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Effect of hydrogen bond of hydroxyl-functionalized ammonium ionic liquids on cycloaddition of CO_2

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ABSTRACT

A synergistic effect of the hydrogen bond on the cycloaddition of CO_2 and epoxides to form cyclic carbonates was investigated through experimental study and characterization. A highly effective homogeneous system of hydroxyl-functionalized quaternary ammonium ionic liquids with a different number of the hydroxyl group in the cation was developed for the fixation of CO_2 to form cyclic carbonates. A mechanism via the hydrogen bond activation for the cycloaddition was proposed based on both experimental data and modeling. This research enhances the understanding of the promotion of reaction via hydrogen bonding and forms the basis for the rational design of catalytic systems for the fixation of CO_2 into organic compounds.

Carbon dioxide, which has been released annually to the atmosphere at ca. 30,000 Mt,[1] is also an attractive C1 feedstock as it is nontoxic, abundant, and inexpensive. An important application is the fixation of CO_2 with epoxides to yield cyclic carbonates, which are used to produce a wide range of commercial and industrial products, including polar aprotic solvents, intermediates, and electrolytes in lithium-ion batteries. Various catalysts have been developed for the production of cyclic carbonates including metal oxides,[2] alkali metal salts,[3] quaternary onium salts,[4] transition metal complexes,[5] functional organic polymers,[6] and ionic liquids (ILs).[7] Among these catalysts, ILs are demonstrated to be effective and environmentally benign. It is worth mentioning that functionalized ILs are more efficient as a synergistic effect of the combination of the functional groups of cations and anions accelerates the cycloaddition reactions of epoxides.

Recently, synergistic effect of ILs catalytic system has received more and more attention for promoting the cycloaddition reactions of epoxides. Functional groups in catalysts such as hydroxyl groups,[8] amino groups,[9] and carboxylic groups[10] have been widely developed. Hydrogen bond donors (HBD) based on functional groups promote the reaction. The HBD such as cellulose,[11] H_2O,[12] carboxylic acid imidazolium,[13] and hydroxyl-functionalized imidazolium,[14] show a positive influence on the reaction due to the synergistic effect. Specifically the hydroxyl-functionalized ionic liquids (HFILs) have a positive effect on the ring-opening of epoxide and accelerate the reaction as its energy barrier is much lower than that without a hydroxyl group. Much effort was put into investigating the hydroxyl group effect on the reaction. However, details of the hydrogen bond-promoted mechanism were still unclear.

As a part of our continuing efforts on understanding the effect of the hydrogen bond of ILs on promoting the conversion of CO_2 into cyclic carbonates, a series of quaternary ammonium ILs with different number of the hydroxyl group in the cation were synthesized[15] and their activity and reusability toward the coupling of epoxide and CO_2 without any additional co-catalyst and organic solvent were investigated. In this letter, a synergistic effect of the combination of hydroxyl groups of the cation and anion on promoting the cycloaddition reactions of epoxides was discussed. The mechanistic details of the synergistic effect were elucidated by FT-IR and DFT.

Catalyst screening experiments were carried out using propylene oxide (PO) as a model substrate.[16] Reactions were reacted with CO_2 using a variety of ILS under certain reaction conditions without any additional co-catalyst and organic solvent. The effect of hydroxyl groups of catalysts on the cycloaddition is characterized in Table 1. The number of hydroxyl groups in quaternary ammonium ILs varies from 0 to 4. The reaction catalyzed by the tetraethyl ammonium bromide (NEt_4Br) exhibited low activity. When one ethyl group was substituted by the hydroxyethyl (HE) group, the resulting hydroxyethyltriethyl ammonium bromide (NEt_3HEBr)

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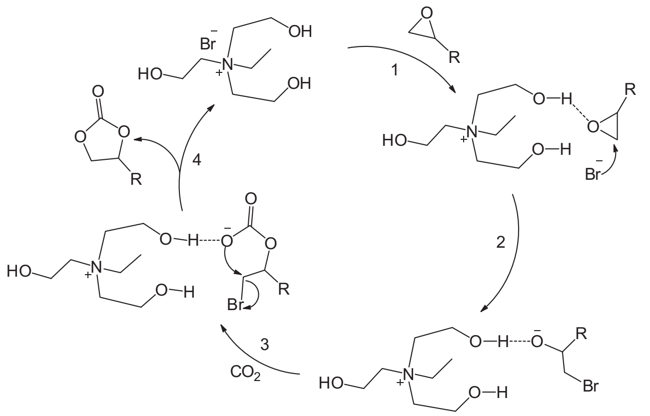
Table 1
Catalyst screen for the synthesis of propylene carbonate[a,b]

Entry	Catalyst	PO conversion (%)	PC yield (%)
1	NEt_4Br	64	63
2	$NEt_3(HE)Br$	82	81
3	$NEt_2(HE)_2Br$	89	88
4	$NEt(HE)_3Br$	93	92
5	$N(HE)_4Br$	78	77
6[c]	$NEt(HE)_3Br$	98	97
7[d]	NEt_4Br/Ethanol	75	74
8[d]	NEt_4Br/Glycol	92	91
9[d]	NEt_4Br/Glycerol	94	93
10[d]	NEt_4Br/propanol	69	68
11[d]	NEt_4Br/1,2-propanediol	77	76
12[d]	NEt_4Br/propanetriol	95	94

[a] Conditions: PO (0.014 mol), catalyst (1 mol %), 120 °C, 1.5 MPa, 1 h.
[b] Results determined by GC and GC–MS.
[c] Reaction temperature: 130 °C.
[d] The molar ratio = 1:1.

showed much higher activity than that of NEt_4Br (entries 1 and 2). With an increase of the number of hydroxyl groups in the cation from 1 to 3, the activity of the catalyst increased steadily. The reaction catalyzed by $NEt(HE)_3Br$ reached 98% PO conversion with 97% PC yield (entry 6). A HBD of the hydroxyl group group, which could remarkably reduce the activation energy, showed a synergistic effect with Br^- and accelerated the ring opening of epoxides.[14] Interestingly, the tetrakis(2-hydroxyethyl)ammonium bromide ($N(HE)_4Br$) with four hydroxyl groups did not show the highest activity among the catalysts employed. In fact the corresponding PO conversion is only 78%, which is lower than that of $NEt_3(HE)Br$ (entry 5, Table 1). It is possible that the additional hydroxyl group groups in the cation of the catalyst prefer to form the hydrogen bond with the halide anion which reduces the nucleophilic behavior of the anion rather than to promote the ring opening of epoxide.[17] Hence, apparently there is an optimal hydrogen bonding effect on enhancing the ring opening of epoxides. Based on the results, the activity order of the functionalized ILs is as follows: $NEt(HE)_3Br > NEt_2(HE)_2Br > NEt_3(HE)Br$ while $N(HE)_4Br > NEt_4Br$ (entries 1–5). In order to further verify that the hydroxyl group can promote the cycloaddition reaction, experiments were carried out with the NEt_4Br catalytic system with ethanol, ethylene glycol, glycerol, propanol, 1,2-propanediol, and propanetriol as co-catalyst (Table 1, entries 7–12). It could be seen from Table 1 that with the increase of the number of hydroxyl groups in the co-catalyst molecule, the activity of catalysts also increased accordingly. The alcohol with one or two hydroxyl groups and a shorter alkyl chain length is more effective in promoting the reaction (Table 1, compare entries 7 and 10; 8 and 11). Thus, a synergistic effect, which polarizes the oxygen atom by hydrogen-bonding of hydroxyl group groups and nucleophilic activation of the carbon atom by anion (Br^-), enhances the catalytic performance of quaternary ammonium ILs.

A possible mechanism for the fixation of CO_2 with epoxide to form cyclic carbonate catalyzed by hydroxyl-functionalized quaternary ammonium ILs was proposed (Scheme 1). Firstly, the epoxide is activated by hydrogen bond interaction, which facilitates the ring opening. The hydrogen bond interaction is studied by a DFT calculation (Fig. S1). The distance of H···O of $N(HE)_3^+$ cation is 0.9702 Å, but the distance of H···O of $N(HE)_3^+$–PO is 1.742 Å due to the hydrogen bond between $N(HE)_3Br^+$ cation and the substrate PO. The hydrogen bond interaction is also confirmed by IR technique. It can be seen in the IR spectra (Fig. 1) that the characteristic sharp absorbance of the hydroxyl groups at 3388 cm^{-1} due to the stretching vibrations of OH groups of $NEt(HE)_3Br$ shifts to 3320 cm^{-1}. That suggests the formation of the hydrogen bond between the OH group and PO. It is important to note that in the DFT study, the frequency of OH groups also shifts from 3534 cm^{-1} to 3212 cm^{-1} due to the hydrogen bond between the $N(HE)_3Br^+$ cation and the substrate PO. Meanwhile, the formation of hydrogen bonds between the OH groups and styrene oxide leads to a shift of the OH group to 3319 cm^{-1} (Fig. S2). Moreover, in IR spectra of catalyst with styrene oxide, the signal of the stretching vibrations of OH groups shifts downfield gradually with an increase of temperature. That also suggests stronger interaction between the OH groups and O atom of styrene oxide (Fig. 2). Then, the epoxide ring opens via a synergistic effect of the combination of the hydroxyl groups and the Br^-, and the CO_2 is inserted. Subsequent cyclization via an intramolecular nucleophilic attack leads to the cyclic carbonate and the catalyst is regenerated.



Scheme 1. Proposed mechanism for the synthesis of propylene carbonate.

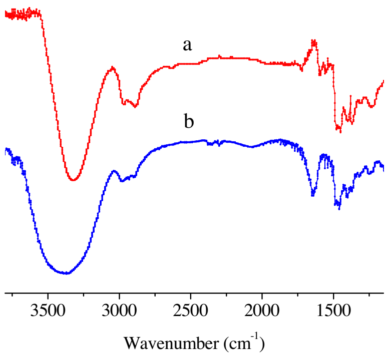


Figure 1. The IR spectrum of $NEt(HE)_3Br$ with and without PO (a) $NEt(HE)_3Br$ with PO, (b) $NEt(HE)_3Br$ without PO.

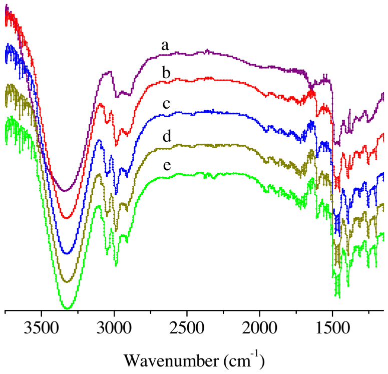


Figure 2. The IR spectra of $NEt(HE)_3Br$ with styrene oxide at different temperatures. (a) 40 °C, (b) 60 °C, (c) 80 °C, (d) 100 °C, (e) 120 °C.

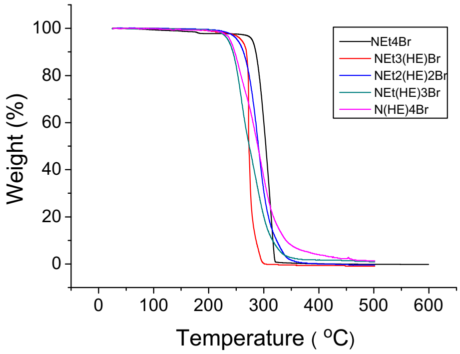


Figure 3. TGA curves of ammonium ionic liquids.

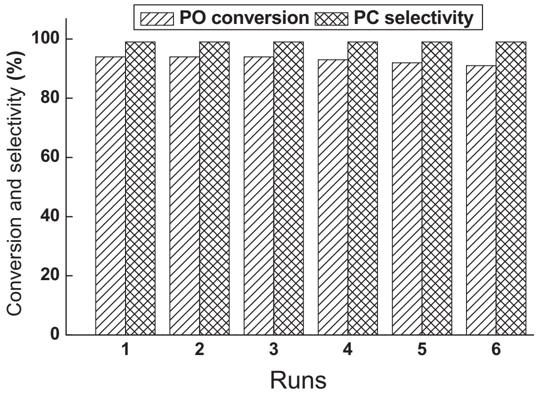
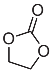
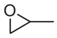
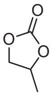
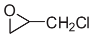
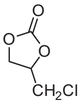
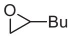
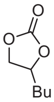
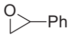
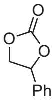
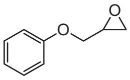
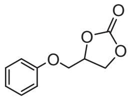
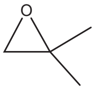
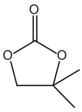


Figure 4. Recycling experiments for NEt(HE)$_3$Br. Conditions: PO (0.285 mol), catalyst (1 mol %), 130 °C, 1.5 MPa, 1 h.

Table 2
Synthesis of other cyclic carbonates catalyzed by NEt(HE)$_3$Br[a]

Entry	Epoxide	Product	*T* (h)	Conv.[b] (%)	Selec.[b] (%)
1	 **1a**	 **2a**	1	99	99
2	 **1b**	 **2b**	1	98	99
3	 **1c**	 **2c**	1	99	99
4	 **1d**	 **2d**	6	98	99
5	 **1e**	 **2e**	2	97	99
6	 **1f**	 **2f**	2	99	99
7	 **1g**	 **2g**	14	91	99

[a] Reaction conditions: epoxides (0.0143 mol), catalyst (1 mol %), CO_2 1.5 MPa, 130 °C.
[b] Determined by GC.

TGA data (Fig. 3) show that the synthesized hydroxyl-functionalized ammonium ILs are all stable up to 200 °C, which is much higher than the reaction temperature of 130 °C. The stability of the different ILs are dependent on the degree of the substitution of the hydroxyl group: NEt$_4$Br > NEt$_3$HEBr > NEt$_2$(HE)$_2$-Br > NEt(HE)$_3$Br, N(HE)$_4$Br.

The recycling experiment of the catalyst was carried out by using PO as the substrate. After each experiment, the catalyst was separated by distillation under vacuum and then recycled directly for the next running experiment. The catalysts were quite stable as no decrease in PC yields was observed even after six recycling runs (Fig. 4).

The highly efficient NEt(HE)$_3$Br catalyst was also found to be effective for conversion of a variety of terminal epoxides to cyclic carbonates under the optimal reaction conditions found for PO. The results are summarized in Table 2. Disubstituted epoxides (entry 7) showed lower activity than mono-substituted terminal epoxides (entries 7 vs 1–6), and required a long time (14 h) to obtain a high yield.

In conclusion, a series of hydroxyl-functionalized quaternary ammonium ILs with a different number of the hydroxyl group in the cation were found to be highly efficient for the coupling of epoxide and CO_2 to form cyclic carbonates without any additional co-catalyst and organic solvent. The catalyst showed reusability and could be recycled six times without loss in activity and selectivity. A synergistic effect, due to the polarization of the oxygen atom via the hydrogen-bonding of OH groups and nucleophilic activation of the carbon atom by the anion, was proposed for promotion of the cycloaddition reactions of CO_2 and epoxides. A proposed mechanism based on both experimental data and modeling provides an increased understanding of the promotional effect of hydrogen bonding on the fixation of CO_2 into organic compounds in ionic liquids.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.01.174.

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15. Typical synthesis procedure of hydroxyl-functionalized ionic liquids: For the synthesis of *N*,*N*,*N*-triethyl-2-hydroxyethanaminium bromide ($NEt_3(HE)Br$), a mixture of triethylamine (0.03 mol), 2-bromoethanol (0.04 mol) and dry toluene (10 mL) was heated at 110 °C for 12 h in a 50 ml single flask with vigorous stirring. Then the mixture was cooled down to room temperature, and a white solid formed rapidly. The resultant crude solid was filtered off, washed with acetone (5×20 ml) and dried at 70 °C for 12 h under vacuum. Yield: 90%, white solid, mp: 123.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ 5.25 (t, J = 5.4 Hz, 1H); 3.76 (t, J = 4.8 Hz, 2H); 3.32 (q, J = 7.2 Hz, 6H); 3.30 (t, J = 5.2 Hz, 2H); 1.17 (t, J = 7.0 Hz, 9H). Anal. Calcd for $NEt_3(HE)Br$: C, 42.49; H, 8.91; N, 6.19. Found: C, 42.41; H, 8.93; N, 6.17. Other hydroxyl-functionalized ionic liquids were prepared by the same method. *N*,*N*-Diethyl-2-hydroxy-*N*-(2-hydroxyethyl)ethanaminium bromide ($NEt_2(HE)_2Br$), Yield: 78%; white solid; 91.8 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.20 (tm, J = 5.0 Hz, 2H), 3.74 (dt, J = 5.4 Hz, J = 5.0 Hz, 4H), 3.23 (m, 8H), 1.21 (t, J = 7.2 Hz, 6H). Anal. Calcd for $NEt_2(HE)_2Br$: C, 39.68; H, 8.32; N, 5.78; Found: C, 39.65; H, 8.35; N, 5.74. *N*-Ethyl-2-hydroxy-*N*,*N*-bis(2-hydroxyethyl)ethanaminium bromide ($NEt(HE)_3Br$), yield: 81%, white solid; 62.8 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.20 (tm, J = 5.0 Hz, 3H), 3.80 (dt, J = 5.4 Hz, J = 5.0 Hz, 6H), 3.51 (q, J = 7.0 Hz, 2H), 3.48 (t, J = 5.4 Hz, 6H), 1.24 (t, J = 7.0 Hz, 3H). Anal. Calcd for $NEt(HE)_3Br$: C, 37.22; H, 7.81; N, 5.43; found: C, 37.02; H, 7.82; N, 5.44. Tetrakis(2-hydroxyethyl)ammonium bromide ($N(HE)_4Br$), Yield: 98%; white solid; 48.7 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.16 (br, 4H), 3.81 (br, 8H), 3.57 (br, 8H), Anal. Calcd for $N(HE)_4Br$: C, 34.3; H, 7.39; N, 5.12. Found: C, 35.05; H, 7.35; N, 5.11.
16. A cycloaddition procedure for the reaction of propylene oxide (PO) with CO_2: the coupling reactions were conducted in a 25 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_2 (1.0 MPa) was added to a mixture of PO (0.014 mol) and catalyst (1 mol %) at room temperature. Then, the temperature was raised to 130 °C with the addition of CO_2 from a reservoir tank to maintain a constant pressure (1.5 MPa). After the reaction had proceeded for 1.0 h, the reactor was cooled to room temperature, and the remaining CO_2 was removed slowly. The recycling experiment of the catalyst was carried out in a 100 ml stainless-steel reactor. The catalyst was separated by distillation under vacuum and then recycled directly for the next running experiment. The products were 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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