



A green catalysis of CO₂ fixation to aliphatic cyclic carbonates by a new ionic liquid system



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ABSTRACT

A mixed ionic liquid system has been developed for the efficient catalysis of CO₂ addition to aliphatic epoxides without involving any transition metal catalysts or other additives. The ionic liquid integrated with pyridinium and pyrrolidinium groups (**1-(Br)₃**) together with a non-polar ionic liquid (**3-(Ntf)₂**) effectively transformed non-polar aliphatic epoxides to cyclic carbonates by the reaction with CO₂ under mild CO₂ pressure (3.0 MPa) and reaction temperature (80 °C). The presence of **3-(Ntf)₂** remarkably improved the catalytic activity of **1-(Br)₃** towards non-polar epoxides by increasing the miscibility of catalyst with the substrates. The mixed ionic liquid system is robust enough to be recycled without any significant loss of catalytic activity. GC–MS studies were performed to reveal the reaction pathways to the cyclic carbonates and a feasible model accounting for the effective CO₂ activation in the ionic liquid system was proposed using density functional theory (DFT) calculations.

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1. Introduction

The ever-growing accumulation of carbon dioxide (CO₂) in the atmosphere has caused serious environmental problems over the past decades. Transformation of CO₂ into useful chemicals and fuels through efficient and recyclable catalytic systems is considered a promising approach to reduce this greenhouse gas in the environment [1–18]. Organic carbonates, which are widely used as solvents in the chemical industries, starting materials in polymer synthesis, and intermediates in the manufacture of pharmaceuticals and fine chemicals [19–21], are one of those targeted chemicals that can be directly synthesized from CO₂ and epoxides. Aliphatic polycarbonates, in particular, represent a new class of biodegradable materials for medical applications [4,20,22].

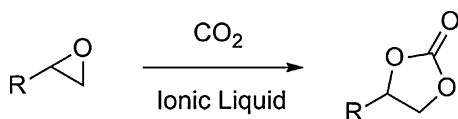
The addition of CO₂ to epoxides (Scheme 1), a reaction of 100% atom efficiency, is regarded as an efficient and environmentally benign way for CO₂ fixation. This reaction offers an alternative way to produce cyclic carbonates without involving the hazardous phosgenes that are used in industry. There have been intensive investigations in search for effective catalytic systems for this reaction that can work under mild reaction conditions, such as low CO₂

pressure, mild processing temperature, and short reaction time with good product selectivity [23–25]. The reaction is known to be catalyzed by certain organic bases in organic solvents [26–29], ammonium and phosphonium salts immobilized in polymers or silica [30–37], metal halides under high temperature [38–40], metal oxides with DMF as a co-catalyst at high temperature [41–43], and some transition metal complexes in organic solvents [44–59]. Recently, some ionic liquids [60–68] have been reported as both media and catalysts for the transformation of CO₂ to organic carbonates. In particular, ionic liquids supported on polymers or silica with/without metal catalysts are considered as green protocols for this process [35,69–76].

We have previously reported an ionic liquid containing pyridinium and pyrrolidinium groups (**1-(Br)₃**) that can function as an efficient organocatalyst as well as a reaction medium for cyclic carbonates synthesis using CO₂ as the feedstock [77]. This ionic liquid catalyzes the conversion of CO₂ and epoxides to cyclic organic carbonates under low CO₂ pressures, mild temperature, and short reaction time with high yield. However, **1-(Br)₃** showed limitations towards non-polar substrates, such as aliphatic epoxides, due to their poor solubility in the ionic liquid medium. Efficient catalytic systems for the preparation of aliphatic carbonates from the reaction of CO₂ and aliphatic epoxides is still scarce [4,13,78], especially under mild reaction conditions. We herein report an ionic liquid mixture system consisting of **1-(Br)₃** plus an aliphatic dicationic pyrrolidinium ionic liquid that can effectively catalyze the

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Scheme 1. Transformation of epoxides into cyclic carbonates with the addition of CO_2 .

CO_2 addition to aliphatic epoxides. This ionic liquid system overcomes the shortcomings of using **1-(Br)₃** alone in catalyzing the non-polar substrates under mild conditions. We also present the results of mechanistic study and density functional theory (DFT) calculations which help to understand the reaction mechanism and high reactivity of the catalyst.

2. Experimental

2.1. Chemicals and instruments

Chemicals and solvents used are of analytical reagent grade and used without further purification. Epoxides were purchased from Aldrich or Acros Organic and used as received unless otherwise noted. Hewlett–Packard 8900 equipped with an EC-1 or EC-WAX column (Alltech Associates, Inc.) was used for GC–MS analysis. ^1H and ^{13}C NMR spectra were collected with Bruker DPX-400 MHz spectrometer. ESI-MS analysis was carried out by using a VG Micro-mass 7070F Mass Spectrometer. The X-ray crystal structure analysis was performed on Bruker CCD area detector diffractometer using MoKa radiation from a generator operating at 50 kV with 30 mA condition. The intensity data were collected and corrected for SAD-ABS (Sheldrick, 1996) program. The structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full matrix least squares on F2 using the Bruker Smart and Bruker SHELXT1 program packages. All non-hydrogen atoms were refined anisotropically. The catalytic reactions were carried out in a 45 mL autoclave reactor.

2.2. Preparation of 1-(3-bromopropyl)-1-methylpyrrolidinium bromide salt

The intermediate was prepared according to the reported method [72] and obtained in quantitative yields. ^1H NMR (400 MHz D_2O): δ 2.14–2.25 (m, 4H), 2.30–2.41 (m, 2H), 3.08 (s, 3H), 3.51–3.62 (m, 8H). ESI-MS m/z : $[\text{M}^+] = 206, 208$.

2.3. Preparation of 1-(6-bromohexyl)-1-methylpyrrolidinium bromide salt

The intermediate of 1-(6-bromohexyl)-1-methylpyrrolidinium bromide was prepared by the slow addition of 1-methylpyrrolidine (20 mmol, 2.1 mL in 10 mL CH_3CN) to 100 mL acetonitrile solution with an excess amount of 1,6-dibromohexane (200 mmol, 30 mL) at refluxing temperature for 24 h. After the reaction, acetonitrile was removed and 50 mL of diethyl ether was added to form white precipitates. The solid was collected by filtration and washed with diethyl ether. After dried under vacuum, the product was obtained as a white hygroscopic powder with 95% yields (6.4 g). ^1H NMR (400 MHz D_2O): δ 1.38–1.48 (m, 2H), 1.48–1.58 (m, 2H), 1.79–1.95 (m, 4H), 2.23 (s, 4H), 3.06 (s, 3H), 3.32–3.40 (m, 2H), 3.45–3.59 (m, 6); ^{13}C NMR (400 MHz D_2O): δ 21.27, 22.90, 24.77, 26.76, 31.66, 34.84, 48.03, 64.12, 64.23; ESI-MS m/z : $[\text{M}^+] = 248, 250$.

2.4. Preparation of ionic liquid **1-(Br)₃**

A mixed solution of 2,2'-dipyridylamine (10 mmol, 1.71 g) in dichloromethane (4.0 mL), 1-(3-bromopropyl)-1-methylpyrrolidinium bromide salt (25 mmol, 7.2 g), and

N,N-diisopropylethylamine (8.0 mL) was heated to 130°C for 10 h. The reaction mixture was then allowed to cool down to room temperature, followed by the addition of 20 mL acetone. The organic solvent was decanted to obtain an oily mixture. The mixture was then washed with chloroform for several times to remove unreacted starting materials. A pale yellow hygroscopic solid of ionic liquid, **1-(Br)₃**, was obtained with 90% yield (6.2 g) after dried under vacuum. ^1H NMR (400 MHz D_2O): δ 2.25 (s, 8H), 2.40–2.62 (m, 4H), 3.09 (s, 6H), 3.43–3.80 (m, 12H), 4.58 (t, 4H, $J = 8$ Hz), 7.02 (t, 2H, $J = 8$ Hz), 7.46 (d, 2H, $J = 8$ Hz), 7.911 (t, 2H, $J = 8$ Hz), 8.14 (d, 2H, $J = 8$ Hz); ^{13}C NMR (400 MHz, D_2O): δ 21.25, 23.42, 48.13, 50.53, 61.03, 64.64, 114.48, 116.49, 140.98, 143.22, 156.31; ESI-MS m/z : $[\text{M} - 3\text{Br}^-]^{3+} = 141.5$, $[\text{M} - 2\text{Br}^-]^{2+} = 251.6$, 252.6; Elemental analysis: Calcd. for $\text{C}_{26}\text{H}_{42}\text{N}_5\text{Br}_3 \cdot \text{H}_2\text{O}$: C, 47.00; H, 6.37; N, 10.54. Found: C, 47.05; H, 6.40; N, 10.56.

2.5. Preparation of ionic liquid **2-(Br)₃**

A mixed solution of 2,2'-dipyridylamine (10.3 mmol, 1.8 g) in dichloromethane (4.0 mL), 1-(6-bromohexyl)-1-methylpyrrolidinium bromide salt (22 mmol, 7.4 g), and *N,N*-diisopropylethylamine (4.0 mL) was heated to 130°C for 10 h. The reaction mixture was then allowed to cool down to room temperature. After 20 mL of THF was added, the organic solvent was decanted to obtain an oily mixture. The mixture was then washed with acetonitrile for several times to remove unreacted starting materials. A pale yellow hygroscopic solid of ionic liquid, **2-(Br)₃**, was obtained with 80% yield (6.2 g) after dried under vacuum. ^1H NMR (400 MHz D_2O): δ 1.39–1.53 (m, 8H), 1.74–1.85 (m, 4H), 1.85–1.94 (m, 4H), 2.15–2.30 (m, 8H), 3.01 (s, 6H), 3.41–3.59 (m, 12H), 4.34–4.38 (t, 4H, $J = 7$ Hz), 6.88–6.92 (t, 2H, $J = 7$ Hz), 7.30 (d, 2H, $J = 9$ Hz), 7.78–7.83 (t, 2H, $J = 7$ Hz), 8.02 (d, 2H, $J = 9$ Hz); ^{13}C NMR (400 MHz, D_2O): δ 21.21, 22.93, 25.10, 25.29, 28.22, 48.02, 53.35, 63.96, 64.20, 113.53, 115.91, 140.98, 142.19, 155.94; ESI-MS m/z : $[\text{M} - 3\text{Br}^-]^{3+} = 169$, $[\text{M} - 2\text{Br}^-]^{2+} = 293.5$, 294.5; Elemental analysis: Calcd. for $\text{C}_{32}\text{H}_{54}\text{N}_5\text{Br}_3 \cdot \text{H}_2\text{O}$: C, 50.14; H, 7.36; N, 9.14. Found: C, 50.22; H, 7.41; N, 9.19.

2.6. Preparation of ionic liquid **3-(Ntf)₂**

To 100 mL THF were added 1-methylpyrrolidine (135 mmol, 15 mL) and 1,6-dibromohexane (54 mmol, 13.2 g). The solution was heated to reflux for 24 h. After the reaction, 50 mL of diethyl ether was added to the solution and the resulting white precipitates were collected by filtration. After washing with diethyl ether and drying under vacuum, the product of bromide salt, **3-(Br)₂**, was isolated with 98% yield (22.4 g) as a white hygroscopic powder. The compound of **3-(Ntf)₂** was obtained quantitatively via ion-exchange with lithium bis(trifluoromethane)sulfonimide salt (LiNtf) in water. Characterization for **3-(Br)₂**: ^1H NMR (400 MHz D_2O): δ 1.43–1.57 (m, 4H), 1.84–1.98 (m, 4H), 2.25 (s, 8H), 3.09 (s, 6H), 3.34–3.47 (m, 4H), 3.48–3.66 (m, 8H); ESI-MS m/z : $[\text{M}^{2+}] = 127$, $[\text{M} - \text{Br}^-]^+ = 333$, 335.

2.7. Preparation of single crystals of **1-(Br)₃** for X-ray analysis

The ionic liquid **1-(Br)₃** (250 mg) was completely dissolved in hot acetonitrile. After cooling down the mixture to room temperature, ethylacetate was added dropwise until the solution just started to get cloudy. The single crystal suitable for X-ray crystal structure analysis was obtained by the slow diffusion of diethyl ether to the solution at room temperature. CCDC-709110 contains the supplementary crystallographic data for this paper. The detailed parameters are also available in the supporting information.

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