

## Short communication

One-pot reaction of CO<sub>2</sub>, epichlorohydrin and amine to synthesize 4-(phenylamino)methyl-ethylene carbonate catalyzed by ionic liquids

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## ABSTRACT

Ionic liquids were firstly used as catalysts for one-pot synthesis of 4-(phenylamino)methyl-ethylene carbonate from CO<sub>2</sub>, epichlorohydrin and aniline without the utilization of any solvents or additives. The effects of the ratio of epichlorohydrin and aniline, catalyst amount, reaction temperature, time and initial CO<sub>2</sub> pressure were investigated. The catalytic activity of the reaction was affected by the anions of ionic liquids and followed the order of Cl<sup>-</sup> > Br<sup>-</sup> > OAc<sup>-</sup> > BF<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup>. The possible reaction mechanism was proposed based on the reaction results.

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## 1. Introduction

CO<sub>2</sub> from combustion of fossil fuels is regarded as the main greenhouse gas. Reduction of CO<sub>2</sub> emissions has attracted intense attention from governments and scientists. However, with the growth of world population and the improvement of modernization, it is apparent that atmospheric CO<sub>2</sub> concentration will continue to monotonically increase for the foreseeable future due to energy demand. Therefore, besides minimizing CO<sub>2</sub> emissions, it is significant to utilize CO<sub>2</sub> as a renewable feedstock for generating energy, material and fine chemicals [1–3].

One of the promising routes using CO<sub>2</sub> as a raw material is the production of cyclic carbonates by the cycloaddition of CO<sub>2</sub> with epoxides. This is partially because cyclic carbonates are useful as intermediates for polycarbonates, electrolytes in lithium ion batteries, green solvents and important intermediates in organic synthesis. Various catalysts have been developed for the process, including metal halides, metal oxides, metal complexes, Schiff base and so on [4–6]. With the unique properties including negligible vapor pressure, good thermal stabilities, wide liquid temperature ranges, unlimited structural variations, ionic liquids have also received much attention in the field of cycloaddition of

CO<sub>2</sub> with epoxides recently [7]. The reported ionic liquids for cycloaddition of CO<sub>2</sub> with epoxides include imidazolium salts [8–10], quaternary ammonium salts [11], quaternary phosphonium salts [12], metal halide ionic liquids [13–16], supported ionic liquids [17–28].

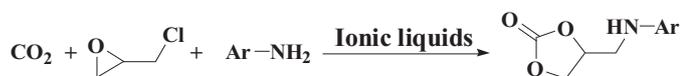
Although significant studies have been made for synthesis of cyclic carbonates, the reports related to synthesize amino functionalized cyclic carbonate with one-pot reaction involving CO<sub>2</sub> are still very rare. Herein we report, firstly, the one-pot reaction of CO<sub>2</sub>, epichlorohydrin and amine to synthesize amino functionalized cyclic carbonates in the presence of catalytic amount of ionic liquids (Scheme 1).

## 2. Experimental

## 2.1. Reagents

All chemicals were purchased commercially and used without further purification. The imidazolium ionic liquids such as 1-butyl-3-methyl-imidazolium chloride (BmimCl), 1,2-dimethyl-3-butyl-imidazolium chloride (BmmimCl), 1-butyl-3-methyl-imidazolium acetate (BmimOAc), 1,2-dimethyl-3-butyl-imidazolium acetate (BmmimOAc), 1-butyl-3-methyl-imidazolium bromide (BmimBr), 1,2-dimethyl-3-butyl-imidazolium bromide (BmmimBr), 1-butyl-3-methyl-imidazolium tetrafluoroborate (BmimBF<sub>4</sub>), 1-butyl-3-methyl-imidazolium hexafluorophosphate (BmimPF<sub>6</sub>) were synthesized according to the literature.

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E-mail address: [ghgao@chem.ecnu.edu.cn](mailto:ghgao@chem.ecnu.edu.cn) (G. Gao).



**Scheme 1.** One-pot reaction to synthesize amino functionalized cyclic carbonate.

### 2.2. A representative procedure for the reaction of CO<sub>2</sub>, epichlorohydrin and aniline to synthesize 4-(phenylamino)methyl-ethylene carbonate catalyzed by BmimCl

The reaction of CO<sub>2</sub>, epichlorohydrin and aniline was carried out in a stainless-steel autoclave reactor with an inner volume of 50 mL. BmimCl (0.1 mmol, 0.018 g), epichlorohydrin (6 mmol, 0.555 g) and aniline (2 mmol, 0.186 g) were added to the autoclave. The reactor was purged with CO<sub>2</sub> two times and pressurized with CO<sub>2</sub> to 0.5 MPa at ambient temperature. The reaction mixture was heated to 60 °C and kept for 6 h under stirring. The reactor was cooled to room temperature and depressurized to an atmospheric pressure. Dodecane was added to the reaction mixture as an internal standard for GC analysis. GC analyses were performed on a Shimadzu GC-14B equipped with a capillary column CBP1-M25-025. The yields of 4-(phenylamino)methyl-ethylene carbonate (**1**) and 1-chloro-3-phenylamino-propan-2-ol (**2**) were calculated based on the amount of aniline. The pure products were obtained by chromatography on silica gel and characterized by <sup>1</sup>H NMR and GC-Mass. NMR spectra were recorded on Bruker with tetramethylsilane as the internal standard.

## 3. Results and discussion

### 3.1. One-pot reaction of CO<sub>2</sub>, epichlorohydrin and aniline to synthesize 4-(phenylamino)methyl-ethylene carbonate catalyzed by various ionic liquids

Reaction of CO<sub>2</sub>, epichlorohydrin and aniline in the presence catalytic amount of ionic liquids afforded amino functionalized cyclic carbonate (**1**) and the ring opening product, 1-chloro-3-phenylamino-propan-2-ol (**2**) smoothly. It is reasonably assumed that the ring opening product was formed by the aminolysis of epichlorohydrin with aniline [29,30]. Various ionic liquids with different cations and anions have been applied to catalyze the reaction and the results were summarized in Table 1. BmimCl and BmmimCl gave **1** and **2** in the combined yields of 90% and 87%, and

relative higher selectivity of **1** among the various ionic liquids, respectively (Table 1 entries 1, 2). Other ionic liquids such as BmimBr, BmmimBr, BmimOAc and BmmimOAc also afforded **1** and **2** in relatively good combined yields of 72–80% (Table 1 entries 3–6). However, BmimBF<sub>4</sub> and BmimPF<sub>6</sub> showed the low catalytic activity for this reaction and gave the combined yields in 59% and 33%, respectively (Table 1 entries 7, 8). These results indicate that anions of imidazolium based ionic liquids play an important role in the reaction, and the catalytic activity follows the order of Cl<sup>-</sup> > Br<sup>-</sup> > OAc<sup>-</sup> > BF<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup>. Meanwhile, with same anions, Bmmim based ionic liquids, in which the C2-proton of imidazolium is replaced by a methyl group, gave similar catalytic activity compared with Bmim based ionic liquids. These results apparently differ from our previous works, in which C2-proton of imidazolium plays a dominating role in the reactions involving carbonates [31,32]. In addition, both BmimCl and BmmimCl had higher catalytic activity than Bu<sub>4</sub>NCl (Table 1 entries 1, 2, 9). This indicates that the imidazolium-based cations of the ionic liquids also play a momentous role in catalyzing the reaction of CO<sub>2</sub>, epichlorohydrin and aniline. Conclusively, BmimCl was selected as a model catalyst for further investigation.

### 3.2. Optimization of reaction conditions

To optimize the reaction parameters, the effects of ratio of the epichlorohydrin and aniline, catalyst amount, temperature, reaction time and initial CO<sub>2</sub> pressure were investigated.

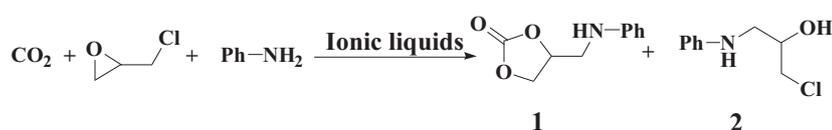
#### 3.2.1. Effect of ratio of the epichlorohydrin and aniline

The influence of the molar ratio of epichlorohydrin and aniline was shown in Fig. 1. The yield of **1** increased dramatically with increasing molar ratio of epichlorohydrin and aniline from 1 to 3 and almost leveled off with further increase of epichlorohydrin, and reached to the highest yield of 65% at the molar ratio of 8. However, the yield of **2** increased from the ratio of 1 to 2, then decreased from ratio of 2 to 8. Considering economical efficiency, the reactant molar ratio of 3 was used in the following investigation.

#### 3.2.2. Effect of catalyst amount

The influence of the catalyst amount was shown in Fig. 2. Without any catalyst, the reaction cannot go smoothly. With the increase of the amount of BmimCl from 0 to 5 mol%, the yields of

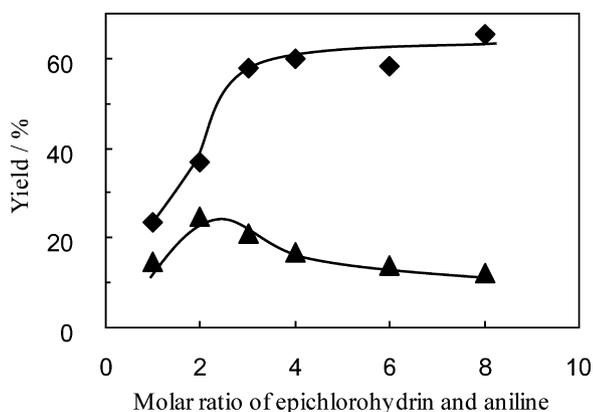
**Table 1**  
Reaction of CO<sub>2</sub>, epichlorohydrin and aniline catalyzed by various ionic liquids.<sup>a</sup>



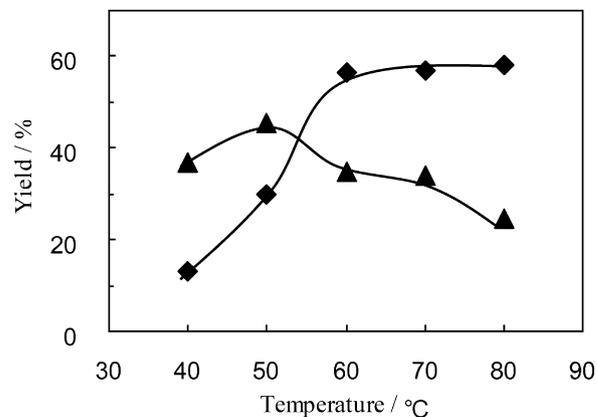
Entry	Ionic liquid	Yield/% <sup>b</sup>	
		<b>1</b>	<b>2</b>
1	BmimCl	58	32
2	BmmimCl	53	34
3	BmimBr	31	49
4	BmmimBr	36	44
5	BmimOAc	46	30
6	BmmimOAc	44	28
7	BmimBF <sub>4</sub>	22	37
8	BmimPF <sub>6</sub>	<1	32
9	Bu <sub>4</sub> NCl	36	32

<sup>a</sup> Reaction conditions: aniline: 2 mmol, epichlorohydrin: 6 mmol, ionic liquid: 0.1 mmol, 60 °C, 6 h, 0.5 MPa CO<sub>2</sub>.

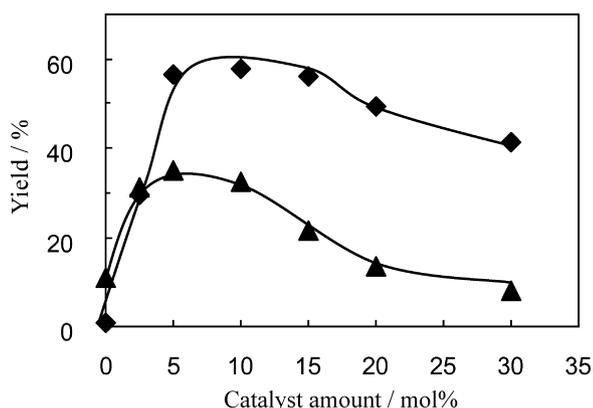
<sup>b</sup> GC yield.



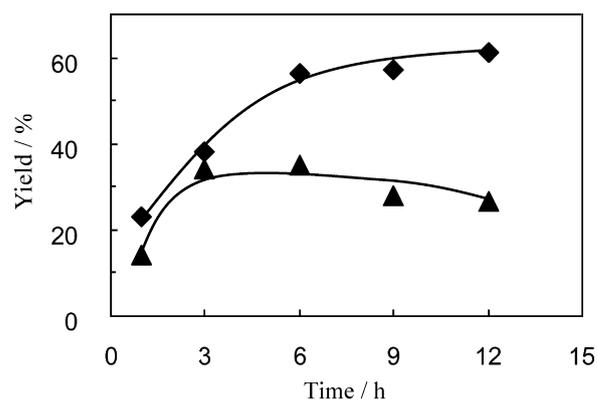
**Fig. 1.** Effect of molar ratio of the epichlorohydrin and aniline. Reaction conditions: aniline: 2 mmol, BmimCl: 0.2 mmol, 60 °C, 6 h, 1.5 MPa CO<sub>2</sub>. (◆) Yield of 1; (▲) yield of 2.



**Fig. 3.** Effect of reaction temperature. Reaction conditions: aniline: 2 mmol, epichlorohydrin: 6 mmol, BmimCl: 0.1 mmol, 6 h, 1.5 MPa CO<sub>2</sub>. (◆) Yield of 1; (▲) yield of 2.



**Fig. 2.** Effect of catalyst amount. Reaction conditions: aniline: 2 mmol, epichlorohydrin: 6 mmol, 60 °C, 6 h, 1.5 MPa CO<sub>2</sub>. (◆) Yield of 1; (▲) yield of 2.



**Fig. 4.** Effect of reaction time. Reaction conditions: aniline: 2 mmol, epichlorohydrin: 6 mmol, BmimCl: 0.1 mmol, 60 °C, 1.5 MPa CO<sub>2</sub>. (◆) Yield of 1; (▲) yield of 2.

**1** and **2** improved dramatically. However, with further increase of the amount of BmimCl, the yields of **1** and **2** almost leveled off and then decreased. In the meanwhile, 4-chloromethyl-ethylene carbonate, which was formed by the reaction of CO<sub>2</sub> with epichlorohydrin, increased dramatically with increase of the amount of BmimCl. The decrease of yields of **1** and **2** was probably due to the acceleration of the cycloaddition of CO<sub>2</sub> with epichlorohydrin under high concentration of BmimCl, which consume epichlorohydrin and led to less epichlorohydrin reacted with aniline.

### 3.2.3. Effect of reaction temperature

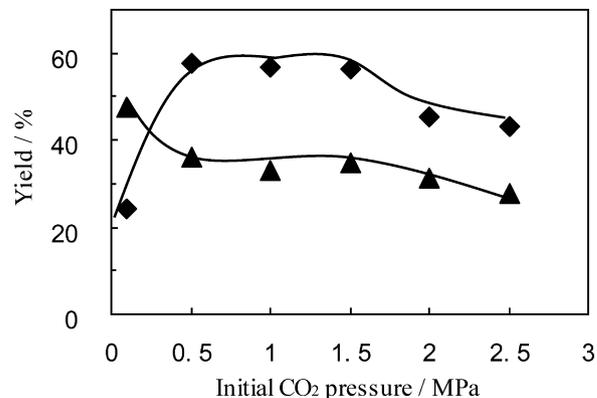
The influence of the reaction temperature was shown in Fig. 3. The yield of **1** increased with the rise in temperature from 40 to 60 °C, and almost leveled off with further rise in temperature from 60 to 80 °C. Meanwhile, the yield of **2** increased with the rise in temperature from 40 to 50 °C and then decreased with further increase of the temperature.

### 3.2.4. Effect of reaction time

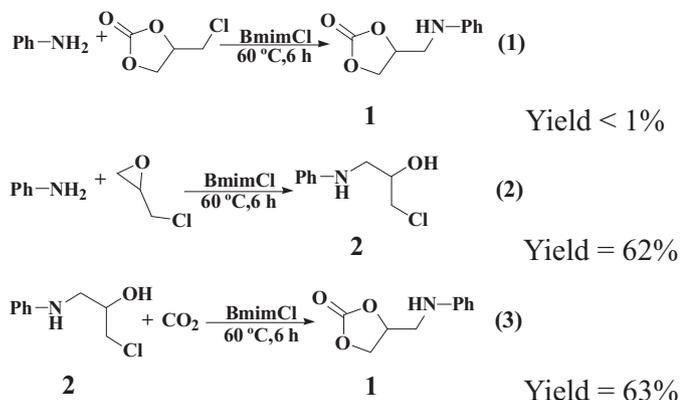
The influence of the reaction time was shown in Fig. 4. The yield of **1** increased dramatically before 6 h and increased slowly when further prolonged the reaction time to 12 h. Meanwhile, the yield of **2** increased in the first 6 h, and then decreased slightly with prolonged reaction time from 6 to 12 h. It was noted that the increase of the yield of **1** was consistent with the decrease of the yield of **2**. Presumably, **1** was formed from the reaction of **2** with CO<sub>2</sub>. The details of the reaction mechanism will be discussed in Section 3.3.

### 3.2.5. Effect of initial CO<sub>2</sub> pressure

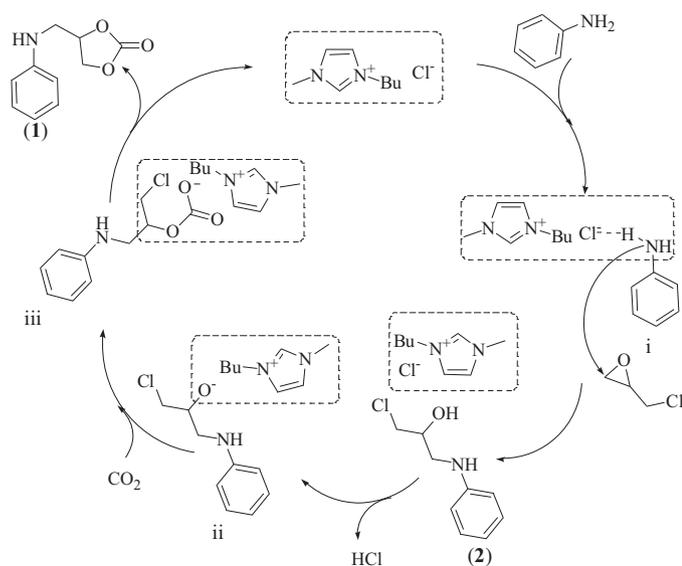
The influence of the initial CO<sub>2</sub> pressure was shown in Fig. 5. The yield of **1** was very low under atmospheric pressure (CO<sub>2</sub> continuously fed into the reactor). The yield of **1** increased first and almost leveled off from 0.5 to 1.5 MPa initial CO<sub>2</sub> pressure. The yield of **1** decreased with the further increase of CO<sub>2</sub> pressure from 1.5 to 2.5 MPa. Meanwhile, the yield of **2** decreased with increase of CO<sub>2</sub> pressure. With high initial CO<sub>2</sub> pressure (>1.5 MPa), the yields of **1** and **2** decreased. A possible explanation is that high CO<sub>2</sub> pressure may retard the interaction between epoxide and the catalyst [18,33].



**Fig. 5.** Effect of initial CO<sub>2</sub> pressure. Reaction conditions: aniline: 2 mmol, epichlorohydrin: 6 mmol, BmimCl: 0.1 mmol, 60 °C, 6 h. (◆) Yield of 1; (▲) yield of 2.



Scheme 2. Model reactions.

Scheme 3. Proposed reaction mechanism of CO<sub>2</sub>, epichlorohydrin and aniline catalyzed by BmimCl.

### 3.3. Studies of the reaction mechanism

To investigate the reaction course, three model reactions were carried out as shown in Scheme 2. Aniline did not react with 4-chloromethyl-ethylene carbonate in the presence of catalytic amount of BmimCl. This indicated that **1** was not afforded by the reaction of aniline and “intermediate” of 4-chloromethyl-ethylene carbonate which can be obtained by the cycloaddition of CO<sub>2</sub> with epichlorohydrin [9,10]. However, aniline reacted with epichlorohydrin smoothly and the ring opening product **2** was obtained in the yield of 62% in the presence of BmimCl. The ring opening reaction of aniline and epichlorohydrin also occurred in the presence of ammonium salt catalysts [29,30]. The reaction of **2** and CO<sub>2</sub> was carried out in the presence of BmimCl, and **1** was obtained in a yield of 63%.

Based on the above results, a possible mechanism for the BmimCl-catalyzed one-pot synthesis of 4-(phenylamino)methyl-ethylene carbonate from CO<sub>2</sub>, epichlorohydrin and aniline is proposed (Scheme 3). Firstly, anion of ionic liquid activates the N–H bond of aniline by acceptance of hydrogen-bond and forms an intermediate (i). Secondly, nucleophilic attack of activated aniline on the  $\beta$ -carbon atom of epichlorohydrin that is sterically less hindered occurs. Simultaneously, the ring opening product **2** is formed as a by-product. Thirdly, **2** undergoes dissociation of HCl to form an intermediate (ii). Fourthly, the insertion of CO<sub>2</sub> into an

intermediate (ii) results in the formation of an intermediate (iii). Finally, cyclization via an intramolecular nucleophilic attack leads to the formation of **1** and the regeneration of the catalyst.

## 4. Conclusion

In summary, we have described a simple and eco-friendly procedure for the one-pot synthesis of 4-(phenylamino)methyl-ethylene carbonate from CO<sub>2</sub>, aniline and epichlorohydrin catalyzed by ionic liquids under solvent-free conditions. The catalytic activity is affected by the anions of ionic liquids and follows the order of Cl<sup>−</sup> > Br<sup>−</sup> > OAc<sup>−</sup> > BF<sub>4</sub><sup>−</sup> > PF<sub>6</sub><sup>−</sup>.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcou.2013.02.001.

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