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A green catalysis of CO_2 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 CO_2 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 CO_2 under mild CO_2 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 CO_2 activation in the ionic liquid system was proposed using density functional theory (DFT) calculations.

1. Introduction

The ever-growing accumulation of carbon dioxide (CO_2) in the atmosphere has caused serious environmental problems over the past decades. Transformation of CO_2 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 CO_2 and epoxides. Aliphatic polycarbonates, in particular, represent a new class of biodegradable materials for medical applications [4,20,22].

The addition of CO_2 to epoxides (Scheme 1), a reaction of 100% atom efficiency, is regarded as an efficient and environmentally benign way for CO_2 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 CO_2 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 CO_2 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 CO_2 as the feedstock [77]. This ionic liquid catalyzes the conversion of CO_2 and epoxides to cyclic organic carbonates under low CO_2 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 CO_2 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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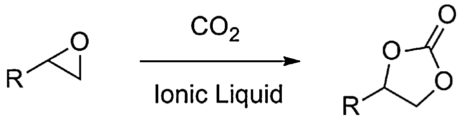


Scheme 1. Transformation of epoxides into cyclic carbonates with the addition of CO_2.

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 Micromass 7070F Mass Spectrometer. The X-ray crystal structure anaylsis 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 SADABS (Sheldrick, 1996) program. The structure was solved by direct methods, expended 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*: $[M^+]=206$, 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*: $[M^+]=248$, 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*: $[M\ -3Br^-]^{3+}=141.5$, $[M\ -2Br^-]^{2+}=251.6$, 252.6; Elemental analysis: Calcd. for $C_{26}H_{42}N_5Br_3{\cdot}H_2O$: 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)$_3$*

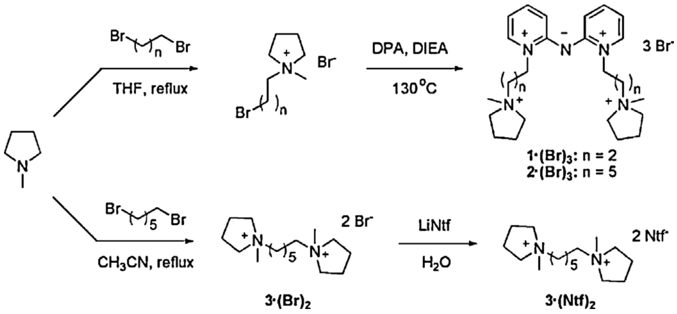
A mixed solution of 2,2′-dipyridylamine (10.3 mmol, 1.8 g) in dichloromethane (4.0 mL), 1-(6-bromohexyl)-1-methylpyrrolidinium bromide salt (22 mmol, 7.4 g), and *N,N*-diisopropylethylamine (4.0 mL) was heated to 130 °C for 10 h. The reaction mixture was then allowed to cool down to room temperature. 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*: $[M\ -3Br^-]^{3+}=169$, $[M\ -2Br^-]^{2+}=293.5$, 294.5; Elemental analysis: Calcd. for $C_{32}H_{54}N_5Br_3{\cdot}H_2O$: 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(trifluromethane)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*: $[M^{2+}]=127$, $[M\ -Br^-]^+=333$, 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.



Scheme 2. Synthetic routes to the ionic liquids.

2.8. General procedure for the catalytic additions of epoxides to CO_2 in ionic liquids

The epoxide (8 mmol), ionic liquid **1·(Br)$_3$** (4.4 mmol, 2.7 g), and **3·(Ntf)$_2$** (2.5 mmol, 2.0 g) were thoroughly mixed in an autoclave. The compressed CO_2 was directly charged into the autoclave at room temperature. The mixture was allowed to react at 80 °C for 0.5–3 h with stirring. After the completion of reaction, the autoclave was cooled down with cold water and the pressure was slowly released. The reaction mixture was extracted with 15 mL of hot ethyl acetate, and the solution was then decanted from the autoclave. The extraction process was repeated five times to ensure the complete removal of the product. The cyclic carbonates were analyzed with GC–MS. The residual catalyst in the autoclave was recycled and reused in the following run after the removal of ethyl acetate under vacuum. The ethyl acetate solvent was collected and reused for extraction.

2.9. Conditions for the reaction of 2-(chloromethyl)oxirane with CO_2 in mechanistic studies

2-(Chloromethyl)oxirane (8 mmol, 0.75 g) in ionic liquid **1·(Br)$_3$** (4.0 mmol, 2.7 g) and de-ionized water (60 mL, 2% w/w of ionic liquid) were thoroughly mixed in an autoclave. The compressed CO_2 (1.5 MPa) was directly charged into the autoclave at room temperature. The mixture was allowed to react at 80 °C for 0.5 h. The reaction was then ceased by quickly cooling the mixture to 0 °C. After pressure was completely released, the reaction product was immediately extracted with 15 mL of ethyl acetate. The extract was analyzed by GC–MS and two isomers of cyclic carbonates were observed in a ratio of 97: 3. GC–MS *m/z*: [M^+] (major product) = 136, 138; [M^+] (minor product) = 180, 182.

2.10. Density functional theory (DFT) calculations

All the DFT calculations were carried out using the b3lyp level of density functional theory with the Gaussian 03 software package [78–81]. The effective core potentials (ECPs) of Hay and Wadt with double-ζ valence basis sets (LanL2DZ) [82,83] with polarization functions ($\zeta_d = 0.428$) [84] was chosen to describe Br. All of the other atoms are described by the 6–31G basis sets.

3. Results and discussion

3.1. Synthesis and characterization of ionic liquids

The procedures for the preparation of ionic liquids with pyridinium and pyrrolidinium groups are straightforward (Scheme 2). Quantitative amount of ionic liquids can be obtained easily from inexpensive and commercially available starting materials under mild and simple synthetic conditions. The reaction starts with 1-methylpyrrolidine (50 mmol scale) and dibromoalkanes (1,3-dibromopropane and 1,6-dibromohexane) in THF under refluxing conditions. The intermediate, 1-(3-bromopropyl)-1-methylpyrrolidinium bromide, was obtained in a quantitative yield. In the case of 1-(6-bromohexyl)-1-methylpyrrolidinium bromide, a non-separable ionic liquid **3·(Br)$_2$** was also produced. These two compounds of obviously different molar masses were identified with the positive mode ESI-MS analysis (see Figure S4 in supporting information). The formation of **3·(Br)$_2$** is probably due to the long alkyl chain of 1,6-dibromohexane that lowers its reactivity towards 1-methylpyrrolidine in THF. More importantly, the 1-(6-bromohexyl)-1-methylpyrrolidinium bromide, which is relatively non-polar and more soluble in THF, was further attacked by 1-methylpyrrolidine during the reaction. In order to reduce the formation of **3·(Br)$_2$** in the preparation of the intermediate, a large excess amount of 1,6-dibromohexane (10 equivalents to 1-methylpyrrolidine) was used and THF was replaced with acetonitrile for a higher reaction temperature. The isolated yield of 1-(6-bromohexyl)-1-methylpyrrolidinium bromide was improved to 95% under these conditions and no **3·(Br)$_2$** was detected in the reaction. The excess 1,6-dibromohexane was easily separated by the extraction with petroleum ether (40–60 °C) after the reaction, and reused as the starting reagent for the synthesis of another ionic liquid (1,1′-hexane-1,6-diylbis(1-methylpyrrolidinium) bis(trifluromethane)sulfonamide, **3·(Ntf)$_2$**).

After the preparation of intermediates, the ionic liquids **1·(Br)$_3$** and **2·(Br)$_3$** were obtained in both high yields and purity without using flash column chromatography. Isolated yields of 90% for **1·(Br)$_3$** and 80% for **2·(Br)$_3$** were obtained respectively in the synthesis (Scheme 2) through the reaction of the corresponding intermediates with 2,2′-dipyridylamine (DPA) at 130 °C for 10 h. It is worthy to note that the addition of base, *N,N*-diisopropylethylamine (DIEA), speeded up the reaction and enhanced the yields. Both **1·(Br)$_3$** and **2·(Br)$_3$** are highly polar ionic liquids and insoluble in most organic solvents except for alcohols (methanol and ethanol) and water. As a result, pure compounds could be easily obtained by simply washing away the unreacted starting materials with acetone and acetonitrile (in the case of **2·(Br)$_3$**, ethylacetate and acetonitrile were used). **1·(Br)$_3$** and **2·(Br)$_3$** were isolated as pale yellow hygroscopic solids at room temperature.

The synthesis of **3·(Ntf)$_2$** is relatively simple compared to those of **1·(Br)$_3$** and **2·(Br)$_3$**. The reaction started with 1-methylpyrrolidine (135 mmol) and 1,6-dibromohexane (54 mmol) in 100 mL THF. It is essential to use 1-methylpyrrolidine in slightly excess (1.25 equivalents to each alkyl-bromide) to avoid incomplete reaction and the production of mono-adduct which is non-separable from ionic liquid **3·(Br)$_2$**. After 24 h under reflux conditions, **3·(Br)$_2$** was obtained as white precipitates (98% yield) by adding diethyl ether to the reaction solution. Subsequent two-phase ion-exchange with lithium bis(trifluromethane)sulfonimide salt (LiNtf) in water-ethyl acetate yielded a room temperature ionic liquid **3·(Ntf)$_2$**.

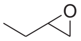
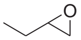
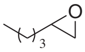
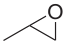
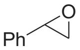
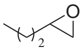
The ionic liquids were characterized with ^1H and ^{13}C NMR, ESI-MS, and elemental analysis. The analytical results indicated that both compounds contain one DPA and two 1-methylpyrrolidinium groups that are linked to DPA through two alkyl bridges. The proposed structure shown in Scheme 2 perfectly matched the experimental data acquired from ESI-MS and elemental analysis. Interestingly, two 1-methylpyrrolidinium groups were linked to the nitrogen atoms of two pyridine units, not to the secondary amine position of DPA. This could explain the remarkable chemical shifts observed in the aromatic region of their ^1H NMR spectra. In particular, the protons on the ortho- and para-positions of the pyridine units showed chemical shifts in a great extent compared with those on the same positions in DPA (see Figure S3 in supporting information). However, even with all these information, it was still difficult to have the precise structures of the ionic liquids. Solid state analysis was further carried out to confirm the structure of the ionic liquids.

A single crystal of **1·(Br)$_3$** was obtained by the recrystallization in a mixed solution of acetonitrile and ethyl acetate with the slow diffusion of diethyl ether at room temperature (Figure S1 in supporting information). The solid state structure determined from X-ray crystal analysis exactly matched the proposed one in Scheme 2. The crystal structure clearly shows that each pyridine unit in DPA is independently associated with two 1-methylpyrrolidinium moieties through a propylene bridge. The lengths of C—N bonds in the propylene bridge, which connects the pyridinium and pyrrolidinium, shows the covalent characteristics (C6—N2 = 1.486 Å, C8—N3 = 1.503 Å; the average C—N bond length for alkylammonium salt is 1.499 Å). These C—N bond lengths indicate that the pyridine rings and pyrrolidine units are connected covalently *via* the propylene bridge. In addition, the C—N bonds of the pyridylamine unit exhibit a strong double-bond characteristics, as indicated by their shorter bond distances (C1—N1 = 1.335 Å) than those in DPA ligand (1.380 Å) [85]. This is probably due to the negative charge developed on the nitrogen atom (N1) which is delocalized on two positively charged pyridinium rings and significantly strengthens the C—N bonding. Moreover, the crystal data of the cationic part (1^{3+}) indicate a number of torsion angles within the molecule (see Table S3 in supporting information). These multiple torsion angles imply that the structure of **1·(Br)$_3$** is conformationally flexible. The pyridine unit of 1^{3+} shows a slight distortion as there is a small torsion angle developed on the ring (N(2)—C(1)—C(2)—=C(3) = 2.1°), and its planar structure is retained as in DPA ligand. However, the orientation of the two pyridine units is non-planar with a dihedral angle of 30°, which is much larger than that of the regular DPA ligand. The angle of twist is obviously the consequence of the steric effects between two propylene-bridged pyrrolidinium units. In addition, the higher conformational flexibility of ionic liquid **1·(Br)$_3$** may stem from the propylene bridge that has multiple torsion angles in the range of −56.2–97.8°. Although the compound is solid at room temperature, it liquefies readily on the absorption of moisture from air at room temperature. The physical properties of the ionic liquid are also strongly affected by its counter anions. For example, the exchange of bromide anions of the ionic liquid with bis(trifluoromethane)sulfonimide ($^{-}$Ntf) resulted in lowering its melting point to 60 °C.

3.2. *The use of ionic liquids as a reaction medium in the addition reaction of CO$_2$ to epoxides*

The potential use of ionic liquid **1·(Br)$_3$** as an excellent organocatalyst and a reaction medium for the chemical fixation of CO$_2$ to the epoxides has previously been demonstrated [77]. However, good isolated yields (>94%) were limited to the terminal epoxides with a polar terminal group, such as 2-(phenoxymethyl)oxirane, 2-(chloromethyl)oxirane, and 2-methyloxirane. The low reactivity of ionic liquid **1·(Br)$_3$** towards the non-polar substrates, particularly the epoxides with an alkyl chain, is due to the poor compatibility of the highly polar ionic liquid with the substrates. An elevated CO$_2$ pressure (3.0 MPa) and a longer reaction time (3 h) only slightly improved the yields in the reactions with 2-ethyloxirane and 2-butyloxirane (Table S4, entry 1: 80% in supporting Information). Preliminary results listed in Table S4 in supporting Information indicate that **1·(Br)$_3$** is a very efficient organocatalyst and reaction medium for synthesis of certain cyclic carbonates, but not suitable for the non-polar epoxides. Further improvement of this ionic liquid system for the alkyl-chained cyclic carbonates synthesis is essential, as the aliphatic polycarbonates are attractive biodegradable materials, particularly for biomedical applications in recent years [4,20,22].

Table 1
The addition reaction of CO$_2$ with the non-polar epoxides in a mixed ionic liquid system **1·(Br)$_3$/3·(Ntf)$_2$** at 80 °C[a].

Entry	Epoxide	Scale (mmol)	*P* (MPa)	Time (h)	Yield[b] (%)
1[c]		8	3.0	3	0
2		8	3.0	1.5	98
3		8	4.0	3	100
4		50	3.0	4	94
5		50	3.0	1.5	96
6		50	3.0	4	96

[a] Reaction conditions: 2.0 g of **3·(Ntf)$_2$** and 3.0 g of **1·(Br)$_3$** for the catalysis; All ionic liquids were reused after each experiment.

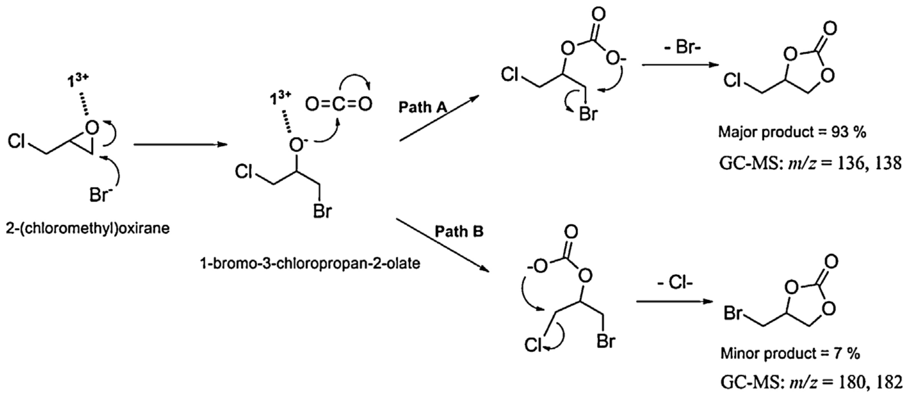
[b] Isolated yield; Selectivity of cyclic carbonates was >99% in all cases based on GC–MS analysis.

[c] Control experiment with using **3·(Ntf)$_2$** only.

Our first attempt to improve the compatibility with the non-polar epoxides was to modify the alkyl chain bridge between the DPA and 1-methylpyrrolidinium groups in **1·(Br)$_3$**. Although the elongated alkyl chain bridge, from propyl to hexyl, in the modified ionic liquid **2·(Br)$_3$** made itself less polar, more flexible, and therefore miscible with aliphatic epoxides such as 2-ethyloxirane and 2-butyloxirane, it also increased the viscosity of **2·(Br)$_3$**. It was necessary to add 2–5% (w/w) water in order to stir the reaction mixture. As the hydroxyl group in the catalyst or reaction media was reported to assist the ring-opening process of epoxides [86], the catalytic activity was enhanced with the addition of water. Still, the complete conversion of 2-ethyloxirane required a prolonged reaction time [87]. In the case of 2-butyloxirane, even poorer catalytic performance was observed in **2·(Br)$_3$** than in **1·(Br)$_3$**.

The structural modification of the ionic liquid seems not an effective way to enhance the catalytic reaction of alkyl-chained terminal epoxides with CO$_2$. A possible solution is to introduce a non-polar ionic liquid to compensate the low miscibility of the ionic liquid catalytic system [64]. Another simple ionic liquid **3·(Ntf)$_2$**, a room temperature ionic liquid with low viscosity, was thus prepared (Scheme 2). The structural similarity of **3·(Ntf)$_2$** granted by two 1-methylpyrrolidinium groups makes it very miscible with **1·(Br)$_3$**, while retaining non-polar property by having a hexyl bridge and two non-polar anions ($^{-}$Ntf). The addition of **3·(Ntf)$_2$** to **1·(Br)$_3$** remarkably improved the catalytic efficiency and yields for the non-polar alkyl-chained epoxides (Table 1, entries 2–3). Under the optimized conditions, 2-ethyloxirane and 2-butyloxirane in 8 mmol scales were transformed to their corresponding cyclic carbonates with 98 and 100% yields, respectively. Compared to **1·(Br)$_3$** alone, this new **1·(Br)$_3$/3·(Ntf)$_2$** ionic liquid mixture system increased the catalytic activity more than double and reduced the reaction time for the complete conversion. In the control experiments where only **3·(Ntf)$_2$** was used without **1·(Br)$_3$**, no catalytic activity was observed. The remarkable enhancement of the catalytic activity was achieved by the addition of **3·(Ntf)$_2$** that allowed mixing of **1·(Br)$_3$** with the non-polar substrates.

The catalytic ability of the new mixed ionic liquid system (**1·(Br)$_3$/3·(Ntf)$_2$**) was also examined for 50 mmol-scale reactions under the same mild CO$_2$ pressure and reaction temperature conditions. Three industrially useful organic carbonates, propylene oxide, styrene oxide, and 2-propyleoxirane, were selected for the investigation and the results are shown in Table 1 (entry 4-6). A



Scheme 3. Proposed reaction pathways in the addition reaction of CO_2 with epoxide in **1·(Br)**$_3$.

short chain epoxide, propylene oxide, was successfully transformed to propylene carbonate with an excellent isolated yield of 94%. The reaction conditions used for the catalytic process (3.0 MPa of CO_2 at 80 °C for 4 h) are very mild for such a large scale reaction. The transformation of 50 mmol styrene oxide, which is relatively inert to CO_2 addition, to the corresponding carbonate was extremely rapid and efficient to achieve 96% yield within 1.5 h. An epoxide with a longer aliphatic chain, 2-propyloxirane, was also smoothly converted into aliphatic carbonates with 96% isolated yield within 4 h. The excellent performances of the **1·(Br)₃**/**3·(Ntf)₂** system in large-scale reactions demonstrate the potential use of these ionic liquids for industry.

3.3. Mechanistic studies for the CO_2 addition reaction to epoxides in ionic liquid

The reaction mechanism for the addition of CO_2 to epoxides in the presence of quaternary ammonium catalyst has been proposed by quite a number of studies in recent years [34,65–68,88]. However, the experimental proofs were rarely discussed. Ionic liquids **1·(Br)₃**, which contains multiple quaternary ammonium groups, appears to follow the Lewis acid-base catalytic mechanism. The mechanism most probably involves Lewis acid activation of epoxide by the cation of the ionic liquid, followed by the nucleophilic attack by Lewis base (Br^-) which opens up the epoxide ring to form an oxy-anion species. This intermediate further reacts with CO_2 to give a cyclic carbonate after the intra-molecular cyclic elimination. The cation of **1·(Br)₃** presumably acts as a very good Lewis acid that renders this ionic liquid an efficient catalyst for the activation of epoxides and CO_2 in the reaction.

Attempts to collect the information of reaction intermediates using ESI-MS and ^1H NMR were unsuccessful, probably due to their transient characteristics. In order to understand the reaction pathways of the CO_2 addition reaction with epoxides, we thus took an indirect approach using GC–MS as illustrated in Scheme 3. As a model substrate for this study, 2-(chloromethyl)oxirane was selected, for it possesses a chloride functional group, a good leaving group upon the attack by nucleophiles. The reaction proceeds from a nucleophilic attack by the Br^- ion of **1·(Br)₃**, and the subsequent ring opening of the epoxide gives an oxy-anion intermediate, 1-bromo-3-chloropropan-2-olate. The oxy-anion intermediate contains two potential leaving groups (Cl and Br) on the backbone. This reactive intermediate further reacts with CO_2, and an intramolecular cyclic elimination gives a cyclic carbonate as the final product. At the stage of intra-molecular cyclic elimination, there are two possible pathways (path A and B) to generate the cyclic carbonates; two isomers with either Cl or Br.

The oxy-anion intermediate was not observed throughout the reaction. However, GC–MS clearly identified the final products that can illuminate the reaction pathway (for the full GC–MS spectra, see supporting information). From the GC–MS analysis, two isomers of the cyclic carbonate with distinct molecular mass and isotopic patterns were found in the reaction. Both the mass and the isotopic distribution of the molecular ions exactly matched the proposed products in Scheme 3. The chloro-isomer with $m/z = 136$ and 138 and the bromo-isomer with $m/z = 180$ and 182 were observed in a ratio of 3:1 and 1:1, respectively. The path A was determined to be the favored pathway as the cyclic carbonate with a chloride group was the major product (93%). This result is as expected because the bromide group is a much better leaving group than the chloride in the intra-molecular cyclic elimination process. This is also in accordance with the anion effects of the catalysts. The catalytic activity diminished noticeably when the bromide anions in **1·(Br)₃** were replaced with chlorides, and no cyclic carbonate was formed when they were replaced with the $^-$Ntf anions.

In view of the structure of the ionic liquid component molecules, a CO_2 activation mode was proposed [77]. It was postulated that the amide nitrogen of the ionic liquid molecule, which carries formally a negative charge, plays an important role to interact with the CO_2 carbon. Cooperatively, the two iminium nitrogen atoms, which each carry formally a positive charge, help to hold the two CO_2 oxygens. An epoxide molecule, which is held by the remaining two amonium nitrogen atoms (each formally carrying a positive charge also), acts as a nucleophile to be ready to form bond with the CO_2 carbon. Recently, the ionic liquid of Bu_4NBr was reported to be able to catalyze the same cycloaddition reaction [89]. In the report, DFT calculations have also been used to study the mode of CO_2 activation. Following the similar thinking, we carried out DFT studies to see how CO_2 is activated in the ionic liquid system by designing a system which includes **1·(Br)₃** together with a $N(CH_3)_4{\cdot}Br$ molecule, modeling a part of the ionic liquid molecule in the real situation. The results of our DFT calculations are presented in Fig. 1. We found that the mode of CO_2 activation is slightly different from what we expected. The amide nitrogen atom seems to play no role in the activation process. Instead, the high degree of conjugation stabilizes the amide nitrogen effectively. The positive charges associated with the ammonium and iminium nitrogen atoms spread over the N-bonded C — H hydrogen atoms. It is these hydrogen atoms that show weak interactions with bromides and the CO_2 oxygen atoms. With the model system, we calculated the activation free energy of 17.8 kcal/mol. When we use Bu_4NBr, instead of **1·(Br)₃**, in our calculations, an activation free energy of 24.5 kcal/mol was calculated. The lower energy barrier of the current system implies that **1·(Br)₃** is a more efficient system for the CO_2 activation. This is because **1·(Br)₃** provides more active sites to interact with CO_2 as well as with the epoxide molecule.

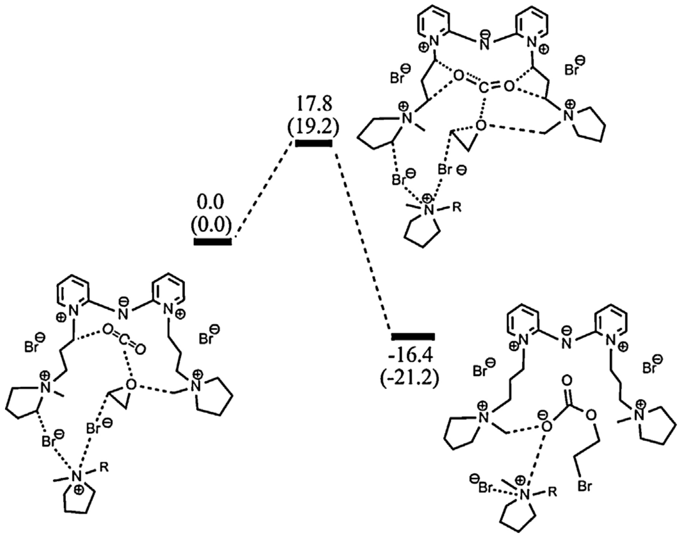


Fig. 1. The energy profile calculated for the CO_2 activation step. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

4. Conclusions

The pyridinium and pyrrolidinium-integrated ionic liquids have been successfully prepared via simple synthetic process and their applications in the synthesis of aliphatic cyclic carbonates under metal-free and mild reaction conditions were demonstrated. A new mixed ionic liquid system of **1·(Br)$_3$/3·(Ntf)$_2$** played dual role as both catalyst and reaction medium in the addition reaction of relatively inert aliphatic terminal epoxides to CO_2. This organocatalytic system showed excellent enhancement, particularly for the non-polar epoxides which are difficult to transform to the cyclic carbonates even with the transition-metal. This mixed ionic liquid system was also efficient for the larger scale (50 mmol) preparation of cyclic carbonates under mild CO_2 pressure and temperature conditions and could be recycled continuously without any significant loss in their catalytic activity. GC–MS studies indicate that the oxy-anion intermediates formed by nucleophilic attack by Br^- react with CO_2 to give the product via the intra-molecular cyclic elimination of Br^-. The results of DFT calculations suggest that the N-bonded C—H hydrogen atoms in the ionic liquid system interact with the CO_2 oxygen atoms, increasing the electrophilicity of the CO_2 carbon atom and facilitating its reactions with epoxides.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.12.027.

References

[1] C.-S. Song, Catal. Today 115 (2006) 2–32.
[2] I. Omae, Catal. Today 115 (2006) 33–52.
[3] R. Zevenhoven, S. Eloneva, S. Teir, Catal. Today 115 (2006) 73–79.
[4] C.M. Rayner, Org. Process Res. Dev. 11 (2006) 121–132.
[5] M. Aresta, A. Dibenedetto, Dalton Trans. (2007) 2975–2992.
[6] C. Oloman, H. Li, ChemSusChem 1 (2008) 385–391.
[7] F. Joó, ChemSusChem 1 (2008) 805–808.
[8] S. Enthaler, ChemSusChem 1 (2008) 801–804.
[9] K.-M.K. Yu, I. Curcic, J. Gabriel, S.-C.E. Tsang, ChemSusChem 1 (2008) 893–899.
[10] A. Behr, Angew. Chem. Int. Ed. 27 (1988) 661–678.
[11] D.H. Gibson, Chem. Rev. 96 (1996) 2063–2095.
[12] W. Leitner, Coord. Chem. Rev. 153 (1996) 257–284.
[13] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155–174.
[14] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951–976.
[15] X.L. Yin, J.R. Moss, Coord. Chem. Rev. 181 (1999) 27–59.
[16] D. Walther, M. Ruben, S. Rau, Coord. Chem. Rev. 182 (1999) 67–100.
[17] G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6618–6639.
[18] S.-J. Zhang, Y.-H. Chen, F.-W. Li, X.-M. Lu, W.-B. Dai, R. Mori, Catal. Today 115 (2006) 61–69.
[19] X.-D. Xu, J.A. Moulijn, Energy Fuels 10 (1996) 305–325.
[20] J.P. Parrish, R.N. Salvatore, K.W. Jung, Tetrahedron 56 (2000) 8207–8237.
[21] J.H. Clements, Ind. Eng. Chem. Res. 42 (2003) 663–674.
[22] G. Rokicki, Prog. Polym. Sci. 25 (2000) 259–342.
[23] N. Aoyagi, Y. Furusho, T. Endo, J. Polym. Sci. Part A: Polym. Chem. 51 (2013) 1230–1242.
[24] C. X. Liu, Y. Cao, L.P. Guan, L. Yang, Y. Shi, Synlett 23 (2012) 1343–1348.
[25] Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda, K. Mashima, Catal. Sci. Tech. 2 (2012) 509–513.
[26] H. Kawanami, Y. Ikushima, Chem. Commun. (2000) 2089–2090.
[27] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartrio, Tetrahedron Lett. 44 (2003) 2931–2934.
[28] J.-L. Jiang, R. Hua, Synth. Commun. 36 (2006) 3141–3148.
[29] R.A. Shiels, C.W. Jones, J. Mol. Catal. A: Chem. 261 (2007) 160–166.
[30] P. Gros, P. Le Perchec, J.P. Senet, J. Org. Chem. 59 (1994) 4925–4930.
[31] H. Xie, H. Duan, S. Li, S. Zhang, New J. Chem. 29 (2005) 1199–1203.
[32] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, Chem. Commun. (2006) 1664–1666.
[33] J.-Q. Wang, D.-L. Kong, J.-Y. Chen, F. Cai, L.-N. He, J. Mol. Catal. A: Chem. 249 (2006) 143–148.
[34] T. Chang, H.-W. Jing, L.-L. Jin, W.-Y. Qiu, J. Mol. Cat. A: Chem. 264 (2007) 241–247.
[35] X. Chen, J. Sun, J. Wang, W. Cheng, Tetrahedron Lett. 53 (2012) 2684–2688.
[36] J. Song, B. Zhang, P. Zhang, J. Ma, J. Liu, H. Fan, T. Jiang, B. Han, Catal. Today 183 (2012) 130–135.
[37] B. Ochiai, T. Endo, J. Polym. Sci., Part A: Polym. Chem. (2007) 5673–5678.
[38] R. Nomura, A. Ninagawa, H. Matsuda, J. Org. Chem. 45 (1980) 3735–3738.
[39] K. Kossev, N. Koseva, K. Troev, J. Mol. Catal. A: Chem. 194 (2003) 29–37.
[40] J. Song, B. Zhang, P. Zhang, J. Ma, J. Liu, H. Fan, T. Jiang, B. Han, Cat. Today 183 (2012) 130–135.
[41] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, Chem. Commun. (1997) 1129–1130.
[42] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526–4527.
[43] B.M. Bhanage, S.-I. Fujita, Y. Ikushima, M. Arai, Appl. Catal. A 219 (2001) 259–266.
[44] W.J. Kruper, D.V. Dellar, J. Org. Chem. 60 (1995) 725–727.
[45] K. Kasuga, N. Kabata, T. Kato, M. Sugimori, M. Handa, Inorg. Chim. Acta (1998) 223–225.
[46] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, Angew. Chem. Int. Ed. 39 (2000) 4096–4098.
[47] M. Ulusoy, E. Çetinkaya, B. Çetinkaya, Appl. Organometal. Chem. 23 (2009) 68–74.
[48] F.-W. Li, C.-G. Xia, L.-W. Xu, W. Sun, G.-X. Chen, Chem. Commun. (2003) 2042–2043.
[49] Y.-M. Shen, W.-L. Duan, M. Shi, J. Org. Chem. 68 (2003) 1559–1562.
[50] X.-B. Lu, Y. Wang, Angew. Chem. Int. Ed. 43 (2004) 3574–3577.
[51] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. García, J. Catal. 228 (2004) 254–258.
[52] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Tetrahedron Lett. 45 (2004) 2023–2026.
[53] M. Kröger, C. Folli, O. Walter, M. Döring, Adv. Synth. Catal. 347 (2005) 1325–1328.
[54] M.-L. Man, K.-C. Lam, W.-N. Sit, S.-M. Ng, Z.-Y. Zhou, Z.-Y. Lin, C.-P. Lau, Chem. Eur. J. 12 (2006) 1004–1015.
[55] K. Nakano, T. Kamada, K. Nozaki, Angew. Chem. Int. Ed. 45 (2006) 7274–7277.
[56] E.K. Noh, S.J. Na, S. Sujith, S.-W. Kim, B.Y. Lee, J. Am. Chem. Soc. 129 (2007) 8082–8083.
[57] W.-L. Wong, K.-C. Cheung, P.-H. Chan, Z.-Y. Zhou, K.-H. Lee, K.-Y. Wong, Chem. Commun. (2007) 2175–2177.
[58] C.-X. Miao, J.-Q. Wang, Y. Wu, Y. Du, L.-N. He, ChemSusChem 1 (2008) 236–241.
[59] S. Sujith, J.K. Min, J.E. Seong, S.J. Na, B.Y. Lee, Angew. Chem. Int. Ed. 47 (2008) 7306–7309.
[60] R. Srivastava, D. Srinivas, P. Ratnasamy, Appl. Catal. A 289 (2005) 128–134.
[61] D.-W. Park, N.-Y. Mun, K.-H. Kim, I. Kim, S.-W. Park, Catal. Today 115 (2006) 130–133.
[62] J. Sun, L. Han, W. Cheng, J. Wang, X. Zhang, S. Zhang, ChemSusChem 4 (2011) 502–507.
[63] Y. Xiong, Y. Wang, H. Wang, R. Wang, Z. Cui, J. Appl. Poly. Sci. 123 (2012) 1486–1493.
[64] S. Kazarian, B.J. Briscoe, T. Welton, Chem. Commun. (2000) 2047–2048.
[65] J.-J. Peng, Y.-Q. Deng, New J. Chem. 25 (2001) 639–941.
[66] Y.J. Kim, R.S. Varma, J. Org. Chem. 70 (2005) 7882–7891.
[67] L.-F. Xiao, F.-W. Li, J.-J. Peng, C.-G. Xia, J. Mol. Catal. A: Chem. 253 (2006) 265–269.

[68] Y. Zhou, S. Hu, X. Ma, S. Liang, T. Jiang, B. Han, J. Mol. Catal. A: Chem. 284 (2008) 52–57.

[69] E.A. Prasetyanto, M.B. Ansari, B.-H. Min, S.-E. Park, Catal. Today 158 (2010) 252–257.

[70] F. Cozzi, Adv. Synth. Catal. 348 (2006) 1367–1390.

[71] M. Avalos, R. Babiano, P. Cintas, J.L. Jiménez, J.C. Palacios, Angew. Chem. Int. Ed. 45 (2006) 3904–3908.

[72] C.H. Christensen, J. Rass-Hansen, C.C. Marsden, E. Taarning, K. Egeblad, ChemSusChem 1 (2008) 283–289.

[73] W.-L. Wong, K.-Y. Wong, Can. J. Chem. 90 (2012) 1–16.

[74] T.-Y. Shi, J.-Q. Wang, J. Sun, M.-H. Wang, W.-G. Cheng, S.-J. Zhang, RSC Adv. 3 (2013) 3726–3732.

[75] J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang, Y. She, Green Chem. 14 (2012) 654–660.

[76] Y. Xiong, Y. Wang, H. Wang, R. Wang, Polym. Chem. 2 (2011) 2306–2315.

[77] W.-L. Wong, P.-H. Chan, Z.-Y. Zhou, K.-H. Lee, K.-C. Cheung, K.-Y. Wong, ChemSusChem 1 (2008) 67–70.

[78] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.

[79] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200–206.

[80] C. Lee, W. Yang, G. Parr, Phys. Rev. B 37 (1988) 785–789.

[81] P.J. Stephens, F.J. Devlin, C.F. Chaobalowski, J. Phys. Chem. 98 (1994) 11623–11627.

[82] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284–298.

[83] P.J. Hays, W.R. Wadt, J. Chem. Phys. 82 (1985) 299–310.

[84] A. Höllwarth, M. Böhme, S. Dapprich, A.W. Ehlers, A. Gobbi, V. Jonas, K.F. Köhler, R. Stegmenn, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 208 (1993) 237–240.

[85] J.E. Johnson, R.A. Jacobson, Acta Crystallogr. B 29 (1973) 1669–1674.

[86] J. Sun, S. Zhang, W. Cheng, J. Ren, Tetrahedron Lett. 49 (2008) 3588–3591.

[87] This is probably due to the accumulation of cyclic carbonates in the reaction medium, which reduces the viscosity of **2·(Br)$_3$** and thus enhances the miscibility of 2-ethyloxirane with **2·(Br)$_3$** as the reaction proceeds.

[88] V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561–2563.

[89] J.-Q. Wang, J. Sun, W.-G. Cheng, K. Dong, X.-P. Zhang, S.-J. Zhang, Phys. Chem. Chem. Phys. 14 (2012) 11021–11026.