

이온성 액체를 촉매로한 Vinyl Cyclohexene Oxide와 CO<sub>2</sub>로부터 5원환 카보네이트의 합성

이은하, M.D. Manju, 안지연, 김경훈, 박대원\*  
부산대학교 응용화학공학부  
(dwpark@pusan.ac.kr\*)

**Synthesis of Five-Membered Carbonate from VCHO and CO<sub>2</sub> Using Ionic Liquid**

Eun-Ha Lee, Manju\_M.D., Ji-Yeon An, Kyung-Hoon Kim, Dae-Won Park\*  
Division of Chemical Engineering, Pusan National University  
(dwpark@pusan.ac.kr\*)

**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<sub>2</sub> continues to be utilized as a feedstock for the production of organic products. One of the most successful processes utilizing CO<sub>2</sub> is the synthesis of cyclic carbonate. The demand for cyclic carbonates is continuously increasing in a wide variety of applications. Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [1]. Room temperature ionic liquids have negligible vapor pressure, excellent thermal stability and special characteristics in comparison with conventional organic and inorganic solvents. In the present work, the effects of structure of ionic liquids, temperature, carbon dioxide pressure, and presence of co-catalyst were studied for the cycloaddition of carbon dioxide to 4-vinyl-1-cyclohexene-1,2-epoxide (VCHO).

**EXPERIMENTAL**

Ionic liquids based on 1-n-ethyl-3-methylimidazolium (EMIm), 1-n-butyl-3-methylimidazolium (BMIm), 1-n-hexyl-3-methylimidazolium (HMIm), 1-n-octyl-3-methylimidazolium (OMIm) with different anions such as Cl<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, PF<sub>6</sub><sup>-</sup> were prepared according to the procedures reported previously [2]. All of ionic liquids and VCHO were used without further purification. The addition reaction was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, ionic liquid (2 mmol) and VCHO (5 mL) were charged into the reactor without

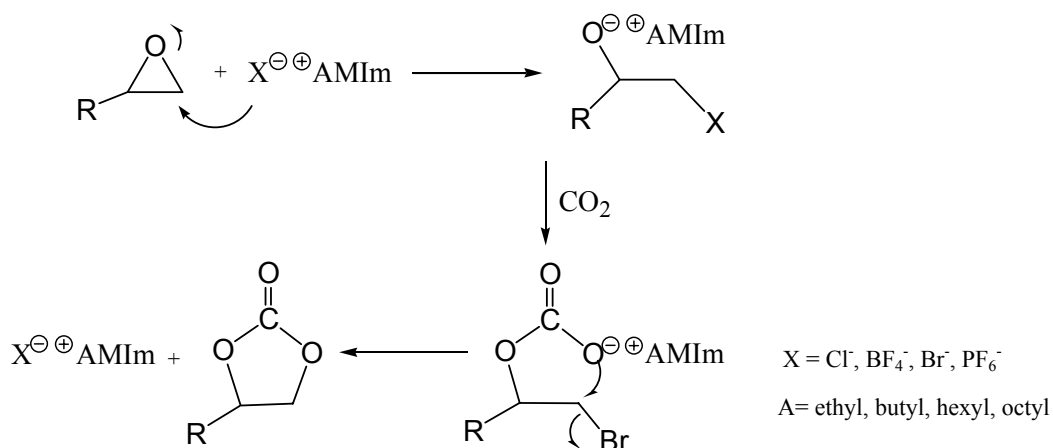
solvent, and the CO<sub>2</sub> was introduced at room temperature to a preset pressure. The reaction was started by stirring when the desired temperature and pressure were attained. The pressure was maintained constant using a back-pressure regulator during the experiments.

## RESULTS AND DISCUSSION

The cyclic carbonate was synthesized from VCHO and carbon dioxide using various ionic liquid catalysts under carbon dioxide pressure.

The conversions of VCHO to the cyclic carbonate with different ionic liquids consisting of cations of EMIm<sup>+</sup>, BMIm<sup>+</sup>, HMIm<sup>+</sup>, OMIm<sup>+</sup> and anions of Cl<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, PF<sub>6</sub><sup>-</sup> are summarized in Table 1. The order of the VCHO conversion increased as the size of the cation of ionic liquid increased from EMIm<sup>+</sup> < BMIm<sup>+</sup> < HMIm<sup>+</sup> < OMIm<sup>+</sup>. Bulky imidazolium salts having longer distances between cations and anions, seem to exhibit higher activity in activating anions. The increase in the solubilities of CO<sub>2</sub> and VCHO in ionic liquid with lengthening alkyl chain of ionic liquid could also be a reason of the increase of VCHO conversion. Kawanami et al. [3] also reported the increase of reactivity when the length of alkyl chain increased from C<sub>2</sub> to C<sub>8</sub> in 1-alkyl-3-methylimidazolium chloride [C<sub>x</sub>MIm]<sup>+</sup>[Cl]<sup>-</sup> for the synthesis of propylene carbonate using CO<sub>2</sub>-ionic liquid system.

The effect of anions in the addition of CO<sub>2</sub> to VCHO are compared in Run 2, 5, 14 and 15. The conversion of VCHO increased in the order of PF<sub>6</sub><sup>-</sup> < BF<sub>4</sub><sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup>, which is consistent with the order of nucleophilicity of anions. The mechanism for the cycloaddition of epoxide and carbon dioxide with ionic liquid catalyst can be suggested as follows [4] :



Therefore, the ionic liquid with bulkier cation having more anion activating ability and that with more nucleophilic anion would exhibit better reactivity.

Table 1. Catalytic activities of ionic liquid in the cyclic reactions of CO<sub>2</sub> with VCHO

Run	Ionic liquid	Temp(°C)	Time(h)	Pressure(psi)	Conversion(%)
1	EMImCl	140	6	140	14.8
2	BMImCl	140	6	140	25.6
3	HMImCl	140	6	140	40.3
4	OMImCl	140	6	140	49.1
5	BMImBr	140	6	140	35.8
6	OMImCl	60	6	140	6.0
7	OMImCl	80	6	140	9.8
8	OMImCl	100	6	140	25.2
9	OMImCl	120	6	140	42.6
10	OMImCl	160	6	140	51.1
11	OMImCl	80	12	140	13.8
12	OMImCl	80	24	140	13.9
13	OMImCl	80	48	140	30.8
14	BMImPF <sub>6</sub>	140	6	140	3.0
15	BMImBF <sub>4</sub>	80	6	140	8.2
16	OMImCl	80	6	atmosphere	1.6
17	OMImCl	80	6	70	4.9
18	OMImCl	80	6	540	13.7
19	ZnBr <sub>2</sub>	140	6	140	-
20	HMImCl+ZnBr <sub>2</sub>	140	6	140	41.3
21	HMImCl+ZnCl <sub>2</sub>	140	6	140	34.2
22	HMImCl+ZnF <sub>2</sub>	140	6	140	28.2

The conversion increased as the temperature increased from 60 °C to 160 °C. It means that there is no severe decomposition of the cyclic carbonate to VCHO and CO<sub>2</sub> even at 160 °C. Table 1 shows that the conversion of VCHO with OMImCl ionic liquid increased from 9.8 % (Run 7, after 6 h) up to 30.8% (Run 13, after 48 h) at 80 °C. The conversion also increased as the pressure increased from atmosphere (Run 16) to 540 psi (Run 18). High pressure generally increases the absorption of carbon dioxide into the solution of VCHO and ionic liquid. The performance of co-catalyst with ionic liquid was studied using zinc halide and the results are compared in Run 19~22. Mixed catalysts of ionic liquid and zinc halide were very effective for the coupling reaction of VCHO and carbon dioxide [5-7]. The counter anion of the zinc halide also affected the catalytic activity. The conversion of VCHO decreased as ZnBr<sub>2</sub> > ZnCl<sub>2</sub> > ZnF<sub>2</sub>. The notable catalytic activity of zinc bromide with HMImCl may

originate from the cooperation of both the acidic site (Zn) for epoxide activation and basic site (Cl<sup>-</sup> in HMIImCl and or Br<sup>-</sup> in ZnBr<sub>2</sub>) for CO<sub>2</sub> activation.

## **CONCLUSION**

In the synthesis of cyclic carbonate from VCHO and carbon dioxide, ionic liquids 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<sub>2</sub> pressure also increased the conversion of VCHO.

## **ACKNOWLEDGEMENT**

This work was supported by the Korea Science and Engineering Foundation (R01-2005-000-10005-0) and Brain Korea 21 program.

## **REFERENCES**

- [1] Welton, T., "Room-temperature ionic liquids. Solvents for synthesis and catalysis", *Chem. Rev.*, **99**, 2071 (1999).
- [2] Bonhote, P., Dias, A., Papageorgiou, N., Kalyanasuodram, K. and Gratzel, M., "Hydrophobic, highly conductive ambient-temperature molten salts", *Inorg. Chem.*, **35**, 1168 (1996).
- [3] Kawanami, H., Sasaki, A., Matsui, K. and Ikushima, Y., "A rapid and effective synthesis of propylene carbonate using a supercritical CO<sub>2</sub>-ionic liquid system", *Chem. Commun.*, 896 (2003).
- [4] Calo, V., Nacci, A., Monopoli, A. and Fanizzi, A., "Cyclic carbonate formation carbon dioxide and oxiranes in tetrabutylammonium halides as solvents and catalysts", *Org. Lett.*, **4**(15), 2561 (2002).
- [5] Yamaguchi, K., Ebitani, K., Yoshida, T., Yoshida, H. and Kaneda, K., "Mg-Al mixed oxides as highly active acid-base catalysts for cycloaddition of carbon dioxide to epoxides", *J. Am. Chem. Soc.*, **121**, 4526 (1999).
- [6] Paddock, R. L., Hiyama, Y., McKay, J. M. and Nguyen, S. T., "Co(III) porphyrin/DMAP: an efficient catalyst system for the synthesis of cyclic carbonate from CO<sub>2</sub> and epoxide", *Tetrahedron Lett.*, **45**, 2023 (2004).
- [7] Sun, J., Fujita, S., Zhao, F. and Arai, M., "Synthesis of styrene carbonate from styrene oxide and carbon dioxide in the presence of zinc bromide and ionic liquid under mild conditions", *Green Chem.*, **6**, 613 (2004).