

Cycloaddition of carbon dioxide to epichlorohydrin using ionic liquid as a catalyst

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Abstract—The cycloaddition of carbon dioxide to epichlorohydrin was performed without any solvent in the presence of ionic liquid as catalyst. 1-Alkyl-3-methyl imidazolium salts of different alkyl group (C_2 , C_4 , C_6 , C_8) and anions (Cl^- , BF_4^- , Br^- , PF_6^-) were used for this reaction carried out in a batch autoclave reactor. The conversion of epichlorohydrin was affected by the structure of the imidazolium salt ionic liquid; the one with the cation of longer alkyl chain length and with more nucleophilic anion showed better reactivity. The conversion of epichlorohydrin increased as the temperature increased from 60 °C to 140 °C. It also increased with increasing carbon dioxide pressure probably due to the increase of the absorption of carbon dioxide into the mixture of epichlorohydrin and the ionic liquid. Zinc bromide was also tested for its use as a cocatalyst in this reaction.

Key words: Cycloaddition, Epichlorohydrin, Ionic Liquid, Carbon Dioxide

INTRODUCTION

Carbon dioxide (CO_2) is the most abundant waste produced by human activities and one of the greenhouse gases. In order to prevent the risky reinforcement of the greenhouse effect, the accumulation of CO_2 in the atmosphere should be controlled by removing it from industrial emissions. On the other hand, CO_2 is recognized to be a naturally abundant, cheap, recyclable and non-toxic carbon source that can sometimes replace toxic chemicals such as phosgene, isocyanates or carbon monoxide [1-4]. Since Russia ratified the Kyoto Protocol in 2004, research in CO_2 recovery and sequestration has attracted public attention across a variety of industrial fields. Under these circumstances, chemical fixation of CO_2 becomes more and more important from the ecological and economic points of view. The synthesis of cyclic carbonate via cycloaddition of CO_2 to epoxide is one of the effective routes of CO_2 chemical fixation. Cyclic carbonates have found extensive use as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc. [5,6].

The synthesis of cyclic carbonates from CO_2 and epoxides has been applied in industrial scale and many excellent reviews in different periods contributed by Rokicki [7], Super [8], Darensbourg [1,9], Coates [10] and Sugimoto [11] on the catalyst development and the reaction mechanisms have described this topic well. However, the activity, stability and recovery of catalysts still remain to be improved [12].

Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [13] due to their

particular properties, especially with the emergence of the *N,N*-di-alkylimidazolium cation derivatives [14]. Both the cationic and the anionic partners can be easily varied, so that these ionic liquid solvents can be designed for particular applications or for particular sets of properties [15]. Room temperature ionic liquids have negligible vapor pressure, excellent thermal stability and special characteristics in comparison with conventional organic and inorganic solvents. Many reactions catalyzed with ionic liquids and showing high performance have been reported [16,17]. In particular, ionic liquids based on imidazolium cations and chloroaluminate anions, such as 1-butyl-3-methylimidazolium aluminium chloride (BMImCl/ $AlCl_3$), have attracted growing interest in the last few years [18,19]. More recently, propylene carbonate has been synthesized from CO_2 and propylene oxide with 1-butyl-3-methylimidazolium (BMIm) salt ionic liquid [13].

In the present work, 1-alkyl-3-methylimidazolium salt ionic liquids of different alkyl groups and different anions were used to investigate the catalytic role of the ionic liquid in the cycloaddition of carbon dioxide to epichlorohydrin (EPCH). The effects of reaction temperature, carbon dioxide pressure, and cocatalyst on this reaction are also discussed.

EXPERIMENTAL

Epichlorohydrin (purity; 99%) was purchased from Aldrich and distilled before use. Ionic liquids based on 1-ethyl-3-methylimidazolium (EMIm), 1-butyl-3-methylimidazolium (BMIm) and 1-hexyl-3-methylimidazolium (HMIm) with different anions such as Cl^- , BF_4^- , PF_6^- were prepared according to the procedures reported previously. The purities of all the ionic liquids were over 96% and the carbon dioxide (purity; 99.99%) was used without further purification.

The synthesis of cyclic carbonate from EPCH and CO_2 using ionic liquid was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical batch operation, ionic liquid (2 mmol) and EPCH (5 mL) were charged into the reactor without

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solvent, and then purged several times with CO₂. The reactor was then pressurized with CO₂ to a preset pressure at room temperature. The reactor was heated to a desired temperature, and then the reaction was started by stirring the solution at 300 rpm. The reactor pressure increased about 34–103 kPa depending on the reaction temperature due to vapor pressure of the reactants.

The product was analyzed by a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-5, 5% phenyl methyl siloxane). The identification of the five membered cyclic carbonates was performed by React-IR (ASI Model 1000, KBr).

RESULTS AND DISCUSSIONS

The cyclic carbonate was synthesized from epichlorohydrin and carbon dioxide by using various ionic liquid catalysts under carbon dioxide pressure as shown in Scheme 1. The formation of the five-membered cyclic carbonate was characterized by IR spectroscopy. Comparing the relative intensities of the two carbonyl bands at 1,750 cm⁻¹ (linear carbonate) and 1,800 cm⁻¹ (cyclic carbonate) in the IR spectrum, the amount of polycarbonate was estimated to be less than 1%.

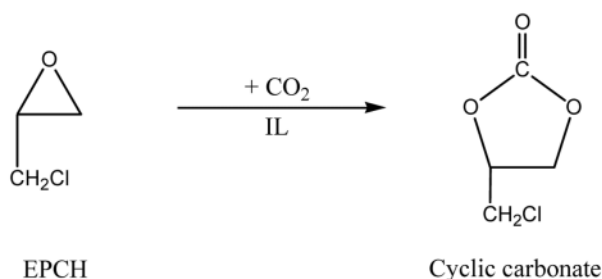
The catalytic activity of ionic liquids usually depends on the corresponding catalyst cation and counter anion [20,21]. In order to understand the effects of cation structure on the conversion of EPCH, 1-alkyl-3-methylimidazolium chloride of different alkyl groups (ethyl, butyl, hexyl, octyl) were used at 80 °C under CO₂ pressure of 928 kPa for 6 h. Table 1 summarizes the effects of ionic liquid structure on the conversion of EPCH. The selectivity of the five membered cyclic carbonate was near to 100% because there was a negligible

amount of byproducts such as polycarbonate and homopolymer of EPCH.

The EPCH conversion increased as the size of the cation of ionic liquids increased from EMIm⁺<BMIm⁺<HMIm⁺<OMImCl⁺. The rate determining step of the epoxide-CO₂ reaction involves nucleophilic attack of the chloride anion to EPCH as shown in Scheme 2 [22]. Bulky ionic liquids, having longer distance between cation and anion, may be considered to have higher anion activation ability. This explains why they are more effective in nucleophilic attack of the anion to the oxirane ring of EPCH. The bulkiness of the alkyl imidazolium cation forces the chloride ion away from the cation, and this weaker electrostatic interaction would render the anion more nucleophilic [22]. Starks et al. [23] also reported that bulkier quaternary ammonium salt had higher anion activation ability due to the longer distance between cation and anion. For example, (C₄H₉)N⁺...Br⁻ (d=62.8 nm) can have reactivity of four orders of magnitude higher than Na⁺...Br⁻ (d=28.5 nm) although the difference in cation-anion interionic distances for the two ion pairs is only about 34.3 nm. The increase in the solubilities of CO₂ and EPCH in ionic liquid with lengthening alkyl chain of the ionic liquid could also be a reason for the increase of EPCH conversion. Kawanami et al. [24] also reported the increase of reactivity when the alkyl chain length increased from C₂ to C₈ in 1-alkyl-3-methylimidazolium tetrafluoroborate (C_xMIImBF₄) for the synthesis of propylene carbonate using a high pressure CO₂-ionic liquid system.

Ionic liquids with different anions (Cl⁻, BF₄⁻, Br⁻, PF₆⁻) were also tested for the addition of CO₂ to EPCH at 80 °C. The EPCH conversions of BMIm ionic liquid with BF₄⁻ and PF₆⁻ were very low at 80 °C. The conversion of EPCH increased in the order of PF₆⁻<BF₄⁻<Br⁻<Cl⁻, which is consistent with the order of the nucleophilicity of the anions. More nucleophilic anion will more easily attack the epoxide ring to form reaction intermediate shown in Scheme 2.

Table 2 lists the conversion of EPCH at different reaction tem-



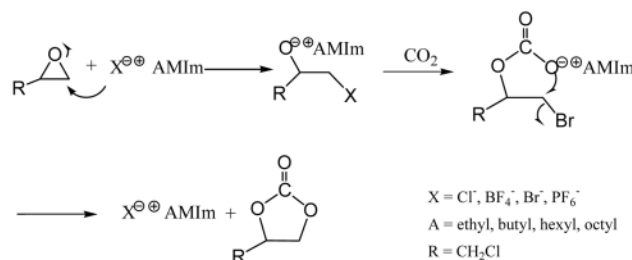
Scheme 1. Synthesis of cyclic carbonate from EPCH and CO₂.

Table 1. Effects of structure of ionic liquid on the conversion of EPCH

Run	Catalyst	Temp (°C)	Time (h)	Pressure (kPa) ^a	Conversion (%)
1	EMImCl	80	6	928	30.6
2	BMImCl	80	6	928	33.6
3	HMImCl	80	6	928	41.3
4	OMImCl	80	6	928	42.5
5	BMImBr	80	6	928	21.8
6	BMImBF ₄	80	6	928	9.2
7	BMImPF ₆	80	6	928	8.0

Reaction condition: EPCH=40 mmol, catalyst=2 mmol.

^aPressure of carbon dioxide at 25 °C.



Scheme 2. Reaction steps for the cycloaddition of CO₂ to EPCH.

Table 2. Effects of reaction temperatures and CO₂ pressure on the conversion of EPCH

Run	Catalyst	Temp (°C)	Time (h)	Pressure (kPa) ^a	Conversion (%)
8	HMImCl	60	6	928	21.5
3	HMImCl	80	6	928	41.3
9	HMImCl	100	6	928	52.7
10	HMImCl	120	6	928	61.4
11	HMImCl	140	6	928	79.0
2	BMImCl	80	6	928	32.6
12	BMImCl	80	6	464	24.3

perature and carbon dioxide pressure. The EPCH conversion increased with increasing reaction temperature from 60 to 140 °C. It means that there is no severe decomposition of the cyclic carbonate to EPCH and CO₂ even at 140 °C. This confirms the advantage of high operation temperature of the ionic liquid compared to other solvents.

The effects of pressure in the addition of CO₂ to EPCH are compared in Runs 2 and 12. The conversion of EPCH increased with increasing carbon dioxide pressure, probably due to the increase of the absorption of CO₂ in the solution of EPCH and ionic liquid. Zhang et al. [25] reported the increase of the solubilities of CO₂ in BMImPF₆ with increasing the pressure of CO₂.

Table 3 summarizes the conversion of EPCH at different reaction time. When the reaction time increased from 6 to 48 h, the EPCH conversion increased. Table 4 lists the conversion of EPCH in the presence of ZnBr₂ as a cocatalyst with BMImCl. No activity was observed with ZnBr₂ alone (Run 16). The combination of ZnBr₂ with the ionic liquid (Run 17-19) exhibited a marked increase in reactivity compared to Runs 2-4, respectively. This may originate from the cooperation action of both the acidic site (Zn) for epoxide activation and basic site (Cl⁻ in ionic liquid and/or Br⁻ in ZnBr₂) for CO₂ activation as proposed previously for several catalyst systems [26,27]. Sun et al. [28] also reported the effect of ZnBr₂ as a cocatalyst for the synthesis of styrene carbonate from styrene oxide and carbon dioxide. The role of ZnBr₂ cocatalyst on the reaction of EPCH and CO₂ can be explained: At initiation stage of the Scheme 2, PGE is coordinated with the Lewis acid site Zn to form the adduct of the metal-epoxide complex (shown in Scheme 3). Then the

Cl⁻ anion of the ionic liquid makes a nucleophilic attack on the less hindered carbon atom of the coordinated epoxide followed by ring opening. Next, CO₂ is coordinated to the complex through interactions with Br⁻ and O⁻. Fuwei et al. [29] also reported an increase of the yield of propylene carbonate from propylene oxide and CO₂ with the use of ZnBr₂ cocatalyst.

CONCLUSIONS

Carbon dioxide can be effectively added to the epoxide ring of epichlorohydrin (EPCH) to produce the corresponding five membered cyclic carbonate without using any solvent. The order of the EPCH conversion increased as the size of the cation of ionic liquids increased from EMIm⁺<BMIm⁺<HMIm⁺<OMImCl⁺. Imidazolium salts, having longer distances between cations and anions, seem to exhibit higher activity in activating anions. The catalytic activity also increased with increasing the nucleophilicity of the anion of BMIm⁺X⁻ ionic liquid: PF₆⁻<BF₄⁻<Br⁻<Cl⁻. Higher carbon dioxide pressure enhanced the EPCH conversion due to the increase of the absorption of carbon dioxide in the solution of ionic liquid and EPCH. The presence of Lewis acidic compound ZnBr₂ as a cocatalyst highly enhanced the activity of ionic liquid for the cyclic carbonate synthesis.

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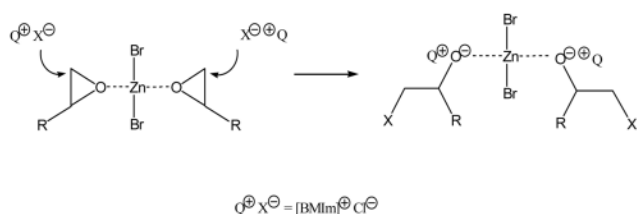
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Table 3. Conversion of EPCH at different reaction times at 80 °C with BMImCl

Run	Catalyst	Temp (°C)	Time (h)	Pressure (kPa) ^a	Conversion (%)
2	BMImCl	80	6	928	33.6
13	BMImCl	80	12	928	41.0
14	BMImCl	80	24	928	54.8
15	BMImCl	80	48	928	64.4

Table 4. Catalytic activity of the ionic liquid and ZnBr₂ at 80 °C

Run	Catalyst	Temp (°C)	Time (h)	Pressure (kPa) ^a	Conversion (%)
16	ZnBr ₂	80	6	928	-
17	BMImCl+ZnBr ₂	80	6	928	54.5
18	HMImCl+ZnBr ₂	80	6	928	57.1
19	OMImCl+ZnBr ₂	80	6	928	58.7



Scheme 3. Coordination of EPCH with ZnBr₂.

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