

# Hydroxyl-functionalized ionic liquid: a novel efficient catalyst for chemical fixation of CO<sub>2</sub> to cyclic carbonate

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## Abstract

A series of hydroxyl-functionalized ionic liquids (HFILs) were synthesized and characterized. They showed efficient reactivity and reusability toward the coupling of epoxide and CO<sub>2</sub> without any additional co-catalyst and organic solvent. Highest activity and selectivity were achieved in the presence of 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMB) in comparison with other similar catalysts investigated. The relationship between the higher catalytic reactivity and OH-functional group was proposed.

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**Keywords:** Ionic liquid; Carbon dioxide; Chemical fixation; Cyclic carbonate

Carbon dioxide is an attractive C1 building block in organic synthesis as it is highly functional, abundant, economical, and nontoxic.<sup>1–4</sup> One of the most attractive synthetic protocols utilizing CO<sub>2</sub> is the coupling reaction of epoxide and CO<sub>2</sub> to afford the five-membered cyclic carbonates,<sup>5–8</sup> which can serve as valuable intermediates for polycarbonates, electrolytes in lithium ion batteries, or green solvents. Numerous catalysts have been developed for this transformation,<sup>9–36</sup> especially including ionic liquids (ILs) which are currently regarded as versatile and novel reaction media.<sup>9–22</sup> Although the advances are significant, most suffer from low catalyst activity,<sup>9–12,26,27</sup> water or air sensitivity of catalyst,<sup>14–16,20–23,31</sup> and the need for toxic co-solvent.<sup>27,34,35</sup> In addition, although the combination of IL with Lewis acid has resulted in many diverse and flexible ‘platform’ to establish a highly effective catalytic system, its big problems are obvious. For example: (1) the activities of ILs are reduced distinctly in the absence of Lewis acids; (2) anhydrous operation is necessary due to the water sensitivity of some Lewis acid; and (3) higher

cost needed compared to single component catalyst system. Therefore, developing water-stable, low-cost, and efficient single component catalyst for the synthesis of cyclic carbonate is still highly required.

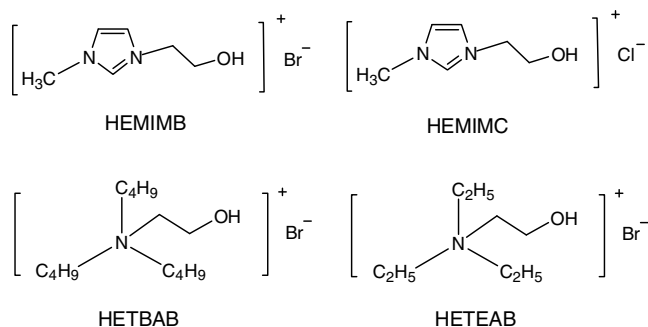
Recently, functionalized ionic liquids (FILs) containing ether or alcohol on the alkyl arms have received much attention in the fields of organic synthesis and catalysis.<sup>36–40</sup> Compared to the traditional ILs, they show additional advantages such as alterable polarity,<sup>36</sup> lower viscosity and higher solubility of inorganic salts,<sup>37</sup> and immobilization potential.<sup>38,39</sup> However, few literatures reported on the synthesis of cyclic carbonate using these FILs except Zhu et al.<sup>41</sup> They found that the supported choline chloride/urea (CH/urea) ionic liquid showed high activity and selectivity for the coupling reaction of epoxide and CO<sub>2</sub> without any solvent. But similar to the aforementioned reports, the disadvantages of this catalytic system are the following: (1) CH alone showed unsatisfied activity in the absence of urea, and (2) urea is a well-known thermal and water sensitive chemical which decomposes to ammonia and isocyanate above its melting point (132 °C) and hydrolyzes to ammonia and CO<sub>2</sub> in water. Since OH group has the positive effect on the ring-opening of epoxy, this

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idea can extend to the corresponding hydroxyl-functionalized ionic liquids (HFILs) directly for the synthesis of cyclic carbonate without using other additives.

Herein, two kinds of HFILs (Scheme 1) were synthesized,<sup>42</sup> and their activities on the synthesis of cyclic carbonates from terminal epoxides and CO<sub>2</sub> were investigated without any additional Lewis acid reagent and solvent.<sup>43</sup>

Under the optimal conditions, the performance of various catalysts was tested using propylene oxide (PO) as a model substrate (Table 1). It is found that HFILs showed higher reactivity (entries 4, 5, 11, and 12) in comparison with other non-functionalized ionic liquids or solid ionic catalysts, such as EMIMBr (1-ethyl-3-methylimidazolium



Scheme 1. Hydroxyl-functionalized ionic liquids (HFILs).

Table 1  
Synthesis of PC catalyzed by different catalysts<sup>a</sup>

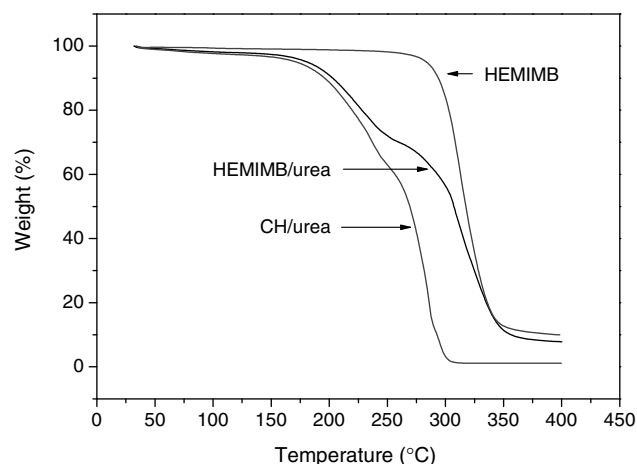
Entry	Catalysts	Conversion (%)	Selectivity (%)
1	1-Methylimidazole	1.5	99.1
2	2-Bromidethanol	2.0	99.2
3	C <sub>2</sub> H <sub>5</sub> OH	1.8	99.1
4	HEMIMB	99.2	99.8
5	HEMIMC	78	99.3
6	EMIMBr	83	99.3
7	EMIMBr/H <sub>2</sub> O <sup>b</sup>	93	99.1
8	EMIMBr/C <sub>2</sub> H <sub>5</sub> OH <sup>b</sup>	92	99.3
9	EMIMBr/DMC <sup>b</sup>	84	99.8
10	EMIMBr/DMF <sup>b</sup>	85	99.6
11	HETBAB	95.8	99.2
12	HETEAB	87.8	99.2
13	TBAB	73.6	99.3
14	PPh <sub>3</sub> EtBr	50.1	99.8
15	KI	34	99.6
16	KBr	2.0	99.4
17	CH	45.1	98.5
18	Urea	trace	—
19	CH/urea	70.9	98.3
20	HEMIMB/urea	99.7	99.3
21 <sup>c</sup>	HEMIMB	94.7	99.3

<sup>a</sup> Reaction conditions: PO (0.2 mol), catalyst (3.2 mmol), temperature: 125 °C, CO<sub>2</sub> pressure: 2.0 MPa, reaction time: 1 h.

<sup>b</sup> Equal catalysis amount (3.2 mmol).


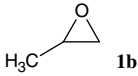

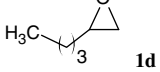
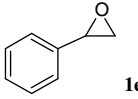
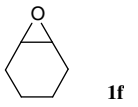
<sup>c</sup> After using four times.

bromine), TBAB (tetrabutylammonium bromide), PPh<sub>3</sub>EtBr (triphenyl(ethyl)phosphonium bromide), KI and KBr (entries 6 and 13–16). By the way, almost no reactivity was observed in the presence of organic base 1-methylimidazole or organic Brønsted acid 2-bromidethanol or C<sub>2</sub>H<sub>5</sub>OH (entries 1–3). HEMIMC (1-(2-hydroxyethyl)-3-methylimidazolium chloride) shows lower activity than HEMIMB (1-(2-hydroxyethyl)-3-methylimidazolium bromide) (entries 4–5). Interestingly, EMIMBr could also show high activity in the presence of equal catalysis amount of H<sub>2</sub>O or C<sub>2</sub>H<sub>5</sub>OH (Table 1, entries 7 and 8). However, its activity is still low in the presence of non-OH group containing chemicals such as DMC (dimethyl carbonate) and DMF (*N,N*-dimethylformamide) (entries 9 and 10). It was proposed that some cooperative effect from the OH group and Lewis basic site of the ionic liquid played an important role in accelerating the synthesis of PC. Among the catalysts, HEMIMB was identified as the most effective one and could be used four times with little loss of activity (entry 21). As also shown in Table 1, the CH/urea mixture could show higher activity than CH or urea alone (entries 17–19), which might be due to the appropriate effect between CH and urea by hydrogen bond.<sup>44</sup> When CH was substituted by HEMIMB to form another two-reagent mixture HEMIMB/urea (molar ratio, 1:2),<sup>45</sup> almost the same value in activity was achieved compared to that of HEMIMB (entries 4 and 20). In addition, TGA experiments (Scheme 2) show that HEMIMB is more stable than CH under heating, and that urea decomposes obviously by increasing temperature above 150 °C. Therefore, the low thermal stability of HEMIMB/urea and CH/urea mixtures would limit the utilization of these catalytic systems in industrial process. Based on the results, single HEMIMB was chosen for the further investigation because of its good performance and thermal stability. It is important to avoid the usage of binary system for convenient and economical operation of industrial synthesis of PC from CO<sub>2</sub> and PO.



Scheme 2. TGA of HEMIM, HEMIMB/urea, and CH/urea.

Table 2  
Synthesis of other cyclic carbonate catalyzed by HEMIMB<sup>a</sup>

Entry	Epoxide	Time (h)	Selectivity (%)	Yield <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1 <sup>d</sup>	 <b>1a</b>	0.7	99	99	87
2	 <b>1b</b>	1	99.8	99	83
3	 <b>1c</b>	0.33	92	92	88
4	 <b>1d</b>	1	99	99	84
5	 <b>1e</b>	1	99	99	83
6	 <b>1f</b>	5	99	99	80

<sup>a</sup> Reaction conditions: Epoxide (0.2 mol), HEMIMB (3.2 mmol), temperature: 125 °C, CO<sub>2</sub> pressure: 2.0 MPa.

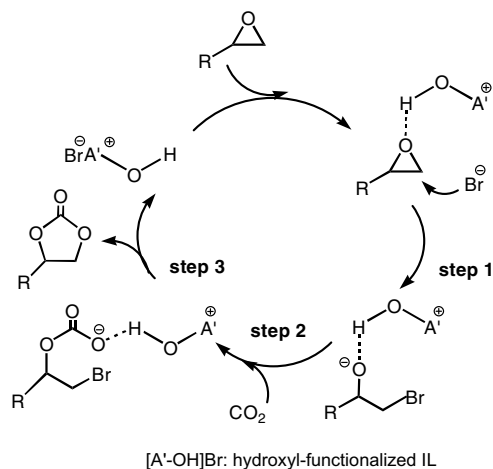
<sup>b</sup> GLC yield.

<sup>c</sup> Catalyst: EMIMBr.

<sup>d</sup> Temperature: 110 °C.

The highly efficient HEMIMB catalyst was also found to be extended to a variety of terminal epoxides (**1a–f**) under the optimal reaction conditions compared to EMIMBr catalyst. The results are summarized in Table 2. Aromatic **1e** and aliphatic **1a**, **1b**, **1d** epoxides are preferred substrates for the reaction. All the reactions could be complete in less than 1.5 h except **1f**, which needs 5 h to reach 90% yield due to the higher hindrance that originated from the two rings. The selectivity of the reactions to the cyclic carbonates was almost >99% except **1c**.

Based on the reports<sup>24,41,46</sup> and the results obtained, a mechanism portraying the probable sequence of events is shown in Scheme 3. It shows that the OH group and the Lewis basic site bromine anion of HFIL coordinately attack the different parts of epoxide firstly. The coordination of the H atom with the O atom of epoxide through a hydrogen bond resulted in the polarization of C–O bonds, and the halide anion made the nucleophilic attack on the less sterically hindered β-carbon atom of the epoxide at the same time. As a result, the ring of the epoxide was opened easily (step 1). Then, the interaction occurred between the oxygen anion and CO<sub>2</sub>, and the alkylcarbonate anion was formed (step 2) that would be transformed into a cyclic carbonate by the intramolecular substitution of the halide in the next step (step 3). OH group plays a similar function like Lewis acid on the ring-opening of epoxy, by which the HFIL could show excellent activity in the absence of Lewis acid. From our experiments (Table 1,



Scheme 3. Proposed mechanism for the reaction.

entries 7–8) other chemicals containing OH groups could also have the same effect on the accelerating activity of the catalyst.

In conclusion, one type of hydroxyl-functionalized ionic liquid was developed and it was found to be an ideal and extremely simple catalyst for the synthesis of cyclic carbonate with high selectivity in the absence of any co-catalyst and any co-solvents. OH groups in the catalyst or reaction media are crucial for the reaction to proceed smoothly due to its cooperation function of ring-opening of epoxide. Among all the catalysts investigated, HEMIMB ionic liquid was the most effective for the cyclic carbonate synthesis with a 99% conversion of PO and 99.8% selectivity of PC under the mild conditions (125 °C, 2.0 MPa, and 1.0 h). The catalyst showed high thermal stability and could be recycled with minor loss in activity and selectivity. Moreover, the catalyst could be applicable to other terminal epoxides. These characteristics make it an ideal catalyst in terms of potential industrial application in chemical carbon dioxide fixation.

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42. Typical synthesis procedure of Hydroxyl-functionalized ionic liquids: For the synthesis of 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMB), a mixture of freshly distilled 1-methylimidazole (0.14 mol), dry toluene (50 mL) and 2-bromidethanol (0.16 mol) was placed in a three-necked glass flask and stirred for 24 h at 70 °C under a nitrogen atmosphere. Then the mixture was cooled down to room temperature, and a white solid formed rapidly. The resultant crude solid was filtered off, washed successively with anhydrous ether (3 × 30 mL), dry MeCN (2 × 20 mL), and dried at 60 °C for 24 h under vacuum. Yield: 96%, mp 90 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600 MHz): δ 3.74 (t, 2H, *J* = 6.6 Hz); 3.9 (s, 3H); 4.27 (t, 2H, *J* = 8.2 Hz); 5.18 (s, 1H); 7.79 (d, 2H); 9.24 (s, 1H). Other hydroxyl-Lewis bases were prepared by the same method. 1-(2-hydroxyl-ethyl)-3-methylimidazolium chloride (HEMIMC), yield: 91%, a white solid, mp 86 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600 MHz): δ 3.72 (t, 2H, *J* = 10.3 Hz); 3.89 (s, 3H); 4.26 (t, 2H, *J* = 10.3 Hz); 5.54 (s, 1H); 7.79 (d, 2H); 9.34 (s, 1H). 2-Hydroxyl-ethyl-tributylammonium bromide (HETBAB), yield: 92%, a yellow liquid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600 MHz) δ 0.93 (t, 9H, *J* = 13.4 Hz); 1.31 (m, 6H); 1.64 (m, 6H); 3.27 (t, 6H, *J* = 16.5 Hz); 3.38 (t, 2H, *J* = 9.66 Hz); 3.78 (t, 2H, *J* = 11.4 Hz); 5.26 (s, 1H). 2-Hydroxyl-ethyl-triethylammonium bromide (HETEAB), yield: 98%, a white solid, mp 120 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600 MHz) δ 1.19 (t, 9H, *J* = 14.4 Hz); 3.30 (t, 6H, *J* = 4.8 Hz); 3.34 (q, 6H, *J* = 7.56 Hz); 3.78 (t, 2H, *J* = 4.8 Hz); 5.27 (s, 1H).
43. Cycloaddition procedure for the reaction of propylene oxide (PO) with CO<sub>2</sub>: All the coupling reactions were conducted in a 100 ml stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. A typical reaction was carried out as follows: in the reactor, an appropriate CO<sub>2</sub> (≈1.0 MPa) was added to a mixture of PO (14.0 ml, 0.2 mol) and catalyst (3.2 mmol) at room temperature. Then, the temperature was raised to 125 °C with the addition of CO<sub>2</sub> from a reservoir tank to maintain a constant pressure (2.0 MPa). After the reaction had proceeded for 1.0 h, the reactor was cooled to 5 °C in an ice-water bath, and the remaining CO<sub>2</sub> was removed slowly. The catalyst was separated by distillation under vacuum, and the products were isolated and analyzed by Agilent 6890/5973B GC-MS equipped with a FID detector and a DB-wax using acetophenone as the internal standard.
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