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Addition of carbon dioxide to allyl glycidyl ether using ionic liquids catalysts

Dae-Won Park *, Na-Young Mun, Kyung-Hoon Kim,
Il Kim, Sang-Wook Park

Division of Chemical Engineering, Pusan National University, Busan 609-735, Republic of Korea

Abstract

The addition of carbon dioxide to allyl glycidyl ether (AGE) was investigated without using any solvent in the presence of ionic liquid as catalyst. 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 used as catalysts. The reaction was performed in a 50 mL stainless steel autoclave. The conversion of allyl glycidyl ether was affected by the structure of imidazolium salt ionic liquids; the one with the cation of bulkier alkyl chain length and with more nucleophilic anion showed better reactivity. Reaction temperature and carbon dioxide pressure enhanced the addition of carbon dioxide to AGE.

Keywords: Allyl glycidyl ether; Carbon dioxide; Addition; Cyclic carbonate

1. Introduction

Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization and environmental problems. Various chemical and biological methods to fix and utilize CO_2 are under study. Among them, the application of carbon dioxide as a monomer for the synthesis of various polymers has received much attention in recent years. The reactions of carbon dioxide with oxiranes leading to five-membered cyclic carbonates are well-known among many examples. These cyclic carbonates can be used as aprotic polar solvents, electrolytes for batteries and sources for reactive polymer synthesis [1]. The polar polymers obtained from the cyclic carbonate and diamine are of interest for optical, magnetic and electronic applications. 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 [2]. But some authors reported the synthesis of five-membered cyclic carbonates under mild condition in the presence of metal halides or phase transfer catalyst [3–5]. In our previous work [6,7], we reported the use of immobilized quaternary ammonium salt catalysts for the synthesis of cyclic carbonates.

Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [8]. 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 [9]. 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 [10,11]. More recently, propylene carbonate has been synthesized from CO_2 and propylene oxide with 1-butyl-3-methylimidazolium (BMIm) salt ionic liquid [8].

In the present work, 1-alkyl-3-methylimidazolium salt ionic liquids of different alkyl groups and different anions were used to understand the catalytic role of the ionic liquids. The effects of reaction temperature and carbon dioxide pressure were also studied for the cycloaddition of carbon dioxide to allyl glycidyl ether (AGE).

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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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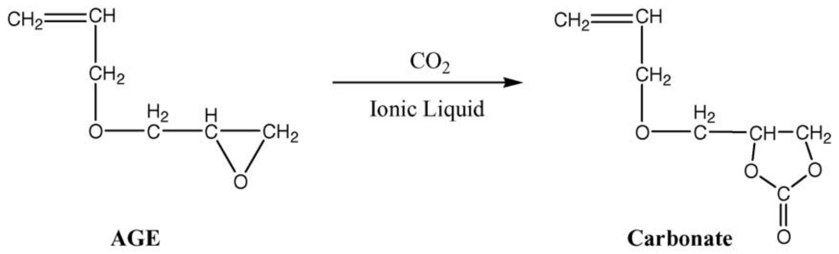


Scheme 1. Synthesis of cyclic carbonate from AGE and CO_2.

2. Experimental

2.1. Material

Allyl glycidyl ether (purity; 99%) was purchased from Aldrich. 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.

2.2. Addition reaction of AGE with carbon dioxide

The synthesis of cyclic carbonate from allyl glycidyl ether (AGE) 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 allyl glycidyl ether (40 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, 70–500 psig, 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 5–15 psia depending on the reaction temperature due to vapor pressure of the reactants. In semi-batch operations, the reaction pressure was maintained constant by a backpressure regulator with a direct connection to high pressure CO_2 supply at the entrance of the reactor.

2.3. Analysis of cyclic carbonate

The 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), ^1H NMR and ^{13}C NMR (Varian Gemini 2000 spectrometer in $CDCl_3$), TMS as an internal standard.

IR (KBr): 1800 (C=O), 1162 (C–O–C), 2860 (–O–CH_2), 1254, 1339, 1420 (–CH_2–), 1648 (C=C), 914 cm^{-1}(C–H).

^1H NMR ($CDCl_3$): δ 5.8–6.0 (1H, –CH=CH_2), 5.0–5.2 (2H, CH_2=CH–), 4.4–4.7 (3H, cyclic –CH–O– and –CH_2–O–), 4.0–4.1 (2H, –CH_2–, d), 3.5–3.8 (2H, –CH_2–O–).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.90 (–OC(O)O–), 133.88 (–C=), 117.47 (=CH_2), 72.05 (>CH–O–), 72.30, 68.92, 66.24 (–CH_2–O–).

3. Results and discussion

The synthesis of cyclic carbonate from AGE 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 as shown in Fig. 1. By comparison of the relative intensities 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%.

It is interesting to note that previous works reported mainly the formation of polycarbonate in the reaction of AGE with carbon dioxide [12–14]. Lukaszczyk et al. [12] used a mixed catalyst system based on $ZnEt_2$ and pyrogallol for the copolymerization of AGE with CO_2 at high CO_2 pressure (ca. 60 atm) for 44 h at 35 °C. Guo et al. [13] also reported copolymer product of AGE–CO_2 using $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$ catalyst under 30–40 atm CO_2 pressure for 24 h at 60 °C. Our previous work [14] also revealed the copolymerization of AGE and CO_2 using Co–Zn double metal cyanide catalyst at 9.6 atm for 36 h at 50 °C. It is generally accepted that the portion of polycarbonate to cyclic carbonate was high at high CO_2

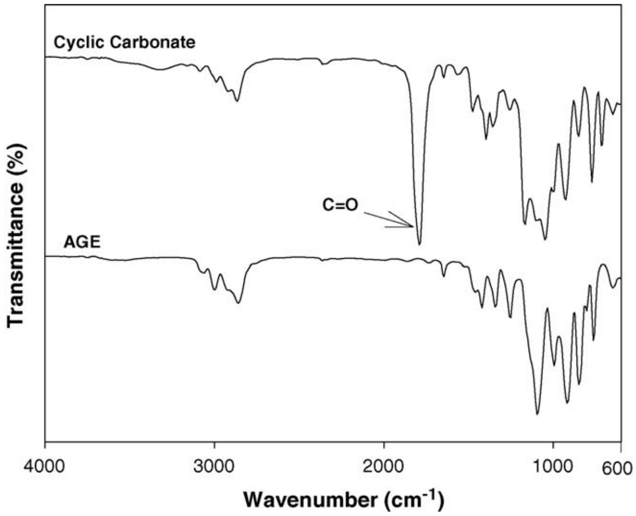


Fig. 1. FT-IR spectrum of cyclic carbonate from AGE and CO_2.

Table 1
Effects of the structure of ionic liquid on the conversion of AGE

Run	Ionic liquid	Temperature (°C)	Time (h)	Pressure (psig)	Conversion (%)[a]	Yield (%)[b]
1	EMImCl	45	48	140	8.6	8.6
2	BMImCl	45	48	140	54.5	53.9
3	HMImCl	45	48	140	57.5	57.0
4	EMImCl	100	48	140	30.5	29.8
5	$EMImBF_4$	100	48	140	16.0	16.0
6	$EMImPF_6$	100	48	140	4.4	4.4

Synthesis conditions: AGE 40 mmol, catalyst 2 mmol.

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

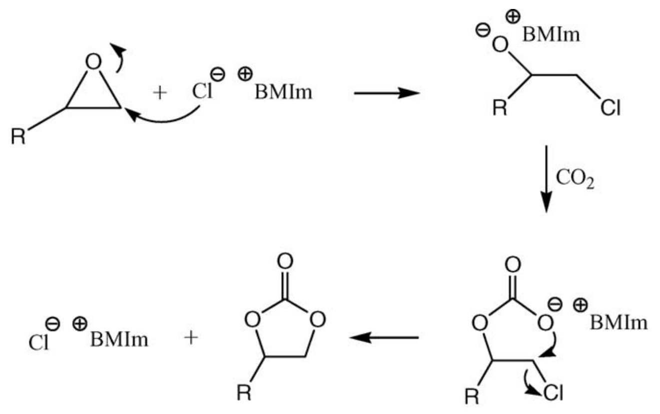
[b] Yield of the cyclic carbonate.

pressure and low reaction temperature [15]. However, ionic liquid catalyst system in this work produced almost only cyclic carbonate even at high pressure such as 500 psig (34 atm). The ^{13}C NMR and ^{1}H NMR analysis also confirmed the synthesis of the cyclic carbonate. No production of the homopolymer of AGE was confirmed by ^{1}H NMR and ^{13}C NMR.

3.1. *Effects of ionic liquid structure*

The catalytic activity of ionic liquids usually depends on the corresponding catalyst cation and counter anion [16,17]. In order to understand the effects of cation structure on the conversion of AGE, 1-alkyl-3-methylimidazolium chloride of different alkyl groups (ethyl, butyl, hexyl) were used at 45 °C under CO_2 pressure of 140 psig for 48 h. Table 1 summarizes the effects of ionic liquid structure on the conversion of AGE. The selectivity of the five-membered cyclic carbonate was near 100% because there was negligible amount of byproducts such as polycarbonate and homopolymer of AGE. Therefore, the yields were very close to the conversion data.

The AGE conversion increased as the size of the cation of ionic liquids increased from $EMIm^+ < BMIm^+ < HMIm^+$. The rate determining step of the epoxide–CO_2 reaction involves nucleophilic attack of the chloride anion to AGE as shown in Scheme 2 [18]. 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 AGE. 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 [18]. Starks et al. [19] also reported that bulkier quaternary ammonium salt had higher anion activation ability due to the longer distance between cation and anion. For example, $(C_4H_9)N^+\cdots Br^-$ ($d = 62.8$ nm) can have reactivity of four orders of magnitude higher than $Na^+\cdots Br^-$ ($d = 28.5$ nm) although the difference in cation–anion interionic distances for the two ion pairs is only about 34.3 nm [19]. The increase in the solubilities of CO_2 and AGE in ionic liquid with lengthening alkyl chain of the ionic liquid could also be a reason of the increase of AGE conversion. Chen et al. [20] reported the increase of CO_2 solubility in imidazolium ionic liquid from butylmethylimidazolium tetrafluoroborate ($BMImBF_4$) to octylmethylimidazolium salt ($OMImBF_4$). Kawanami et al. [21] 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.



Scheme 2. Reaction steps for the cycloaddition of CO_2 to AGE.

Ionic liquids with different anions (Cl^-, BF_4^-, PF_6^-) were also tested for the addition of CO_2 to AGE at 100 °C, since the AGE conversions of EMIm ionic liquid with BF_4^- and PF_6^- were very low at 45 °C. The conversion of AGE 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. *Effects of reaction temperature and CO_2 pressure*

Table 2 lists the conversion of AGE at different reaction temperature and carbon dioxide pressure. The AGE conversion increased with increasing reaction temperature from 45 to 100 °C. But the conversion remained nearly constant over 100 °C, probably due to the partial decomposition of the cyclic carbonate to monomeric AGE at high temperatures. The effects of pressure in the addition of CO_2 to AGE are compared in Run

Table 2
Effects of reaction temperature and CO_2 pressure on the conversion of AGE

Run	Ionic liquid	Temperature (°C)	Time (h)	Pressure (psig)	Conversion (%)[a]	Yield (%)[b]
3	HMImCl	45	48	140	57.5	57.0
7	HMImCl	60	48	140	65.2	64.7
8	HMImCl	80	48	140	77.1	76.6
9	HMImCl	100	48	140	80.5	79.8
10	HMImCl	120	48	140	79.2	78.1
11	HMImCl	100	48	70	71.2	70.6
12	HMImCl	100	48	Atmosphere	43.2	42.7
13	HMImCl	100	48	500	99.2	97.6
14	HMImCl	100	48	140[c]	98.7	97.2
15	HMImCl	100	48	Atmosphere[c]	92.1	91.3

Synthesis conditions: AGE 40 mmol, catalyst 2 mmol.

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

[b] Yield of the cyclic carbonate.

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

Table 3
Effect of reaction time and type of catalysts on the conversion of AGE

Run	Catalyst	Temperature (°C)	Time (h)	Pressure (psig)	Conversion (%)[a]	Yield (%)[b]
9	HMImCl	100	48	140	80.5	79.8
16	HMImCl	100	24	140	50.2	49.5
17	HMImCl	100	6	140	39.6	39.0
18	TBAC	100	48	140	65.0	64.2
19	TBAC	100	48	140[c]	91.0	89.6

Synthesis conditions: AGE 40 mmol, catalyst 2 mmol.

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

[b] Yield of the cyclic carbonate.

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

9, Run 11, Runs 12 and 13. The conversion of AGE increased with increasing carbon dioxide pressure, probably due to the increase of the absorption of CO_2 in a solution of AGE and ionic liquid. Zhang et al. [22] reported the increase of the solubilities of CO_2 in $BMImPF_6$ with increasing the pressure of CO_2. It is also reported, in the CO_2/cyclohexene oxide coupling reaction catalyzed by chromium salen complexes, that high CO_2 pressure increased turnover number of the reaction [23]. Runs 14 and 15 were performed in a semi-batch reactor system using a backpressure regulator. One can see that the semi-batch operations in Runs 14 and 15 exhibited higher conversions than the corresponding batch operations, Run 9 and Run 12, respectively. The carbon dioxide pressure can be maintained high during its reaction with AGE in the semi-batch operations.

Table 3 summarizes the conversion of AGE at different reaction time. When the reaction time increased from 6 to 48 h, the AGE conversion greatly increased. Table 3 also shows the performance of the quaternary ammonium salt tetrabutyl ammonium chloride (TBAC), widely used as catalyst in the addition of CO_2 to epoxides [4,5]. TBAC showed lower AGE conversion than HMImCl at the same reaction condition. Run 19 also shows an increased reactivity compared to the corresponding batch operation, Run 18. In these two operations with TBAC catalyst, no formation of polycarbonate was observed.

4. Conclusions

Carbon dioxide can be effectively added to the epoxide ring of allyl glycidyl ether (AGE) to produce the corresponding five-membered cyclic carbonate without using any solvent. The order of the AGE conversion increased as the size of the cation of ionic liquids increased from $EMIm^+ < BMIm^+ < HMIm^+$. 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 $EMIm^+X^-$ ionic liquid: $PF_6^- < BF_4^- < Cl^-$. Higher carbon dioxide pressure enhanced the AGE conversion due to the increase of the absorption of carbon dioxide in the solution of ionic liquid and AGE.

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References

[1] S. Inoue, N. Yamazaki, Organic and Bioorganic Chemistry of Carbon dioxide, Kodansha Ltd., Tokyo, 1981.
[2] R. Nomura, A. Ninagawa, H. Matsuda, J. Org. Chem. 45 (1980) 3735.
[3] G. Rokicki, W. Kuran, B.P. Marciniak, Monatsh. Chem. 115 (1984) 205.
[4] N. Kihara, T. Endo, Makromol. Chem. 193 (1992) 1482.
[5] T. Nishikubo, A. Kameyama, M. Sasano, J. Polym. Sci. A: Polym. Chem. 32 (1994) 301.
[6] D.W. Park, B.S. Yu, E.S. Jeong, I. Kim, M.I. Kim, K.J. Oh, S.W. Park, Catal. Today 98 (2004) 499.
[7] B.S. Yu, E.S. Jeong, K.H. Kim, D.W. Park, S.W. Park, J.W. Lee, React. Kinet. Catal. Lett. 84 (2005) 175.
[8] T. Welton, Chem. Rev. 99 (1999) 2071.
[9] C.E. Song, W.H. Shim, E.J. Roh, J.H. Choi, Chem. Commun. (2000) 1695.
[10] K.R. Seddon, Kinet. Catal. 37 (1996) 693.
[11] A.S. Larsen, J.D. Holbery, F.S. Tham, C.A.J. Reed, J. Am. Chem. Soc. 122 (2000) 7264.
[12] J. Lukaszczyk, K. Jaszcz, W. Kuran, T. Listos, Macromol. Rapid Commun. 21 (2000) 754.
[13] J.T. Guo, X.Y. Wang, Y.S. Xu, J.W. Sun, J. Appl. Polym. Sci. 87 (2003) 2356.
[14] I. Kim, M.J. Yi, S.H. Byun, D.W. Park, B.U. Kim, C.S. Ha, Macromol. Symp. 224 (2005) 181.
[15] D.J. Darensbourg, J.C. Yarbrough, C. Ortiz, C.C. Fang, J. Am. Chem. Soc. 125 (2003) 7586.
[16] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem. 182 (2002) 419.
[17] D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157.
[18] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561.
[19] C.M. Starks, C.L. Littoa, M. Halpern, Phase Transfer Catalysis, Chapman and Hall, New York, 1994.
[20] Y. Chen, S. Zhang, X. Yuan, in: Proceedings of the 7th World Congress on Recovery Recycling and Reintegration, Beijing, China, 25–29 September, (2005), p. 2.
[21] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, Chem. Commun. (2003) 896.
[22] S. Zhang, X. Yuan, Y. Chen, X. Zhang, J. Chem. Eng. Data 50 (2005) 1582.
[23] D.J. Darensbourg, R.M. Mackiewicz, D.R. Billodeaux, Organometallics 24 (2005) 144.