

Catalytic performance of pyridinium salt ionic liquid in the synthesis of cyclic carbonate from carbon dioxide and butyl glycidyl ether

Hye-Young Ju, Ji-Yeon Ahn, Mamparambath-Dharman Manju, Kyung-Hoon Kim and Dae-Won Park[†]

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

(Received 30 July 2007 • accepted 17 September 2007)

Abstract—The catalytic performance of pyridinium salt ionic liquids in the reaction of butyl glycidyl ether and carbon dioxide was investigated in this study. The catalytic activity was studied in a batch reactor with different 1-alkylpyridinium salt ionic liquids at 60–140 °C. The conversion of butyl glycidyl ether was affected by the structure of the ionic liquid; the one with the cation of bulkier alkyl chain length showed better reactivity. The effect of carbon dioxide pressure, reaction temperature and zinc bromide co-catalyst on this reaction was also discussed.

Key words: Pyridinium Salt, Ionic Liquid, Butyl Glycidyl Ether, Carbon Dioxide

INTRODUCTION

Using carbon dioxide as an environmentally benign, safe, and cheap C₁ building block in synthetic chemistry is a great challenge in “green chemistry” [1]. The coupling reaction of CO₂ and epoxides to produce valuable cyclic carbonates is of great importance in industry. The five-membered cyclic carbonates can find extensive applications as monomers, aprotic polar solvents, and sources for reactive polymer synthesis [2]. 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 CO₂ with oxirane has been performed using Lewis acids, transition-metal complexes, and organometallic compounds as catalysts under high pressure [3]. But some authors reported the synthesis of five-membered cyclic carbonates under mild condition in the presence of metal halides or phase transfer catalyst [4–6]. In our previous work [7–9], we reported the use of immobilized quaternary ammonium salt catalysts for the synthesis of cyclic carbonates.

Recently, the use of ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [10]. 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 [10–13]. In particular, ionic liquids based on imidazolium cations and chloroaluminate anions, such as 1-butyl-3-methylimidazolium aluminium chloride (BMImCl/AlCl₃), have attracted growing interest in the last few years [14,15]. Propylene carbonate has been synthesized from CO₂ and propylene oxide with 1-butyl-3-methylimidazolium (BMIm) salt ionic liquid [16]. In spite of the extensive literature reported about the cycloaddition of CO₂ to epoxides using imidazolium salt catalysts [10–12], there are no works in which pyridinium salt ionic liquids were used as catalysts for the reaction of butyl glycidyl ether (BGE) and CO₂.

In the present work, 1-alkyl-pyridinium 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, carbon dioxide pressure, and the presence of ZnBr₂ co-catalyst were also studied for the cycloaddition of carbon dioxide to BGE.

EXPERIMENTAL

BGE (purity: 95%) was purchased from Aldrich. Pyridinium salts ionic liquids based on 1-ethylpyridinium (EPy), 1-propylpyridinium (PPy), 1-butylpyridinium (BPy), 1-hexylpyridinium (HPy) with different anions such as Cl[−], Br[−], PF₆[−], were prepared according to the procedures reported previously [14]. The ionic liquids were dried and degassed under vacuum at 100 °C for 4 h prior to use.

Experiments for the synthesis of cyclic carbonate from BGE and carbon dioxide were performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. The reactor was charged with 40 mmol of BGE, 2 mmol of catalyst and then purged several times with CO₂. Then it was pressurized with CO₂ to a fixed pressure, heated to a desired temperature, and the reaction was started by stirring the reactant mixture. To determine the structure and the composition of the products, NMR spectra in deuteriochloroform at room temperature were measured with a Burkert AM-400 NMR spectrometer using tetramethylsilane as the standard, and IR spectra were measured by a React IR spectrometer (ASI Model 1000). The conversions of BGE were determined with a GC (HP 6890) with a FID.

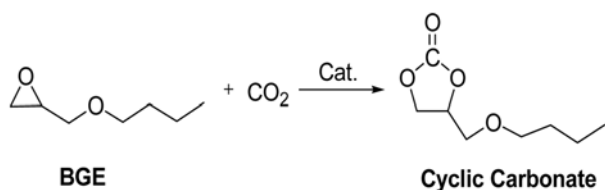
RESULTS AND DISCUSSIONS

Cycloaddition of CO₂ to BGE leads to the formation of the cyclic carbonate shown in Scheme 1.

The product of the reaction analyzed by ¹H-NMR is shown in Fig. 1, and the characteristic peaks from ¹H-NMR analysis (CDCl₃) were as follows: 4.1–4.4 (3H, cyclic -CH-O- and CH₂-O-), 3.4–3.8 (2H, -CH₂-O-). The formation of cyclic carbonate was confirmed by IR analysis. The spectra showed absorption at 1,800 cm^{−1} (C=O of carbonate group) and the consumption of BGE was verified by

[†]To whom correspondence should be addressed.

E-mail: dwpark@pusan.ac.kr



Scheme 1. Synthesis of cyclic carbonate from BGE and carbon dioxide.

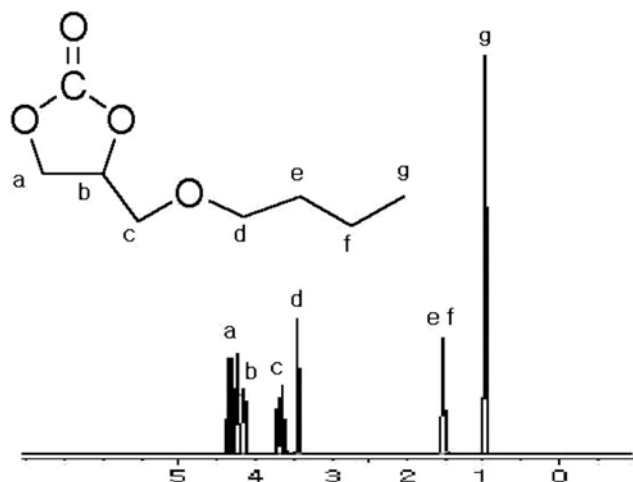


Fig. 1. ¹H-NMR of cyclic carbonate formed from CO₂ and BGE.

Table 1. Effect of catalyst structure on the conversions of BGE

| Run | Catalyst | BGE conv. (%) | Run | Catalyst | BGE conv. (%) |
|-----|----------|---------------|-----|----------------------|---------------|
| 1 | EPyCl | 68.2 | 5 | BPyBr | 73.5 |
| 2 | PPyCl | 78.6 | 6 | BPyPF ₆ | 48.2 |
| 3 | BPyCl | 79.7 | 7 | TBABr ^a | 60.2 |
| 4 | HPyCl | 79.9 | 8 | BMIImCl ^b | 69.8 |

Reaction conditions: BGE=40 mmol, catalyst=2 mmol, T=100 °C, P_{CO2} (25 °C)=120 psig, time=6 h.

^aTBABr=tetrabutylammonium bromide

^bBMIImCl=1-butyl-3-methylimidazolium chloride

the disappearance of the absorption at 910 cm⁻¹ (C-O-C of epoxide ring).

Table 1 summarizes the conversions of BGE with different ionic liquid catalysts. The structure of pyridinium salt ionic liquids affected the conversion of BGE. When the size of cations increased from EPyCl to PPyCl, the BGE conversion after 6 h of reaction increased from 68.2 to 78.6%. The rate-determining step of the epoxide and CO₂ reaction involves nucleophilic attack of anion to the epoxide ring. Therefore, bulky ionic liquid, having longer distance between cation and anion, may have higher anion activation capacity [17]. For more bulky ionic liquids BPyCl and HPyCl, however, the increase of BGE conversion was very small. This may originate from the steric hindrance of these bulky ionic liquids, which compensates the increase of the anion activation ability with increasing alkyl chain length.

The effects of anions of the ionic liquid were studied by using BPy salts. The order of the BGE conversion increased in the order of PF₆⁻ < Br⁻ < Cl⁻. The nucleophilicity and the steric hindrance of Br⁻ is greater than Cl⁻, and the two conflicting factors may make the interaction of Cl⁻ with carbon atom of CO₂ stronger than Br⁻ and carbon atom, rendering the carbon atom more positive [18].

Different types of ionic liquids such as tetrabutylammonium bromide (TBABr) and 1-butyl-3-methylimidazolium chloride (BMIImCl) were also tested in this reaction. TBABr (Run 7) and BMIImCl (Run 8) showed lower BGE conversion than the corresponding pyridinium salt ionic liquid, BPyBr (Run 5) and BPyCl (Run 4), respectively.

Table 2 shows the effects of reaction temperature and carbon dioxide pressure on the conversion of BGE after 1 h of reaction. The increase of temperature from 60 °C to 140 °C increased the BGE conversion from 35.5 to 74.3%. The effects of pressure in the addition of carbon dioxide to BGE are compared in Runs 11, 14-16. The conversion of BGE increased with increasing carbon dioxide pressure from 80 to 200 psig due to the increase of carbon dioxide absorption into the solution of BGE and ionic liquid.

Fig. 2 shows the variation of the conversion of BGE as a function of reaction time with BPyCl catalyst at different reaction temperatures. At 100 °C, the BGE conversion increased continuously

Table 2. Effect of carbon dioxide pressure and reaction temperature on the conversion of BGE

| Run | Catalyst | Temp. (°C) | Pressure (psig) ^a | BGE conv. (%) |
|-----|----------|------------|------------------------------|---------------|
| 9 | BPyCl | 60 | 120 | 35.5 |
| 10 | BPyCl | 80 | 120 | 49.7 |
| 11 | BPyCl | 100 | 120 | 54.3 |
| 12 | BPyCl | 120 | 120 | 72.0 |
| 13 | BPyCl | 140 | 120 | 74.3 |
| 14 | BPyCl | 100 | 80 | 45.1 |
| 15 | BPyCl | 100 | 160 | 68.5 |
| 16 | BPyCl | 100 | 200 | 76.2 |

Reaction conditions: BGE=40 mmol, catalyst=2 mmol, time=1 h.

^aPressure of CO₂ at 25 °C

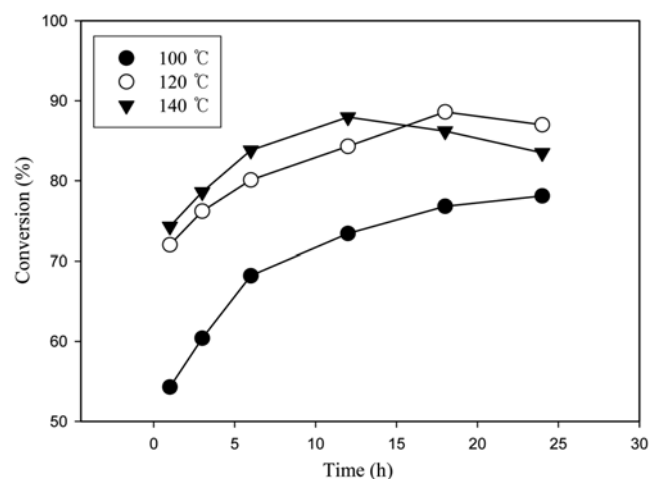


Fig. 2. Time variant conversion of BGE at different temperatures (BGE=40 mmol, BPyCl=2 mmol, P_{CO2} (25 °C)=120 psig).

Table 3. The effect of cocatalyst on the conversion of BGE

| Run | Catalyst (mmol) | Co-catalyst (mmol) | BGE conv. (%) |
|-----|-----------------|-------------------------|---------------|
| 17 | BPyCl (2) | 0 | 64.8 |
| 18 | BPyCl (2) | ZnBr ₂ (0.5) | 79.0 |
| 19 | BPyCl (2) | ZnBr ₂ (1) | 82.4 |
| 20 | BPyCl (2) | ZnBr ₂ (2) | 82.9 |
| 21 | BPyCl (1) | ZnBr ₂ (0.5) | 68.2 |

Reaction conditions: BGE=40 mmol, catalyst=BPyCl, co-catalyst=ZnBr₂, Temp.=100 °C, P_{CO₂} (25 °C)=120 psig, time=2 h.

from 1 h to 24 h of reaction. However, the BGE conversion showed maximum at higher temperatures (18 h at 120 °C, 12 h at 140 °C). The BGE conversion at 140 °C after 24 h was lower than that at 120 °C after 24 h. Therefore, one can see that the cyclic carbonate can be decomposed to BGE and CO₂ at long reaction time and at high reaction temperature.

In order to investigate the effect of co-catalyst on the catalytic performance, ZnBr₂ was tested. Table 3 shows the effect of ZnBr₂ co-catalyst on the conversion of BGE. The mixture catalysts of ZnBr₂ and BPyCl showed improved conversions. This may originate from the cooperative action of both the acidic site (Zn) for epoxide activation and basic site (Cl⁻ in BPyCl and/or Br⁻ in ZnBr₂) for CO₂ activation as postulated previously [19].

CONCLUSION

Ionic liquid showed good catalytic activity for the synthesis of cyclic carbonate from BGE and CO₂. Pyridinium salt ionic liquid with larger cation exhibited higher reactivity. The conversion of BGE also increased with increasing carbon dioxide pressure and reaction temperature. Zinc bromide co-catalyst mixed with BPyCl showed improved reactivity for the addition of CO₂ to BGE.

ACKNOWLEDGMENT

This work was supported for two years by Pusan National Uni-

versity Research Grant.

REFERENCES

1. A. Behr, *Angew. Chem. Int. Ed.*, **27**, 661 (1988).
2. S. Inoue and N. Yamazaki, *Organic and bioorganic chemistry of carbon dioxide*, Kodansha Ltd., Tokyo (1981).
3. R. Nomura, A. Ninagawa and H. Matsuda, *J. Org. Chem.*, **45**, 3735 (1980).
4. G. Rokicki, W. Kuran and B. P. Marciniak, *Monatsh. Chem.*, **115**, 205 (1984).
5. N. Kihara and T. Endo, *Makromol. Chem.*, **193**, 1482 (1992).
6. T. Nishikubo, A. Kameyama and M. Sasano, *J. Polym. Sci. A: Polym. Chem.*, **32**, 301 (1994).
7. D. W. Park, B. S. Yu, E. S. Jeong, I. Kim, M. I. Kim, K. J. Oh and S. W. Park, *Catal. Today*, **98**, 499 (2004).
8. B. S. Yu, E. S. Jeong, K. H. Kim, D. W. Park, S. W. Park and J. W. Lee, *React. Kinet. Catal. Lett.*, **84**, 175 (2005).
9. D. H. Shin, J. J. Kim, B. S. Yu, M. H. Lee and D. W. Park, *Korean J. Chem. Eng.*, **20**, 71 (2003).
10. C. E. Song, W. H. Shim, E. J. Roh and J. H. Choi, *Chem. Commun.*, 1695 (2000).
11. N. Y. Mun, K. H. Kim, D. W. Park, Y. Choe and I. Kim, *Korean J. Chem. Eng.*, **22**, 556 (2005).
12. E. H. Lee, S. W. Cha, M. D. Manju, Y. Choe, J. Y. Ahn and D. W. Park, *Korean J. Chem. Eng.*, **24**, 547 (2007).
13. D.-S. Kim and W.-S. Ahn, *Korean J. Chem. Eng.*, **20**, 39 (2003).
14. K. R. Seddon, *Kinet. Catal.*, **37**, 693 (1996).
15. A. S. Larsen, J. D. Holbery, F. S. Tham and C. A. J. Reed, *J. Am. Chem. Soc.*, **122**, 7264 (2000).
16. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
17. H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A. Chem.*, **182**, 419 (2002).
18. J. Sun, S. I. Fujita, F. Zhao and M. Arai, *Appl. Catal. A. General*, **287**, 221 (2005).
19. J. Sun, S. I. Fujita, F. Zhao and M. Arai, *Green Chem.*, **6**, 613 (2004).