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ScienceDirect
Catalysis Today 131 (2008) 130–134
CATALYSIS TODAY
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Synthesis of cyclic carbonate from vinyl cyclohexene oxide and CO_2 using ionic liquids as catalysts

Eun-Ha Lee, Ji-Yun Ahn, Manju Mamparambath Dharman, Dae-Won Park *, Sang-Wook Park, Il Kim

Division of Chemical Engineering, Pusan National University, Jangjeon-dong, Kumjeong-gu, Busan 609-735 Republic of Korea

Abstract

Synthesis of cyclic carbonate from 4-vinyl-1-cyclohexene-1,2-epoxide (VCHO) and carbon dioxide was investigated without using any solvent in the presence of ionic liquid as a catalyst. Ionic liquids based on 1-alkylmethylimidazolium salts of different alkyl groups (ethyl, butyl, hexyl, octyl) and different anions (Cl^-, BF_4^-, PF_6^-) were used as catalysts. The conversion of VCHO was affected by the structure of the imidazolium salt ionic liquids; the ones with the cations of bulkier alkyl chain length and with more nucleophilic anion showed better reactivity. Reaction temperature, carbon dioxide pressure, and zinc halide cocatalyst enhanced the addition of CO_2 to VCHO. Semi-batch operation with continuous supply of carbon dioxide showed higher VCHO conversion than batch operation did.

Keywords: Vinyl cyclohexene oxide; Carbon dioxide; Cyclic carbonate; Ionic liquid

1. Introduction

Carbon dioxide, which is considered to be a "green house gas", has received much attention for industrial usage since demand for replacement of chlorinated solvents emerged in the 1980s. Meanwhile, CO_2 continues to be utilized as a feedstock for the production of organic products. The reactions of carbon dioxide with oxiranes leading to five-membered cyclic carbonates are well-known among many examples.

Cyclic carbonates are utilized industrially as polar aprotic solvents, substrates for small molecule synthesis, additives, antifoam agents for antifreeze, and plasticizers [1,2]. The five-membered ring cyclic carbonates (1,3-dioxolan-2-ones) are generally incapable of ring opening polymerization due to their thermodynamic stability, but do undergo polymerization with partial loss of CO_2 to yield macromolecules with both ether and carbonate linkages [3]. Due to such uses, a number of syntheses of cyclic carbonates and polycarbonates have been described over the last 30 years [4–9].

The synthesis of cyclic carbonates from the reaction of CO_2 with oxirane has been performed using Lewis acids, transition-metal complexes, and organometallic compounds as catalysts under high pressure [10]. Some articles reported the synthesis of five-membered cyclic carbonates under mild conditions in the presence of metal halides or quaternary ammonium salts [10–12].

In our previous works, we reported the use of soluble or immobilized quaternary ammonium salts as catalysts in the cycloaddition of carbon dioxide to epoxides such as glycidyl methacrylate [13–15], vinyl glycidyl ether [16], and phenyl glycidyl ether [17].

Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [18]. 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 [19]. In particular, ionic liquids based on imidazolium cations have attracted growing interest in the last few years [20–22].

In the present work, 1-alkyl-3-methylimidazolium salt ionic liquids of different alkyl groups and different anions were used

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* Corresponding author. Tel.: +82 51 510 2399; fax: +82 51 512 8563.
E-mail address: dwpark@pusan.ac.kr (D.-W. Park).

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doi:10.1016/j.cattod.2007.10.012

to understand the catalytic role of the ionic liquids. The effects of reaction temperature and carbon dioxide pressure were studied for the cycloaddition of carbon dioxide to 4-vinyl-1-cyclohexene-1,2-epoxide (VCHO). In order to study cooperative effects of the mixture of the ionic liquid and cocatalyst, zinc halide was selected as a cocatalyst.

2. Experimental

2.1. Material

Ionic liquids based on 1-*n*-ethyl-3-methylimidazolium (EMIm), 1-*n*-butyl-3-methylimidazolium (BMIm), 1-*n*-hexyl-3-methylimidazolium (HMIm) and 1-*n*-octyl-3-methylimidazolium (OMIm) with different anions such as Cl^-, Br^-, BF_4^-, PF_6^- were prepared according to the procedures reported previously. The purities of all ionic liquids were over 96%. 4-Vinyl-1-cyclohexene-1,2-epoxide (Aldrich, 98%) and carbon dioxide (purity; 99.99%) were used without further purification.

2.2. Addition reaction of VCHO with carbon dioxide

The synthesis of cyclic carbonate from vinyl cyclohexene oxide (VCHO) 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 VCHO (38.3 mmol) were charged into the reactor without solvent, and then purged several times with CO_2. The reactor was then pressurized with CO_2 to a preset pressure, 0.58–3.82 MPa, 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 0.03–0.10 MPa depending on the reaction temperature due to vapor pressure of the reactants. In semi-batch operations, the reaction pressure was maintained constant by a back-pressure regulator with a direct connection to high pressure CO_2 supply at the entrance of the reactor.

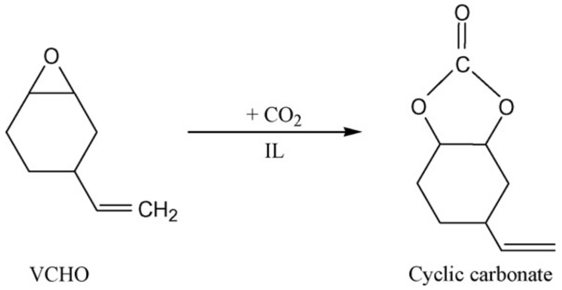
2.3. Analysis of cyclic carbonate

In the reactor, there exists VCHO, cyclic carbonate, ionic liquid and absorbed CO_2 in the liquid solution and gaseous CO_2 under pressure. After reaction the reactor was depressurized at low temperature, then the liquid product was analyzed by a gas chromatograph (HP 6890N) equipped with a FID and a capillary column (HP-5, 5% phenyl methyl siloxane). The identification of the five-membered cyclic carbonates was performed by FT-IR (ASI Model 1000, KBr).

3. Results and discussion

The synthesis of cyclic carbonate from VCHO and CO_2 was carried out using various ionic liquids as shown in Scheme 1.

The formation of the five-membered cyclic carbonate was characterized by IR spectroscopy. By comparison of the relative intensity of the two carbonyl bands at 1750 cm^{-1} (linear carbonate) and 1800 cm^{-1} (cyclic carbonate) in the IR spectrum, the amount of polycarbonate was estimated to be less than 2 %.



Scheme 1. Synthesis of cyclic carbonate from VCHO and CO_2.

3.1. Effects of ionic liquid structure

In order to understand the effects of cation structure on the conversion of VCHO, 1-alkyl-3-methylimidazolium chloride of different alkyl groups (ethyl, butyl, hexyl, octyl) were used at 80 °C under CO_2 pressure of 1.07 MPa for 6 h. Table 1 summarizes the effects of ionic liquid structure on the conversion of VCHO. The selectivity of the five-membered cyclic carbonate was near to 100% because there was negligible amount of byproducts such as polycarbonate and homopolymer of VCHO. Therefore, the yields were very close to the conversion data.

The VCHO conversion increased as the size of the cation of the imidazolium chloride ionic liquids increased from $EMIm^+ < BMIm^+ < HMIm^+ < OMIm^+$. OMImCl showed VCHO conversion of 48.0% at 140 °C after 6 h, which corresponds to a TOF [mol VCHO consumed/(mol catalyst h)] of 1.53 h^{-1}. The rate determining step of the epoxide–CO_2 reaction involves nucleophilic attack of the chloride anion to VCHO as shown in Scheme 2 [23]. Bulky ionic liquids, having longer distance between cation and anion, may be considered to have higher anion activation ability. Therefore, they are more

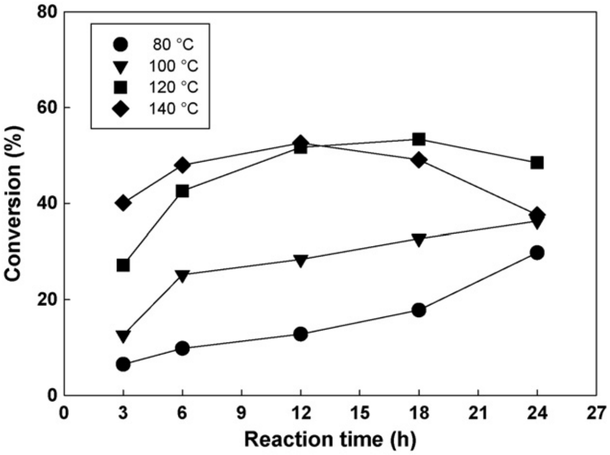


Fig. 1. Conversion of VCHO as a function of reaction time at different temperatures (VCHO = 38.3 mmol, OMImCl = 2 mmol, CO_2 pressure (25 °C) = 1.07 MPa).

Table 1
Catalytic activities of ionic liquid in the cycloaddition of carbon dioxide to VCHO

Run	Ionic liquid	Temperature (°C)	Conversion (%)[a]	Yield (%)[b]
1	EMImCl	80	5.1	5.1
2	BMImCl	80	7.9	7.9
3	HMImCl	80	9.3	9.3
4	OMImCl	80	9.8	9.8
5	EMImCl	140	14.8	14.8
6	BMImCl	140	25.6	25.6
7	HMImCl	140	40.3	40.3
8	OMImCl	140	48.0	48.0
9	$BMImBF_4$	80	6.7	6.7
10	$BMImPF_6$	80	3.3	3.3

Synthesis conditions: VCHO = 5 mL (38.3 mmol), catalyst = 2 mmol, batch operation, CO_2 pressure (25 °C) = 1.07 MPa, reaction time = 6 h.

[a] Conversion is defined on the basis of VCHO.

[b] Yield of the cyclic carbonate.

Table 2
Effect of temperature on the conversion of VCHO

Run	Ionic liquid	Temperature (°C)	Pressure (MPa)	Conversion (%)	Yield (%)
11	OMImCl	60	1.07[a]	6.0	6.0
4	OMImCl	80	1.07[a]	9.8	9.8
12	OMImCl	100	1.07[a]	25.2	25.1
13	OMImCl	120	1.07[a]	42.6	42.1
14	OMImCl	140	1.07[a]	48.0	48.0
15	OMImCl	160	1.07[a]	51.1	50.5
16	OMImCl	60	1.07[b]	10.1	10.0
17	OMImCl	80	1.07[b]	13.8	13.5
18	OMImCl	100	1.07[b]	27.2	27.1
19	OMImCl	120	1.07[b]	47.7	47.4
20	OMImCl	140	1.07[b]	62.7	62.3

Synthesis conditions: VCHO = 5 mL (38.3 mmol), catalyst = 2 mmol, reaction time = 6 h.

[a] Initial pressure of carbon dioxide at 25 °C.

[b] Semi-batch operation with supply of CO_2 using a backpressure regulator.

effective in nucleophilic attack of the anion to the oxirane ring of VCHO. 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 [23].

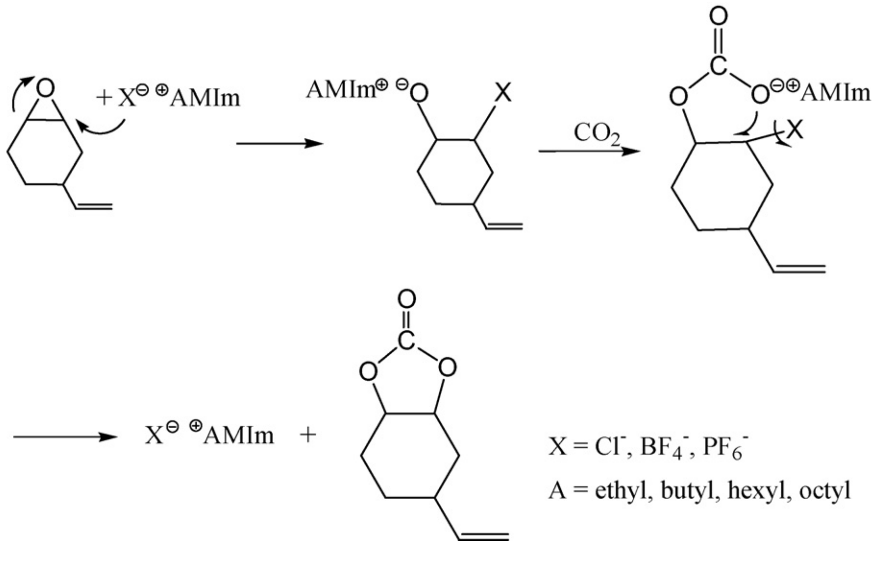
The increase in the solubilities of CO_2 and VCHO in ionic liquid with lengthening alkyl chain of the ionic liquid could also be a reason of the increase of VCHO conversion. Kawanami et al. [24] also reported the increase of reactivity when the alkyl chain length increased from C_2 to C_8 in 1-alkyl-3-methylimidazolium tetrafluoroborate (C_xMImBF_4) for the synthesis of propylene carbonate using a high pressure CO_2–ionic liquid system.

Ionic liquids with different anions (Cl^-, BF_4^-, PF_6^-) were also tested for the addition of CO_2 to VCHO at 80 °C. The conversion of VCHO increased in the order of $PF_6^- < BF_4^- < Cl^-$, 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.

3.2. Effect of temperature and reaction time

Table 2 shows the effect of temperature on the conversion of VCHO after 6 h of reaction using OMImCl catalyst. The conversion increased as the temperature increased from 60 to 160 °C. It means that there is no severe decomposition of the cyclic carbonate to VCHO and CO_2 even at 160 °C during 6 h of reaction. Semi-batch operation shown in Runs 16–20 also exhibited increase of VCHO conversion with increasing temperature. It can be observed that semi-batch operation showed higher conversion of VCHO than the corresponding batch operation.

Fig. 1 shows the variation of VCHO conversion as a function of reaction time with OMImCl catalyst at different reaction temperatures. Below 100 °C, the VCHO conversion increased



Scheme 2. Reaction steps for the synthesis of cyclic carbonate.

continuously from 3 to 24 h of reaction. However, the VCHO conversion showed maximum at higher temperatures (18 h at 120 °C, 12 h at 140 °C). The VCHO conversion at 140 °C after 24 h was lower than that at 120 °C after 24 h. Therefore, one can conclude that the cyclic carbonate can be decomposed to VCHO and CO_2 at long reaction time and at high temperature.

3.3. Effects of carbon dioxide pressure

Table 3 lists the VCHO conversion at 80 °C under different CO_2 pressure using OMImCl catalyst. The VCHO conversion increased as CO_2 pressure increased from atmosphere to 3.82 MPa. High CO_2 pressure could enhance the absorption of CO_2 in the solution of VCHO and OMImCl. Zhang et al. [25] reported the increase of the solubility of CO_2 in $BMImPF_6$ with increasing the pressure of CO_2. It is also reported, in the CO_2/cyclohexne oxide coupling reaction catalyzed by chromium salen complexes, that high CO_2 pressure increased turnover number of the reaction [26]. They explained that the copolymer production increased due to the increase of the amount of adsorbed CO_2 over the pressure range where Henry's law is applicable.

Comparing the results of batch and semi-batch reactor system shown in Table 2, one can see that the semi-batch operations in Runs 16–20 exhibited higher conversions than the corresponding batch operations, Run 4 and Runs 11–14, respectively. The carbon dioxide pressure can be maintained high during its reaction with VCHO in the semi-batch operation. However, in batch operation the carbon dioxide pressure decreased continuously due to its consumption during the reaction.

3.4. Effects of zinc bromide cocatalyst

Table 4 shows the effect of zinc halide cocatalyst on the cyclcoaddition of CO_2 to VCHO. $ZnBr_2$ alone showed no activity for this reaction (Run 25). All the mixture of zinc halide with HMImCl in Runs 27–32 at 140 °C showed an enhanced effect in VCHO conversion compared to the HMImCl itself (Run 26). The VCHO conversion of the mixed catalyst increased in the sequence $ZnF_2 < ZnCl_2 < ZnBr_2$. The nucleophilicity of the halide anions is in the order $F^- < Cl^- < Br^-$. Therefore, more nucleophilic anion could increase the interaction of Br^- and carbon atom of CO_2.

Table 3
Effect of CO_2 pressure on the conversion of VCHO

Run	Ionic liquid	Temperature (°C)	Pressure (MPa)[a]	Conversion (%)	Yield (%)
21	OMImCl	80	Atmosphere	1.6	1.6
22	OMImCl	80	0.58	4.9	4.9
4	OMImCl	80	1.07	9.8	9.8
23	OMImCl	80	2.44	12.0	11.8
24	OMImCl	80	3.82	13.7	13.4

Synthesis conditions: VCHO = 5 mL (38.3 mmol), catalyst = 2 mmol, batch operation, reaction time = 6 h.

[a] Initial pressure of carbon dioxide at 25 °C.

Table 4
Effect of zinc bromide cocatalyst on the cycloaddition of CO_2 to VCHO

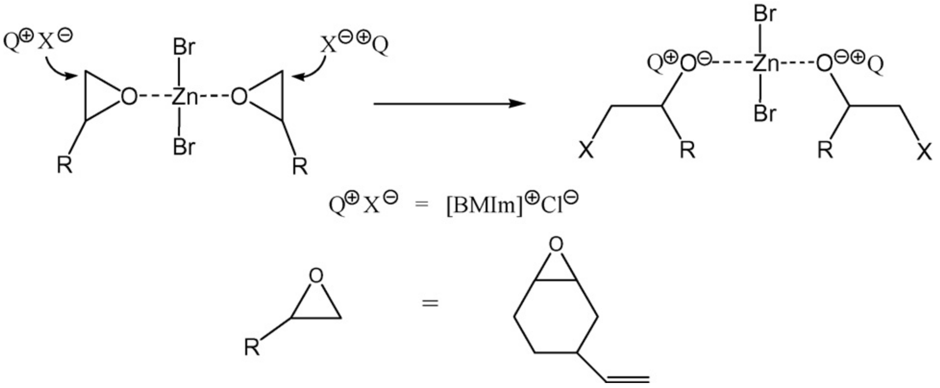
Run	Ionic liquid (mmol)	Cocatalyst (mmol)	Temperature (°C)	Conversion (%)	Yield (%)
25	–	$ZnBr_2$	140	–	–
26	HMImCl(1)	–	140	24.3	23.7
27	HMImCl(1)	$ZnBr_2$(1)	140	41.3	40.3
28	HMImCl(1)	$ZnCl_2$(1)	140	34.2	33.8
29	HMImCl(1)	ZnF_2(1)	140	28.8	28.3
30	HMImCl(2)	$ZnBr_2$(1)	140	54.5	53.1
31	HMImCl(4)	$ZnBr_2$(1)	140	53.9	52.8
32	HMImCl(1)	$ZnBr_2$(2)	140	42.5	42.4
33	HMImCl(1)	$ZnBr_2$(1)	80	13.3	13.2
34	HMImCl(2)	$ZnBr_2$(1)	80	16.6	16.4
35	EMImCl(1)	–	140	9.5	9.5
36	EMImCl(1)	$ZnBr_2$(1)	140	20.3	20.0
37	BMImCl(1)	–	140	14.5	14.1
38	BMImCl(1)	$ZnBr_2$(1)	140	28.9	28.4
39	BMImBr(1)	–	140	18.7	18.5
40	BMImBr(1)	$ZnBr_2$(1)	140	35.6	35.1

Synthesis conditions: VCHO = 5 mL (38.3 mmol), batch operation, CO_2 pressure (25 °C) = 1.07 MPa, reaction time = 6 h.

The increased activity of BMImCl with $ZnBr_2$ may originate from the cooperative action of both the acidic site (Zn) for epoxide activation and basic site (Cl^- in BMImCl and/or Br^- in $ZnBr_2$) for CO_2 activation, as reported previously by Sun et al. [27] for the synthesis of styrene carbonate from styrene oxide and carbon dioxide. The role of $ZnBr_2$ cocatalyst on the addition reaction of CO_2 and VCHO can be explained: At initiation stage of the reaction, VCHO 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, CO_2 is coordinated to the complex through interactions with Br^- and O^-. Fuwei et al. [28] also reported an increase of the yield of propylene carbonate from propylene oxide and CO_2 with the use of $ZnBr_2$ cocatalyst.

The influence of the amount of HMImCl in the mixed catalyst was also studied with the ratios of HMImCl/$ZnBr_2$ from 0.5 to 4. The mixed catalyst with HMImCl/$ZnBr_2$ = 2 showed higher VCHO conversion than the catalyst with equimolar ratio of HMImCl and $ZnBr_2$ at 80 and 140 °C. Excess amount of HMImCl did not show any significant increase in the VCHO conversion. As shown in Scheme 3, two moles of VCHO and one mole of $ZnBr_2$ will form the metal–epoxide complex, and two moles of HMImCl interact with the resulting complex. Therefore, too high amount of HMImCl could not give an additional catalytic effect.

The influence of the structure of ionic liquid on the reaction was also investigated for the mixed catalyst with $ZnBr_2$. The VCHO conversion was in the order of HMImCl > B-BMImCl > EMImCl (compare Runs 27, 36, 38). Probably the bulkier ionic liquid forces the bromide ion away from the cation and makes the interaction between cation and anion weaker, resulting in more nucleophilic nature of the Br^- [27]. Mixture of BMImBr and $ZnBr_2$ in Run 39 also showed higher reactivity than BMImBr alone (Run 38).



Scheme 3. Coordination of VCHO with $ZnBr_2$.

4. Conclusion

In the synthesis of cyclic carbonate from VCHO and carbon dioxide, ionic liquid showed good catalytic activity without using any solvent. The ionic liquid of larger alkyl chain structure and more nucleophilic anion exhibited better reactivity for the cycloaddition of carbon dioxide and VCHO. High temperature, long reaction time, and high CO_2 pressure also increased the conversion of VCHO. Semi-batch operation showed higher conversion of VCHO than batch operation did. The use of zinc halide cocatalyst with the ionic liquid enhanced the reactivity due to the cooperative action of both the acidic site (Zn) and basic site (Br^-).

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (R01-2005-000-10005-0), and Brain Korea 21 program. S.W. Park is also thankful to Applied Rheology Center.

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