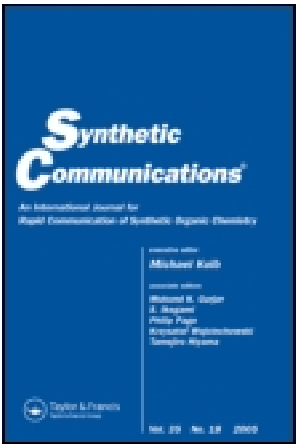

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$ZnBr_2$-Based Choline Chloride Ionic Liquid for Efficient Fixation of CO_2 to Cyclic Carbonate

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$ZnBr_2$-BASED CHOLINE CHLORIDE IONIC LIQUID FOR EFFICIENT FIXATION OF CO_2 TO CYCLIC CARBONATE

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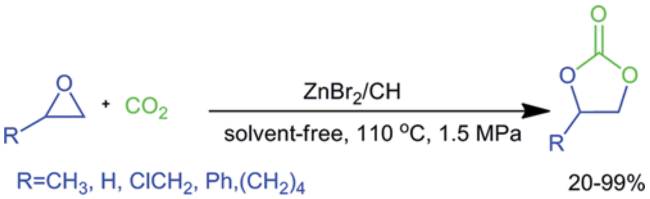
GRAPHICAL ABSTRACT



Abstract *In this work, $ZnBr_2$-based choline chloride (CH) was first investigated to catalyze the synthesis of cyclic carbonates from CO_2 and epoxides under solventless conditions. It was demonstrated that $ZnBr_2$-based CH was very efficient and selective. Under the optimum reaction conditions, 99% yield of propylene carbonate was achieved. The catalyst can be reused five times without loss of catalytic activity. It was proved to be very active in a variety of terminal epoxides with CO_2. In addition, a synergistic catalytic mechanism by Zn^{2+} and -OH was proposed.*

Keywords Carbon dioxide; choline chloride; cycloaddition; epoxide; zinc bromide

INTRODUCTION

As CO_2 is nontoxic, abundant, inexpensive, nonflammable, and highly functional, much attention has been paid to its use as an environmentally benign chemical reagent.[1] One of the applications is the synthesis of cyclic carbonates via cycloaddition of epoxides and CO_2,[2] which have been widely used for various purposes, such as poplar aprotic solvents, intermediates in organic synthesis, monomers for synthesizing polycarbonate, agricultural chemicals, alkylating agents, electrolytic elements of lithium secondary batteries, and chemical ingredients for preparing medicines.[3–6] Moreover, cycloaddition of epoxides and CO_2 are 100% atom-economical reactions.

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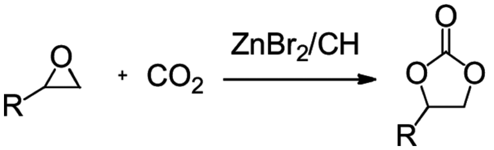


Scheme 1. Cycloaddition of epoxide with CO_2 catalyzed by $ZnBr_2/CH$.

Numerous compounds have already been developed to catalyze these reactions.[7] Heterogeneous catalysts, such as metal oxides[8] and zeolites,[9] suffer from poor activity, rigorous reaction conditions, and poor stability. Although good performance of modified polymers and resins are obtained, the reaction is conducted at longer reaction times under comparative high pressures.[10] Homogeneous catalysts are effective for cyclic carbonate synthesis.[11–23] However, in most cases, organic solvents are used in the reactions over homogeneous catalysts. More important, the procedure of preparing homogeneous catalysts is generally complicated and the cost of catalysts is very high. Therefore, it is desirable to explore a simple, efficient, and available catalyst system for this transformation.

In recent years, ionic liquids (ILs) have received considerable interest because of their unique properties, such as undetectable vapor pressure, wide liquid temperature range, special solubility for many organic or inorganic compounds, and feasibility for designing.[24] On green chemical principles, ILs as catalysts would be composed of biodegradable constituents and exhibit high thermal and chemical stabilities.[25] The bifunctional catalyst based on choline chloride has found great potential in organic synthesis.[26] Recently, bicomponent catalysts, such as CH and urea as well as hexabutylguanidinium salt and zinc bromide,[27] have been reported to efficiently catalyze the synthesis of cyclic carbonates from CO_2 and epoxides. In this respect, the IL composed of Zn^{2+} is probably the most attractive catalyst for CO_2 coupling with epoxides.[28] For example, Zn^{2+} combined with hexabutylguanidinium,[28g] phosphonium,[29] or imidazolium[28g] has shown high catalytic activity. In addition, Zn^{2+}-based CH has been investigated because of its easy preparation, moisture stability, low cost, and biodegradability.[30] Zn^{2+}-based CH has been used in the processes of electrolytic deposition,[31] regiospecific Fischer indole reaction,[32] the protection of carbonyls reaction,[33] and Diels–Alder reaction.[34] To the best of our knowledge, there has no report about this kind of catalyst used for fixation of CO_2 to cyclic carbonate. In this work, we show that $ZnBr_2$-based CH can efficiently catalyze the synthesis of cyclic carbonates from CO_2 and epoxides under solventless condition, and the -OH group of CH plays an important role in the reaction (Scheme 1). In addition, the catalyst can be simply prepared by a combination of CH and Zn^{2+}.

RESULTS AND DISCUSSION

For cycloaddition reaction of CO_2 with epoxide, propylene oxide (PO) was chosen as the standard substrate to investigate the performance of CH with different Lewis acid catalysts. The results are summarized in Table 1. $ZnBr_2$ or CH alone showed very poor activity in the reaction (entries 1 and 2). The behavior of CH with different Lewis acid catalysts varied considerably. The reaction almost did not take place over CH with K^+ or Mg^{2+} (entries 3–5). The yield was unsatisfactory with $CuCl_2 \cdot 2H_2O/CH$, $FeCl_3/CH$, NaCl/CH, and $AlCl_3/CH$ (entries 6–9). However, CH combined with zinc halide showed greater activity than with other metallic halides in accordance with the stronger Lewis acidity of Zn^{2+} (entries 10 and 11). The greatest yield of propylene carbonate (PC) reached 99% over $ZnBr_2$-based CH (entry 11). Furthermore, 92% PC yield could be obtained even with a lower catalyst amount (entry 12). When tetramethylammonium chloride (TMAC) substituted for CH, the corresponding catalyst system showed very poor activity, which indicated that the -OH of CH was crucial for the reaction to proceed smoothly (entry 13).

The performance of $ZnBr_2$-based choline chloride for synthesis of propylene carbonate from CO_2 and propylene is shown in Table 2. The results show that the molar ratio of CH to $ZnBr_2$ has a significant influence on catalytic activity. The yield of PC increased from 31% to 99% with the increase of molar ratios of CH to $ZnBr_2$ from 1 to 5 (entries 1–4), but the yield of PC decreased with the further increase of molar ratio (entry 5). The greatest catalytic activity was obtained when the ratio of CH to $ZnBr_2$ was 5:1. The reaction temperature also has a remarkable effect on the cycloaddition reaction. As the temperature increased from 60 °C to 110 °C, the yield of product increased from 1% up to 99% (entries 6, 7, 8, and 4). However, with further increase of the temperature, the yield of PC decreased from 99% to 93% because of side reactions such as propylene oxide isomerization and polymerization reaction (entries 4 and 9). The results suggested that increasing the reaction time had a positive effect on the PC yield within 60 min. The yield of PC increased sharply with increase of time from 20 min to 60 min (entries 10, 11, and 4). High pressure is dangerous in organic synthesis; however, the reaction proceeded smoothly even under

Table 1. Synthesis of propylene carbonate from CO_2 and propylene oxide catalyzed by CH with different Lewis acid catalysts[a]

Entry	Catalyst	Yield[b] (%)	TOF[c]
1	CH	Trace	Trace
2	$ZnBr_2$	1	5
3	KCl/CH	Trace	Trace
4	KBr/CH	Trace	Trace
5	$MgCl_2 \cdot 6H_2O/CH$	Trace	Trace
6	$CuCl_2 \cdot 2H_2O/CH$	5	25
7	$FeCl_3/CH$	14	70
8	NaCl/CH	21	106
9	$AlCl_3/CH$	33	166
10	$ZnCl_2/CH$	90	451
11	$ZnBr_2/CH$	99	494
12[d]	$ZnBr_2/CH$	92	915
13	$ZnBr_2/TMAC$	1	6

[a] Reaction conditions: PO (140 mmol), CH (1.4 mmol), $ZnBr_2$ (0.28 mmol), CO_2 (1.5 MPa), 110 °C, 60 min.

[b] Isolated yield.

[c] Moles of propylene carbonate produced per mole of catalyst per hour.

[d] $ZnBr_2$ (0.14 mmol).

Table 2. Synthesis of propylene carbonate from CO_2 and propylene oxide catalyzed by $ZnBr_2$-based choline chloride[a]

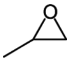
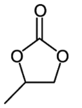
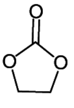
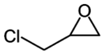
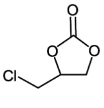
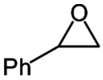
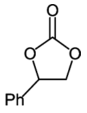
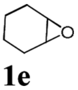
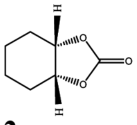
Entry	CH/$ZnBr_2$[b]	Time (min)	Temp. (°C)	Pressure (MPa)	Yield (%)[c]
1	1:1	60	110	1.5	31
2	3:1	60	110	1.5	86
3	4:1	60	110	1.5	91
4	5:1	60	110	1.5	99
5	6:1	60	110	1.5	94
6	1:1	60	60	1.5	1
7	1:1	60	80	1.5	28
8	1:1	60	100	1.5	66
9	1:1	60	120	1.5	95
10	5:1	20	110	1.5	3
11	5:1	40	110	1.5	88
12	5:1	80	110	1.5	97
13	5:1	60	110	2.5	97
14[d]	5:1	60	110	1.5	99
15[e]	5:1	60	110	1.5	99
16[f]	5:1	60	110	1.5	98
17[g]	5:1	60	110	1.5	99
18[h]	5:1	60	110	1.5	99

[a] Reaction conditions: PO (140 mmol) and CH (1.4 mmol).
[b] CH/$ZnBr_2$: molar ratio of CH to $ZnBr_2$.
[c] Isolated yield.
[d] The first run of the catalyst.
[e] The second run of the catalyst.
[f] The third run of the catalyst.
[g] The fourth run of the catalyst.
[h] The fifth run of the catalyst.

pressure as low as 1.5 MPa (entry 4). This can be explained by effects on the concentrations of PO and opening of the oxirane ring.[7,10] At the lower CO_2 pressure, the concentration of PO in the liquid phase was high, which increased the reaction rate.[10] At the same time, lower CO_2 pressure increased the polarity of the reaction medium, resulting in the acceleration of opening the oxirane ring by nucleophilic attack of the catalyst.[7] Therefore, 5:1, 110 °C, 60 min, and 1.5 MPa are the appropriate molar ratio of CH to $ZnBr_2$, temperature, reaction time, and pressure, respectively. To investigate the recycle and reuse of $ZnBr_2$-based CH, the PC and remaining PO were distilled from the product mixture after the reaction, and the remaining catalyst was further used for the next run directly. The catalyst can be repeatedly used five times, and its performance for the fifth run is almost the same as that for the first run (entries 14–18). Because of the good performance of $ZnBr_2$-based choline chloride and simple catalyst system, this system might be used in the industrial process for the manufacture of propylene carbonate.

To survey the applicability of various epoxides to this process, we examined the cycloaddition reactions of other terminal epoxides with CO_2 catalyzed by $ZnBr_2$-based CH. The results are summarized in Table 3. The $ZnBr_2$-based CH catalyst was found to be applicable to a variety of terminal epoxides. The catalyst system

Table 3. Coupling of CO_2 and various epoxides catalyzed by $ZnBr_2$-based choline chloride[a]

Entry	Epoxides	Products	Yield (%)[b]	Selectivity (%)
1	 **1a**	 **2a**	100	99
2	 **1b**	 **2b**	100	99
3	 **1c**	 **2c**	99	98
4[c]	 **1d**	 **2d**	98	86
5[d]	 **1e**	 **2e**	95	20

[a] Reaction condition: epoxide (140 mmol), CH (1.4 mmol), $ZnBr_2$ (0.28 mmol), CO_2 (1.5 MPa), 110 °C, 60 min.

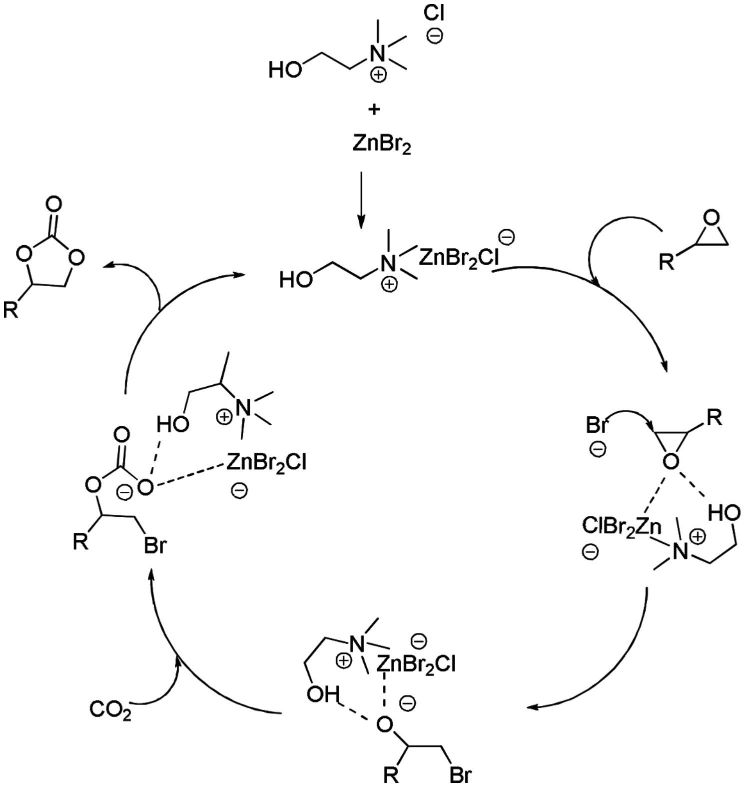
[b] Isolated yield.

[c] 12 h.

[d] 24 h.

provided the corresponding cyclic carbonates in 20–99% yields with excellent selectivity. Propylene oxide (**1a**), ethylene oxide (**1b**), epichlorohydrin (**1c**), and styrene oxide (**1d**) are good substrates to give cyclic carbonates in excellent yields. However, 1,2-cyclohexene oxide (**1e**) exhibited relatively poor activity, due to the greater hindrance of rings.

It has been suggested that the chlorine ion could open the epoxy ring when the ring was activated by formation of hydrogen bonding.[27,35] In our catalyst system, $ZnBr_2$ and CH showed a synergetic effect on promoting the reaction. The tentative mechanism is suggested and shown schematically in Scheme 2. The bromine anion opens the epoxy ring, which is synergistically activated by Zn^{2+} and -OH of CH to give the intermediate. Then, the intermediate reacts with CO_2 to form the corresponding cyclic carbonate and regenerate the catalyst.



Scheme 2. Proposed mechanism for the coupling of epoxides with CO_2 catalyzed by $ZnBr_2$-based CH.

CONCLUSION

A novel catalyst system, $ZnBr_2$-based CH, exhibits excellent catalytic activity for the synthesis of cyclic carbonates from epxides and CO_2. The reaction of the synthesis of PC is carried out under mild condition without any cosolvent. The catalyst system can be reused five times without dropping in yield and selectivity under optimum conditions. In addition, the catalyst system is proven to be excellently active in a variety of terminal epoxides with CO_2, and good yields of cyclic carbonates can be obtained. Furthermore, the catalyst system is simple, economical, and environmentally benign. These characteristics make it an ideal greener catalyst system in terms of potential industrial application in chemical fixation of CO_2.

EXPERIMENTAL

Choline chloride, epichlorohydrin, epoxyethane, $ZnBr_2$, metal chloride, and metal bromide were analytical-reagent grade and obtained from Beijing Chemical Plant. Other epoxides were purchased from Alfa Aesar, and CO_2 with 99.9% purity was purchased from Beijing Bei temperature gas factory.

Coupling Reaction

All reactions were carried out in a 100-mL stainless-steel autoclave equipped with a magnetic stirrer and automatic temperature control system. For a typical reaction, the reactor was charged with the appropriate amounts of catalyst, epoxide, and 1.5 MPa CO_2. The reaction mixture was heated to 110 °C while maintaining the desired CO_2 pressure and reacted for 1 h. After the reaction was completed, the autoclave was cooled to 0 °C in an ice-water bath. The products were isolated and analyzed by gas chromatography (Agilent 6890/5973B) equipped with a RTX-5 capillary column (30 m × 0.25 μm) and a flame ionization detector (FID).

NMR Data for Cyclic Carbonates

The products were also characterized by ^{1}H NMR and ^{13}C NMR spectra, which were recorded on a Varian Mercury Plus 400 spectrometer. Chemical shifts were given as δ values referenced in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard. The structures of the isolated products were also characterized by high-resolution mass spectroscopy (HRMS) as previously reported.[36]

4-Methyl-1,3-dioxolan-2-one (2a). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.49 (d, $J = 6.0$ Hz, 3 H), 4.05 (t, $J = 8.8$ Hz, 1H), 4.60 (t, $J = 8.0$ Hz, 1H), 4.86–4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 400 MHz): 18.95, 70.46, 73.51, 154.95 (C=O). HRMS calcd. for $C_4H_6O_3$: 102.0316; found: 102.0316.

1,3-Dioxolan-2-one (2b). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.2 (t, $J =$ 10 Hz, 4H); ^{13}C NMR ($CDCl_3$, TMS, 400 MHz): 63.3, 155 (C=O). HRMS calcd. for $C_3H_4O_3$: 88.0160; found: 88.0160.

4-Chloromethyl-1,3-dioxolan-2-one(2c). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.490 (d, $J = 6.0$ Hz, 3H), 4.05 (t, $J = 8.4$ Hz, 1H), 4.60 (t, $J = 8.0$ Hz, 1H), 4.86–4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 400 MHz): 18.95, 70.46, 73.51, 154.95 (C=O). HRMS calcd. for $C_4H_5ClO_3$: 135.9927; found: 135.9927.

4-Phenyl-1,3-dioxolan-2-one(2d). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.34 (t, $J = 8.4$ Hz, 1H), 4.80 (t, $J = 8.4$ Hz, 1H), 5.68 (t, $J = 8.0$ Hz, 1H), 7.35–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$, TMS, 400 MHz): 71.10, 77.92, 125.81, 129.12, 129.63, 135.70, 154.81 (C=O). HRMS calcd. for $C_9H_8O_3$: 216.1150; found: 216.1150.

4,5-Tetramethylene-1,3-dioxolan-2-one (2e). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.80–1.86 (m, 2H), 1.97–2.05 (m, 2H), 2.28 (d, $J = 4.8$ Hz, 4H), 5.06–5.11 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS, 400 MHz): 19.00, 26.61, 75.65, 155.27 (C=O). HRMS calcd. for $C_7H_{10}O_3$: 142.0630; found: 142.0630.

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