ = 0.68 (dd, *J* = 7.0 Hz, 3H, $\mathit{CH_3}$CH$_2$–), 1.10–1.18 (m, 10H, CH$_3$($\mathit{CH_2}$)$_5$CH$_2$CH$_2$N), 1.59 (dd, *J* = 8.5 Hz, 2H, –$\mathit{CH_2}$CH$_2$N), 3.07 (s, 6H, N$\mathit{CH_3}$), 3.34–3.37 (m, 2H, CH$_2\mathit{CH_2}$N), 3.99 (s, 2H, N$\mathit{CH_2}$COOH); ^{1}C NMR (125 M, D$_2$O): δ = 13.64, 22.22, 25.58, 28.36, 31.20, 51.71, 65.37, 167.21; ESI-MS: calcd for C$_{12}$H$_{26}$NO$_2$Br *m/z* [M]$^+$ = 216.3, found 216.3.

[(CH$_2$COOH)DMDA]Br (**5a**). mp 140–141 °C, yield 95%, a white solid; ^{1}H NMR (500 M, D$_2$O): δ = 0.70 (d, 3H, $\mathit{CH_3}$CH$_2$–), 1.16 (d, 20H, CH$_3$($\mathit{CH_2}$)$_{10}$CH$_2$CH$_2$N), 1.59 (s, 2H, –$\mathit{CH_2}$CH$_2$N), 3.11 (s, 6H, N$\mathit{CH_3}$), 3.47 (m, 2H, CH$_2\mathit{CH_2}$N), 3.92 (s, 2H, N$\mathit{CH_2}$COOH); ^{1}C NMR (125 M, D$_2$O): δ = 14.01, 22.72, 22.82, 26.41, 29.30, 29.69, 29.81, 29.90, 30.00, 30.07, 32.16, 52.12, 63.96, 167.50; ESI-MS: calcd for C$_{16}$H$_{34}$NO$_2$Br *m/z* [M]$^+$ = 272.4, found 272.4.

[(CH$_2$COOH)DMDA]Cl (**5b**). mp 150–152 °C, yield 95%, a white solid; ^{1}H NMR (500 M, D$_2$O): δ = 0.66 (t, 3H, $\mathit{CH_3}$CH$_2$–), 1.12 (t, 20H, CH$_3$($\mathit{CH_2}$)$_{10}$CH$_2$CH$_2$N), 1.53 (d, 2H, –$\mathit{CH_2}$CH$_2$N), 3.06 (s, 6H, N$\mathit{CH_3}$), 3.41 (t, 2H, CH$_2\mathit{CH_2}$N), 3.91 (s, 2H, N$\mathit{CH_2}$COOH); ^{1}C NMR (125 M, D$_2$O): δ = 14.01, 22.72, 22.82, 26.41, 29.30, 29.69, 29.81, 29.90, 30.00, 30.07, 32.16, 52.12, 63.96, 167.50; ESI-MS: calcd for C$_{16}$H$_{34}$NO$_2$Cl *m/z* [M]$^+$ = 272.4, found 272.4.

[DDPA]Br (**6**). mp 164–165 °C, yield 96%, a white solid; ^{1}H NMR (500 M, D$_2$O): δ = 0.65 (t, 3H, $\mathit{CH_3}$CH$_2$–), 1.06 (s, 16H, CH$_3$($\mathit{CH_2}$)$_8$CH$_2$CH$_2$N), 1.15 (s, 2H, –$\mathit{CH_2}$CH$_2$CH$_2$N), 1.54 (s, 2H, –$\mathit{CH_2}$CH$_2$N), 1.94–2.00 (m, 2H, NCH$_2\mathit{CH_2}$CH$_2$SO$_3$H), 2.71 (t, 2H, NCH$_2$CH$_2\mathit{CH_2}$SO$_3$H), 2.91 (s, 6H, N$\mathit{CH_3}$), 3.13 (t, 2H, –CH$_2\mathit{CH_2}$N), 3.25–3.28 (m, 2H, N$\mathit{CH_2}$CH$_2$CH$_2$SO$_3$H); ^{1}C NMR (125 M, D$_2$O): δ = 13.99, 18.44, 22.41, 22.79, 26.25, 29.26, 29.67, 29.76, 29.90, 29.99, 30.04, 32.12, 47.51, 50.77, 62.22, 64.32; ESI-MS: calcd for C$_{17}$H$_{38}$NSO$_3$Br *m/z* [M]$^+$ = 336.6, found 336.5.

[(CH$_2$COOH)DMHA]Br (**7**). mp 146–147 °C, yield 93%, a white solid; ^{1}H NMR (500 M, DMSO): δ = 0.84 (t, 3H, $\mathit{CH_3}$CH$_2$–), 1.22 (s, 28, CH$_3$($\mathit{CH_2}$)$_{14}$CH$_2$CH$_2$N), 1.63 (s, 2H, –$\mathit{CH_2}$CH$_2$N), 2.44–2.49 (m, 6H, N$\mathit{CH_3}$), 3.21 (t, 2H, CH$_2\mathit{CH_2}$N), 3.34–3.74 (m, 2H, N$\mathit{CH_2}$COOH); ESI-MS: calcd for C$_{20}$H$_{42}$NO$_2$Br *m/z* [M]$^+$ = 328.6, found 328.6.

2.3. Hammett acidity of the BAILs

The Hammett acidity (H_0) function was calculated by the equation: $H_0 = \mathrm{p}K(\mathrm{I_{aq}}) + \lg([\mathrm{I}]_\mathrm{s}/[\mathrm{IH^+}]_\mathrm{s})$. Here, "I" represents the base indicator, and $[\mathrm{IH^+}]_\mathrm{s}$ and $[\mathrm{I}]_\mathrm{s}$ are, respectively, the molar concentration of the protonated and non-protonated forms of the indicator. The value of $[\mathrm{I}]_\mathrm{s}/[\mathrm{IH^+}]_\mathrm{s}$ was determined and calculated from the UV-Vis spectrum. In the experiment, dimethyl yellow (pK_a = 3.3) was chosen as the base indicator and ethanol as the solvent. The maximum absorbance of the non-protonat-