Imidazolium ionic liquids/organic bases: Efficient intermolecular synergistic catalysts for the cycloaddition of CO_2 and epoxides under atmospheric pressure

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ABSTRACT

An intermolecular synergistic catalytic system consisting of ionic liquids and organic bases is developed for the cycloaddition of CO_2 and epoxides. This strategy realizes the cycloaddition takes place under atmospheric pressure of CO_2 with high activity. NMR, FT-IR spectroscopy and DFT calculations are applied to investigate the synergistic effect and reaction mechanism on molecules. Plausible ionic liquids/secondary amines and ionic liquids/tertiary amines catalyzed mechanisms are proposed and further confirmed by more detailed DFT calculations including reaction pathways and energy profiles, respectively. The procedure reported here represents a facile, cost-effective and energy-efficient route for chemical fixation of CO_2 into 5-membered cyclic carbonates.

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1. Introduction

With ceaseless increasing CO_2 emission since last century, it has become the primary reason of global climatic warming. As an abundant, non-toxic, non-flammable and easily available source of C1 building block, CO_2 is also an attractive environmentally friendly chemical reagent [1]. However, due to the low energy level of CO_2, a large energy input is inevitable to transform it [2]. Enormous researchers have dedicated themselves to apply CO_2 as raw material for chemical reactions [3].

CO_2 can be applied to synthesize high value-added compounds or fuel products [4,5]. Particularly, the cycloaddition of CO_2 and epoxides to synthesize cyclic carbonates is one of the most successful and efficient routes for chemical fixation of CO_2 in academia and industry [1,2]. The cyclic carbonates are widely used as green reagents, aprotic solvents, precursors for polycarbonate materials, electrolyte solvents for lithium ion battery and fuel additives [5]. Therefore, a variety of catalysts have been investigated for the coupling reaction, such as, alkali metal salts, transition metal complexes, functional polymers, quaternary ammonium salts, quaternary phosphonium salts and Schiff bases [6]. However, these catalytic systems were still suffered from low reactivity, harsh reaction condition, toxic metals, and/or multistep catalyst preparation.

Newly emerged ionic liquids (ILs) were supposed to solve such problems to some extent when they were applied to catalyze the cycloaddition reaction of CO_2 and epoxides [7]. We also found that phenolic hydroxyl-functionalized imidazolium ILs present excellent performance for the cycloaddition reaction [8]. In these studies, the typical ILs-catalyzed mechanism was established as shown in Scheme 1a [9]. The cations of ILs activate epoxides through the interaction with oxygen and the anions of ILs undergo a nucleophilic attack at the least hindered carbon atom of epoxides, which facilitate the opening of the C—O bond. In this strategy, the activation of CO_2 was ignored. On the other hand, it has been reported that organic bases may provide new opportunities for CO_2 activation through the formation of base-CO_2 adducts [10]. As co-catalysts, organic bases were widely used to activate CO_2 in the cycloaddition of CO_2 and epoxides (Scheme 1b) [11].

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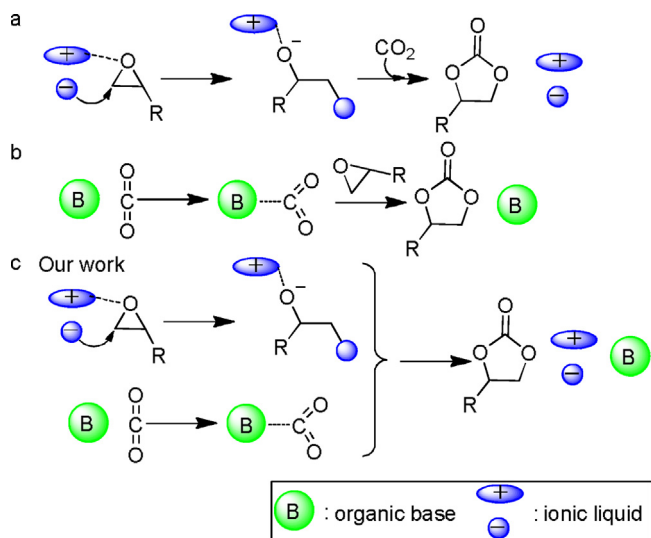
Scheme 1. Mechanism of cycloaddition of CO_2 and epoxides by different catalytic system a) ionic liquids; b) organic bases; c) our proposed dual catalysts.

Table 1
The synergistic effect of organic bases and ionic liquids for the cycloaddition of CO_2 and epichlorohydrin.[a]

Entry	Ionic liquids	Organic bases	Yield[b] [%]
1	BnBimBr	–	50
2	–	DEA	20
3	BnBimBr	DEA	96
4	BmimBr	DEA	82
5	DBnimBr	DEA	95
6	BnMBimBr	DEA	53
7	BnBimBr	DEBA	93
8	BnBimBr	MIm	91
9	BnBimBr	DBU	72
10	BnBimBr	TEA	80
11	BnBimBr	n-BA	81
12	BnBimBr	DABCO	85
13	BnBimBr	Im	78

[a] Reaction conditions: Epichlorohydrin (10 mmol), CO_2 (0.1 MPa), organic base (0.1 mmol), ionic liquids (0.1 mmol), 80 °C, 3 h. [b] GC yield.

Herein, we present a study on the combination of imidazolium ionic liquids and organic bases as synergistic catalytic system for the cycloaddition of CO_2 and epoxides for the first time (Scheme 1c). In this catalytic system, ionic liquids and organic bases are able to activate epoxides and CO_2, respectively. The dual activation facilitates the reaction to proceed under mild conditions. Experimental and theoretical methods on molecules were applied to investigate the synergistic mechanisms of ionic liquids/secondary amines or ionic liquids/tertiary amines.

2. Experimental

2.1. General

1-Benzyl-3-butylimidazolium bromide (BnBimBr), 1,3-dibenzylimidazolium bromide (DBnimBr), 1-benzyl-2-methy-3-butylimidazolium bromide (BnMBimBr) were synesized according to the literature with minor modification (see Supporting Information). 1-Butyl-3-methylimidazolium bromide (BmimBr) was supplied by the Centre for Green Chemistry and Catalysis, LICP, CAS. CO_2 was supplied by Doumaoai Factory with a purity of 99.9%. Epichlorohydrin, epibromohydrin, 2-(phenoxymethyl)oxirane ethylene oxide, propylene oxide, styrene oxide and 1,2-hexene oxide were purchased from TCI. The other reagents were supplied by Sinopharm. All chemicals were used without further purification.
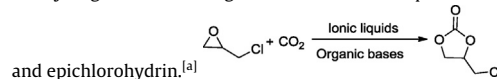
NMR spectra were recorded on Bruker Ascend400 instruments with tetramethylsilane as the internal standard. GC analysis was performed by using a Shimadzu GC–14 B equipped with a capillary column DM-1701 (60 m-0.32 mm-0.25 mm) equipped with a flame ionization detector. FTIR spectra were recorded on a Nicolet nexus 670 instrument.

2.2. Typical procedure for the cycloaddition of CO_2 and epoxide

Typically, epichlorohydrin (0.925 g, 10 mmol), BnBimBr (0.029 g, 0.1 mmol) and DEA (0.007 g, 0.1 mmol) were mixed together and put into a 30 mL stainless steel autoclave equipped with a magnetic stirrer. The reaction was carried out under atmospheric pressure of CO_2 at 80 °C. After the completion of reaction, the autoclave was cooled to room temperature. In order to remove the ionic liquid, Et_2O (40 mL) was added to the reaction mixture and filtered. The filtrate was subsequently analyzed by

gas chromatography to determine yield using dodecane as internal standard. The product was purified by chromatography on silica gel and characterized structurally by NMR spectroscopy.

2.3. Computational methods

The structural optimization by DFT calculations was carried out at the M06-2x/6–31 + G* level using G09 program package [12,13]. The frequency analyses were then performed at the M06-2X/6-311G* level based on the optimized gaseous structures to identify the minima and transition states on potential surfaces. The intrinsic reaction coordinate calculations were conducted to verify that the transition structures connect the correct reactants and products in the forward and reverse directions. The solvent effect on the solute was evaluated using the SMD [14,15] model in G09. All the calculated Gibbs free energies ΔG_{sol} were evaluated under the experimental conditions with the temperature 353 K and pressure 0.1 MPa. More details about the optimized structures are provided in Supporting Information.

3. Results and discussion

3.1. Synergistic catalysis of organic bases and ionic liquids

To investigate the effect of intermolecular synergistic catalytic system, diethylamine (DEA) and BnBimBr were selected as catalysts for the cycloaddition of CO_2 and epichlorohydrin. When BnBimBr was used alone, a moderate yield of 50% of 3-chloro-1,2-propylene carbonate was obtained after 3 h under atmospheric CO_2 pressure (entry 1, Table 1). If DEA was used alone, a poor yield of 20% was obtained (entry 2, Table 1). However, the combination of BnBimBr and DEA gave excellent yield of 96% (entry 3, Table 1), indicating the intermolecular synergistic effect of organic base and ionic liquid for accelerating the cycloaddition reaction. The synergistic effect was also observed in the combination of other ionic liquids and DEA as well. DBnimBr and BmimBr gave yields of 95% and 82%, respectively (entry 4–5, Table 1). However, BnMBimBr, in which the C2-H of the imidazolium ring was replaced by methyl group, provided a lower yield of product (53%) (entry 6, Table 1). These results indicated that C2-H of imidazolium was also crucial for the reaction. NMR spectroscopy and DFT calculations demonstrated the interaction between epoxide and C2-H through hydrogen bonding which led to the activation of epoxide (Fig. S1, S2). The similar observation has been reported by us and others [16]. Various organic bases
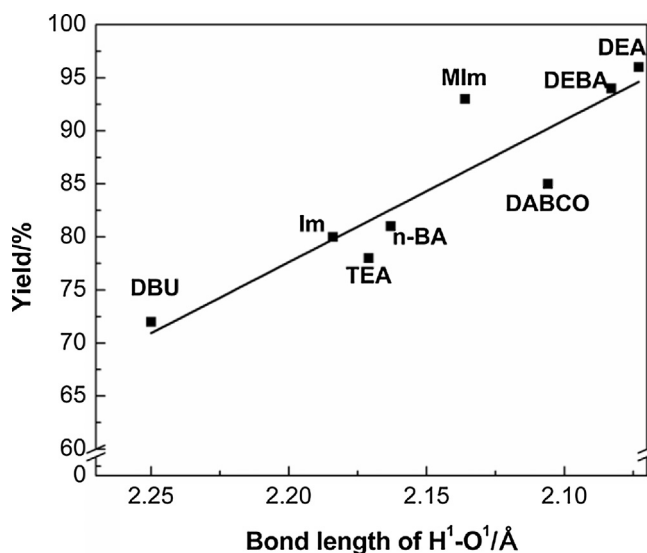
Fig. 1. The correlation of activities and hydrogen bond between C2-H of imidazolium and epichlorohydrin in the presence of various bases. Reaction conditions: Epichlorohydrin (10 mmol), CO_2 (0.1 MPa), BnBimBr (0.1 mmol), organic base (0.1 mmol), 80 °C, 3 h. GC yield.

also showed the synergistic effects to different extent in combination with BnBimBr. Distinctly, N, N-diethylbenzylamine (DEBA) and 1-methylimidazole (MIm) gave the high yields of 93% and 91%, respectively (entry 7–8, Table 1). Other organic bases including 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), triethylamine (TEA), *n*-butylamine (*n*-BA), 1,4-diazabicyclo[2.2.2]octane (DABCO) and imidazole (Im) afforded the product in the yields of 72–85% (entry 9–13, Table 1).

In order to verify the effect of organic base on the cycloaddition reaction in detail, DFT calculations were applied to simulate the hydrogen bond (H^1—O^1) between C2—H of imidazolium and oxygen atom of epichlorohydrin in the mixture of BnBimBr, epoxide and organic bases. The length of H^1—O^1 bond was ranging from 2.07 Å to 2.25 Å in the presence of different organic bases such as DEA, DEBA, MIm, DBU, TEA, *n*-BA, DABCO and Im (Fig. S3), which might be influenced by the basicity and steric hindrance of organic base. Interestingly, an approximately linear negative correlation was obtained between the catalytic activities of organic bases and the lengths of H^1—O^1 bonds (Fig. 1). When the length of H^1—O^1 bond was shorter, the activation of epoxide was more sufficient, which led to the higher reaction activity. These results demonstrated that these organic bases affected the interaction between BnBimBr and epoxide, and further influenced the reaction activity.

3.2. Optimization of reaction parameters

Subsequently, we investigated the effect of other reaction parameters including catalysts amount, reaction temperature and reaction time. In BnBimBr/DEA synergistic catalytic system, when increasing the amount of BnBimBr from 0.5 mol% to 1 mol%, the yield of cyclic carbonate increased from 80% to 96%, and remained the same yield with further increasing the amount of ionic liquid to 2 mol% (entry 1–3, Table 2). With increasing of the amount of organic base from 1 mol% to 2 mol%, the yield did not change obviously, decreasing the amount of organic base to 0.5 mol% resulted in slightly decrease in the yield from 96% to 91% (entry 4–5, Table 2). Lowering reaction temperature to 70 °C and 60 °C led to lower yields of 75% and 45%, respectively (entry 6 and 7, Table 2). In addition, a shorter reaction time of 2 h and 1 h gave the lower yields of 75% and 59%, respectively (entry 8 and 9, Table 2). The optimized reaction conditions of 1 mol% BnBimBr, 1 mol% DEA, 80 °C,

Table 2
Optimization of reaction parameters on the cycloaddition in BnBimBr/DEA catalytic system.[a]

Entry	Ionic liquids [mol%]	Organic bases [mol%]	T[°C]	t [h]	Yield[b] [%]
1	0.5	1	80	3	80
2	1	1	80	3	96
3	2	1	80	3	96
4	1	2	80	3	95
5	1	0.5	80	3	91
6	1	1	70	3	75
7	1	1	60	3	45
8	1	1	80	2	75
9	1	1	80	1	59

[a] Reaction conditions: Epichlorohydrin (10 mmol), CO_2 (0.1 MPa). [b] GC yield.

3 h, 0.1 MPa were obtained. The BnBimBr/DEBA catalytic system showed a similar variation trend (Table S1).

3.3. Synthesis of cyclic carbonates from CO_2 and other epoxides

To investigate the generalities of the dual catalyst system, various epoxides were applied for cycloaddition under the optimized reaction conditions (Table 3). Diverse epoxides were transformed into corresponding cyclic carbonates with good to excellent yields. In BnBimBr/DEA synergistic catalytic system, epibromohydrin and 2-(phenoxymethyl)oxirane (entry 1–2, Table 3) afforded high yields of 95% and 93%, respectively, presumably ascribe to the electron-withdrawing properties of the bromide atom and phenoxyl [11c,17]. Due to their low boiling points, ethylene oxide and propylene oxide reacted with CO_2 under higher pressure and gave yield of 97% (entry 3–4, Table 3). Styrene oxide (entry 5, Table 3) with large steric hindrance also converted into corresponding cyclic carbonate in the yield of 94% under a slight higher temperature (90 °C). 1,2-Hexene oxide afforded a good yield (81%) at 110 °C (entry 6, Table 3). The relative lower reactivity of 1,2-hexene oxide was probably ascribed to the large steric hindrance and electron donating group of butyl, which would hinder nucleophilic attack on the least hindered carbon atom of epoxide ring. The BnBimBr/DEBA system also showed good generalities for various epoxides (Table S2).

Table 3
Reaction of various terminal epoxides with CO_2 under optimized conditions.[a]

Entry	Substate	Product	Yield[e] [%]
1	Br⌒△O	Br⌒(carbonate)	95
2	PhO⌒△O	PhO⌒(carbonate)	93
3[b]	△O	(carbonate)	97
4[b]	⌒△O	(carbonate)	97
[c]	Ph△O	Ph(carbonate)	94
6[d]	Bu⌒△O	Bu⌒(carbonate)	82

[a] Reaction conditions: Epoxide (10 mmol), CO_2 (0.1 MPa), BnBimBr (0.1 mmol), organic bases (0.1 mmol), 80 °C, 3 h, GC yield. [b] 0.5 MPa; [c] 90 °C; [d] 110 °C; [e] GC yield.
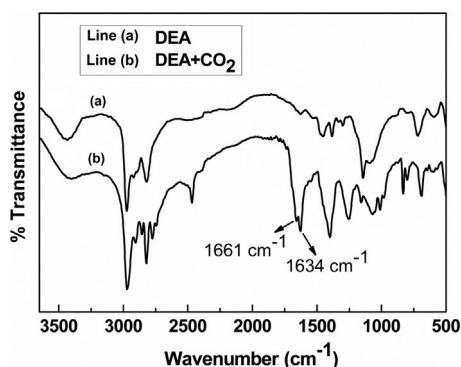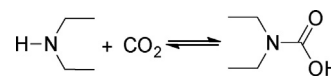
Fig. 2. IR spectrum of DEA before and after reaction with CO_2.

Scheme 2. The reaction of DEA and CO_2.

3.4. Mechanism study

During the studies of synergistic effect of organic bases and ionic liquids, we found that secondary amines and tertiary amines activated CO_2 through different approaches. In order to make a deep insight into the catalytic mechanism, the activation models of CO_2 by secondary amines and tertiary amines and the promotion of ionic liquids were investigated by using experimental and theoretical methods.

3.4.1. Ionic liquids/secondary amines catalyzed mechanism

It has reported that the reaction of secondary amines and CO_2 form carbamic acids or carbamates depending on the reaction conditions. [4a,18] In order to clarify the intermediates in BnBimBr/DEA catalyzed system, FT-IR and NMR investigations were applied to identify the reaction mixture of DEA and CO_2. The FT-IR spectrum of the DEA before and after CO_2-bubbling for 1 h was shown in Fig. 2. Two characteristic peaks centered at $1634\,cm^{-1}$ and $1661\,cm^{-1}$ can be assigned to the new formed –COOH moiety. [19] Besides, the characteristic peak corresponding to dialkylammonium carbamate anion around 1545–$1575\,cm^{-1}$ was not observed. [18c,20] These results indicated that CO_2 could be captured by DEA to generate carbamic acid under the reaction condition. Subsequently, NMR investigations based on the bubbling of CO_2 into DEA were performed to further verify the formation of diethylcarbamic acid (Fig. 3). Upon prolonging the reaction time, the resonance of active proton was shifted downfield gradually from 0.88 ppm to 7.89 ppm and all the peaks were broadened, which were presumably due to the fast proton exchange between continuous formed carbamic acid and free amine. In the ^{13}C NMR spectrum, a new signal at $\delta = 161.89$ ppm was observed, which indicates that a CO_2 molecule was inserted into the N—H bond of DEA to form the carbamic acid. Dijkstra also found similar results that carbamic acid was formed in the organic solvent and in the supercritical CO_2.

[18c] CO_2 could be activated by diethyl amine to form diethyl carbamic acid, which was considered as active intermediate in the cycloaddition of CO_2 and epoxides (Scheme 2).

On the basis of the dual effect of such a binary catalyst on epoxide/CO_2-activation, a reaction mechanism catalyzed by BnBimBr/secondary amines is proposed as illustrated in Fig. 4(a). Correspondingly, a detailed DFT calculation on the reaction pathways was carried out and the calculated free energy profiles are shown in Fig. 4(b). In the first step, the epoxide and BnBimBr can form the stable complex **Int-1** through the hydrogen-bonding interaction between the oxygen atom of epoxide ring and the C2-H of BnBimBr. Then, the bromide anion attacks the carbon atom of epoxide nucleo philically via the transition state **TS-1**, with a remarkable energy barrier of $23.0\,kcal\,mol^{-1}$. The ring opening of epoxide leads to an oxy anion species **Int-2**. On the other hand, CO_2 is activated by DEA via the transition state **TS-2** to afford the species **Int-4** diethyl carbamic acid, where the new nitrogen-carbon bond forms. Our calculated results also indicate that, the energy of another transition state without the water for proton transfer is higher than that of **TS-2** (Fig. S4), since the transition state with a four-member ring is quite unstable in energetics. Subsequently, nucleophilic attack of **Int-2** on **Int-4** via the transition state **TS-3**, yielding a salt **Int-5** which contains alkylcarbonate anion. The DEA is released from **TS-3** by abstracting the proton in diethyl carbamic acid back through a water molecule as a proton shuttle. The activation energy barrier for this step is $21.2\,kcal\,mol^{-1}$ and the salt **Int-5** is quite stable in energetics. Finally, **Int-5** converts to the corresponding cyclic carbonate Pro through the intramolecular ring-closure via **TS-4**, with regenerating the catalyst BnBimBr.

3.4.2. Ionic liquids/tertiary amines catalyzed mechanism

During the study of the mechanism for BnBimBr/DEBA catalyzed the cycloaddition of CO_2 and epoxide, we found that adventitious water could affect the catalytic activity significantly. Accordingly, the effect of additional water on the cycloaddition of CO_2 and epichlorohydrin was investigated. As shown in Fig. 5, without any additional water, a yield of 50% was obtained after 1 h under atmospheric CO_2 pressure. With increasing of additional water from 1 mol% to 4 mol% base on the epoxide, the yields were increased gradually to around 70%. However, with further increasing of additional water from 4 mol% to 10 mol%, the yields were decreased significantly. The effect of water in other BnBimBr/tertiary amine systems was also evaluated. As shown in Fig. 6, in the presence of 4 mol% water, the yields of target product increased about 10% in
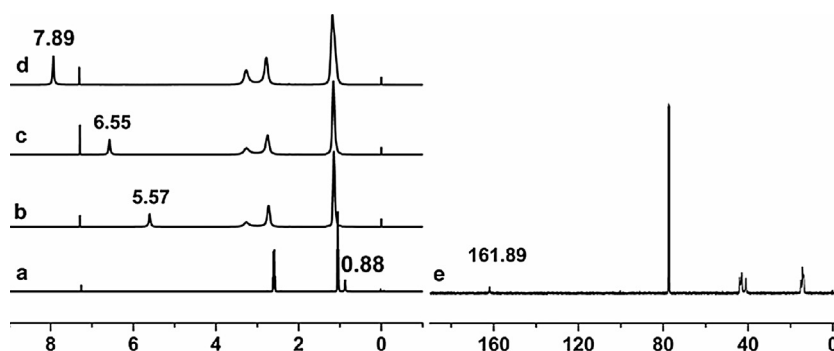

Fig. 3. ^1H NMR spectra of a) only DEA, b) the complex of DEA react with CO_2 for 1 h, c) 2 h, d) 3 h in $CDCl_3$, and e) ^{13}C NMR spectra of the complex of DEA react with CO_2 for 3 h in $CDCl_3$.
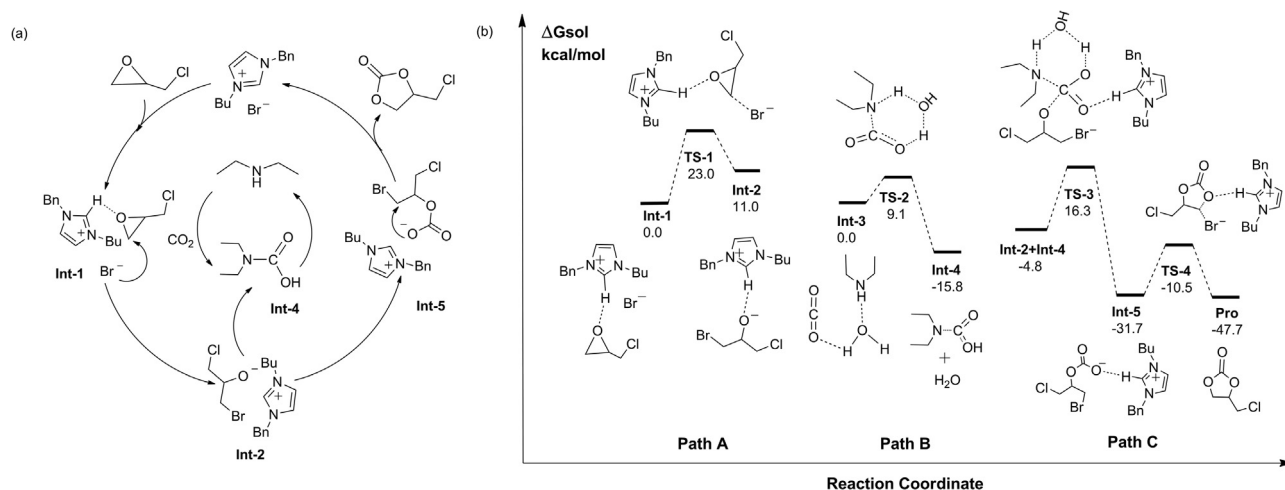
Fig. 4. (a) Proposed Ionic liquids/secondary amines catalyzed mechanism for the cycloaddition of CO_2 and epichlorohydrin. (b) Calculated reaction pathways and energy profiles for the reactions in (a). Path A denotes the ring-opening process of epoxide, Path B denotes the formation of diethyl carbamic acid and Path C denotes the process of yielding the final products.
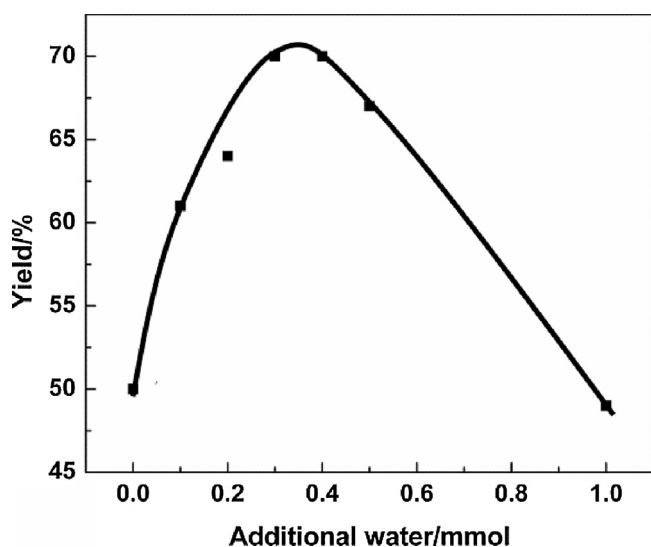

Fig. 5. The effects of additional water in the BnBimBr/DEBA catalytic system for the cycloaddition of CO_2 and epichlorohydrin. Reactin conditions: Epichlorohydrin (10 mmol), CO_2 (0.1 MPa), DEBA (0.1 mmol), BnBimBr (0.1 mmol), 80 °C, 1 h. GC yield.
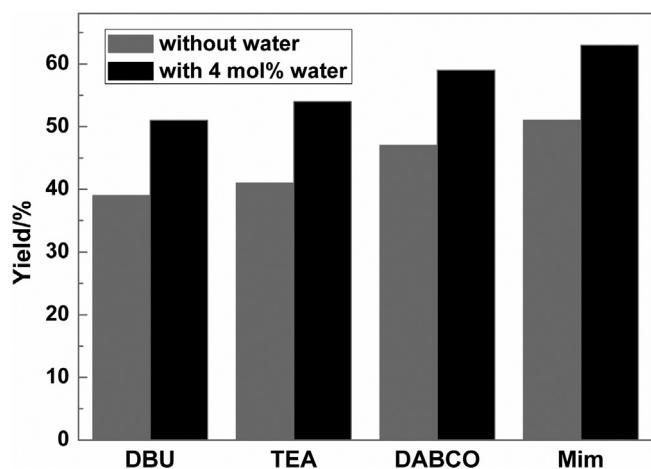

Fig. 6. The effects of additional water in the BnBimBr/organic base catalytic system for the cycloaddition of CO_2 and epichlorohydrin. Reaction conditions: Epichlorohydrin (10 mmol), CO_2 (0.1 MPa), BnBimBr (0.1 mmol), Organic base (0.1 mmol), water (0.4 mmol) 80 °C, 1 h. GC yield.

the BnBimBr/tertiary amines (e.g. DBU, TEA, DABCO, Mim and Im) systems. It has reported that DBU could react with CO_2 to form corresponding bicarbonate salt $[DBUH^+][HCO_3^-]$ in the presence of trace amount of water. [21] Similarly, in the BnBimBr/tertiary amines system, adventitious water was capable of assisting tertiary amines to activate CO_2 through in-situ generation of bicarbonate salts. The appropriate amount of water would facilitate the formation of bicarbonate salts, which were considered to be active species of CO_2 for the cycloaddition, and lead to acceleration of the reaction.

Based on the above results, a reaction mechanism catalyzed by BnBimBr/tertiary amines is proposed as illustrated in Fig. 7(a). Correspondingly, a detailed DFT calculation on the reaction pathways was carried out and the calculated free energy profiles are shown in Fig. 7(b). The ring-opening process of epoxide is the same as Path A shown in Fig. 4(b). Path D denotes the proposed pathway for the activation of CO_2 existing in solution by the tertiary amine. Tertiary amine, CO_2, and water molecules can form stable complex **Int-6** through the hydrogen bonding interactions in solution. Due to the strong basicity of tertiary amine, the nitrogen atom is capable of abstracting the proton from H_2CO_3 through the transition state **TS-5**. The energy barrier for the proton abstraction via **TS-5** is only 5.9 kcal mol^{-1}, which is quite easy to occur in solution. The capture of CO_2 by DEBA with water molecules generates the ion pair $[HDEBA^+][HCO_3^-]$, denoted as **Int-7**. The ion pair **Int-7** reacts with **Int-2** to generate the stable complex **Int-5**, with DEBA and a water molecule liberated. The energy barrier of this step is 21.2 kcal mol^{-1}. In the last intramolecular cyclization step via the transition state **TS-4**, the target product **Pro** is formed and BnBimBr is regenerated.

4. Conclusion

In summary, a simple and efficient intermolecular synergistic catalyst system consisting of imidazolium ionic liquids and organic bases has been developed for CO_2 chemical fixation with epoxides under metal- and solvent-free conditions. The binary system exhibits distinctly higher catalytic activity than using organic bases or imidazolium ionic liquids alone. The combination of imidazolium ionic liquids and organic bases is found to be applicable for the transformation of a range of epoxides under very mild conditions. The mechanism studies based on the NMR, FT-IR investigations and DFT calculations indicate that imidazolium ionic liquids activate epoxides and organic bases activate CO_2, respectively. The appli-
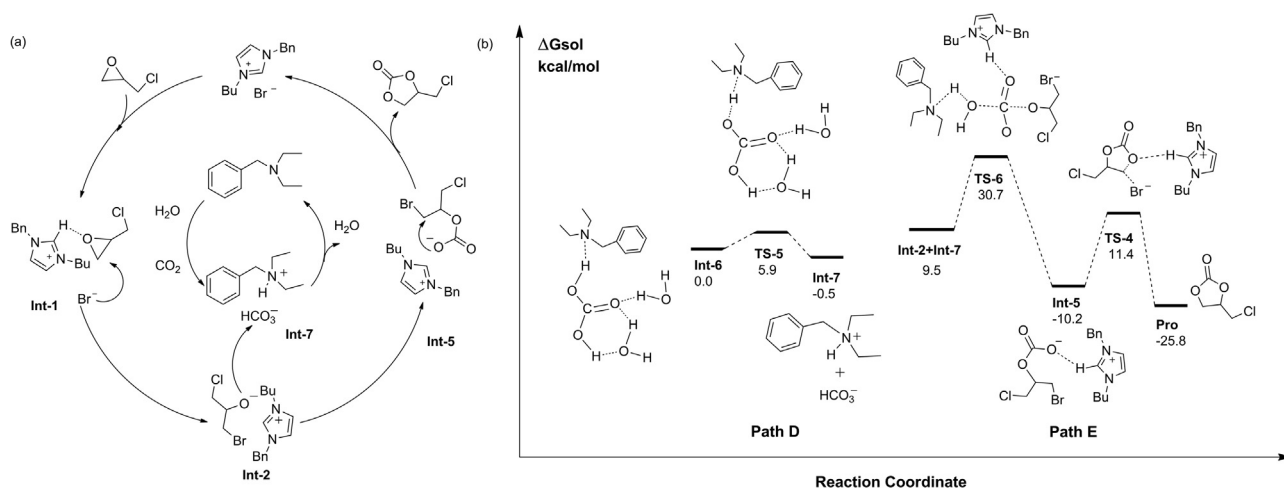
Fig. 7. (a) Proposed Ionic liquids/tertiary amines catalyzed mechanism for the cycloaddition of CO_2 and epichlorohydrin. (b) Calculated reaction pathways and energy profiles for the proposed tertiary amine-catalyzed mechanism. Path D denotes the activation of CO_2 by DEBA and Path E denotes the synthesis of cyclic carbonate.

cation of imidazolium ionic liquids/organic bases catalytic system in the cycloaddition reaction provides a cost-effective and energy-efficient route to obtain 5-membered cyclic carbonates from CO_2 at atmospheric pressure.

Acknowledgements

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.mcat.2017.12.026.

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