이온성 액체를 이용한 이산화탄소와 부틸글리시딜에테르로 부터 5원환 카보네이트의 합성

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

Synthesis of Cyclic Carbonate from Carbon Dioxide and Butyl Glycidyl Ether Using Ionic Liquid as Catalysts

Hye-Young Ju, Manju M.D., Kyung-Hoon Kim, Dae-Won Park*
Division of Chemical Engineering, Pusan National University
(dwpark@pusan.ac.kr*)

INTODUCTION

Using CO_2 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 CO_2 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 intermediates in the production of biomedical materials[2-4]. Recently, the use of ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted. Especially cyclic carbonate has been synthesized from CO_2 and epoxide with 1-alkyl-3-methylimidazolium salts ionic liquids[5].

The aim of this study was to investigate the effects of structure of ionic liquids, reaction temperature, carbon dioxide pressure, and co-catalysts for the synthesis of cyclic carbonate from carbon dioxide and butyl glycidyl ether (BGE) using ionic liquid as catalyst.

EXPERIMENTAL

Ionic liquids based on 1-ethyl-3-methylimidazolium (EMIm), 1-butyl-3-methylimidazolium (BMIm), 1-hexyl-3-methylimidazolium (HMIm), and 1-octyl-3-methylimidazolium (OMIm) with different anions such as Cl^-, BF_4^-, PF_6^- were prepared according to the procedures reported previously. The synthesis of cyclic carbonate from CO_2 to BGE was performed in a batch reactor. The 50 mL autoclave reactor was charged with 40 mmol of BGE, 2 mmol of catalyst and then purged several times with CO_2. Then it was pressurized with CO_2 at room temperature, heated to a desired temperature, and the reaction started. Cyclic carbonate can be synthesized from BGE and CO_2 using imidazolium salt ionic liquid as shown in Scheme 1.

To determine the structure and the composition of the products, the ^{1}H-NMR spectra in deuteriochloroform at room temperature were measured with a Burker AM-400 NMR spectrometer using tetramethylsilane as the standard, and the IR spectra were measured by a React IR spectrometer (Asi Applied system). The conversions of BGE were determined with a 6890 GC.

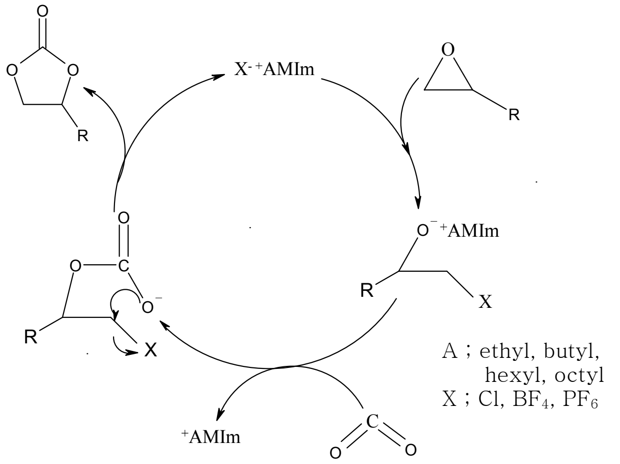
RESULTS AND DISCUSSION

From the proton peaks in the ^{1}H-NMR spectrum, the cyclic carbonate was detected as a reaction product ; ^{1}H-NMR (δ, $CDCl_3$), 4.4 – 4.7 (3H, cyclic -CH-O- and CH_2-O-), 3.5 – 3.8 (2H, -CH_2-O-). The IR spectra also confirmed the structure of the cyclic carbonate.

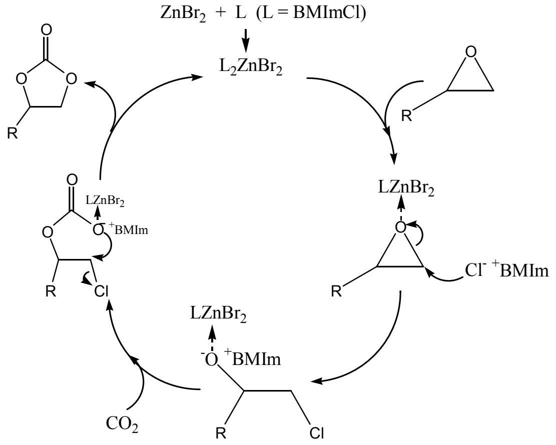
Table 1 summarizes the conversions of BGE and yields of the cyclic carbonate with different ionic liquids after 6 h. The structure of imidazolium salt ionic liquid affected the conversion of BGE ; as the size of cations increased from $EMIm^+$ to $HMIm^+$, the conversion increased. But, large cation $OMIm^+$ decreased the conversion because it is too bulky to form an intermediate with BGE. For the effects of anions, the conversion of BGE increased in the order of $BF_4^- < PF_6^- < Cl^-$, which is consistent with the order of nucleophilicity of anions[6].

High temperature favored the production of the cyclic carbonate, but BGE conversion decreased at 140 ℃ (Run 10) due to the partial decomposition of the cyclic carbonate to BGE. The effects of pressure in the addition of CO_2 to BGE are compared in Run 1 and Run 11 - 13. The conversion of BGE increased with increasing carbon dioxide pressure, probably due to the increase of the absorption of CO_2 in the solution of BGE and ionic liquid. In order to investigate the effect of co-catalyst on the catalytic performance, $ZnBr_2$ was tested. The mixture catalyst of $ZnBr_2$ and BMImCl showed an improved yield (compare Run 14 and 15). This 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 postulated previously[7]. The role of co-catalyst on the mechanism of cyclic carbonate synthesis from BGE and CO_2 is shown in Scheme 2.

Kinetic studies were carried out at 80 – 100 ℃ using BMImCl catalyst at CO_2 pressure of 150 psi for all temperatures. Fig 1 shows the polts of ln[1/(1-X)] vs. time, where X is conversion of BGE. One can see that the experimental data fitted well to the first order rate equation. The pseudo first order reaction rate constants were determined as 0.004967, 0.007695, and 0.008981 min^{-1} for 80, 100, and 120 ℃, respectively. From Arrhenius plot (Fig. 2), the activation energy was estimated as 15.4 kJ/mol.



Scheme 1. Mechanism for the reaction



Scheme 2. Effect of co-catalyst on mechanism

Table 1. The cycloaddition results of BGE/CO_2 using ionic liquid catalysts.

Run	Catalyst	Temp. (℃)	P (psig)^a	BGE conv. (%)	Yield (%)
1	EMImCl	100	150	78.0	78.0
2	BMImCl	100	150	79.1	79.1
3	HMImCl	100	150	81.3	81.1
4	OMImCl	100	150	60.3	60.3
5	$EMImPF_6$	100	150	41.0	40.8
6	$EMImBF_4$	100	150	26.6	26.1
7	EMImCl	60	150	26.7	26.7
8	EMImCl	80	150	42.1	42.1
9	EMImCl	120	150	88.0	87.3
10	EMImCl	140	150	84.9	83.1
11	EMImCl	100	Atmosphere	46.8	46.2
12	EMImCl	100	75	65.5	65.5
13	EMImCl	100	300	91.4	90.2
14	BMImCl^b	100	150	70.7	70.2
15	BMImCl + $ZnBr_2$^{c}	100	150	85.6	85.3

Reaction condition : BGE = 40 mmol, catalyst = 2 mmol, reaction time = 6 h.

a) Pressure of CO_2 at 25 ℃, b) BMImCl = 1 mmol, c) BMImCl = 1 mmol, $ZnBr_2$ = 1 mmol

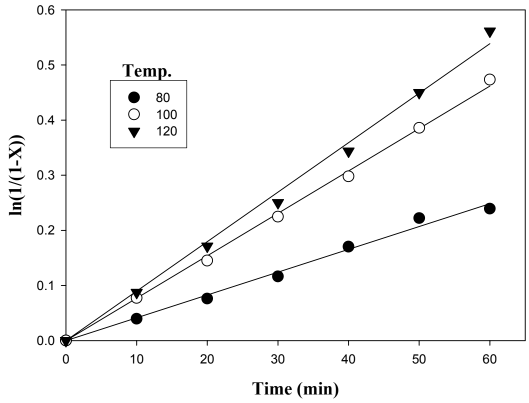


Fig. 1. Plots of ln[1/(1-X)] vs time.

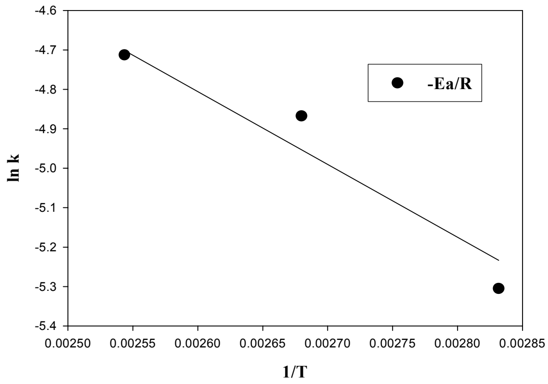


Fig 2. Arrhenius plot.

CONCLUSIONS

Ionic liquid showed good catalytic activity for the synthesis of cyclic carbonate from carbon dioxide and butyl glycidyl ether. Ionic liquid of more nucleophilic anion exhibited higher reactivity. The conversion of BGE increased as reaction temperature and carbon dioxide pressure increased. This reaction can be considered as first order with respect to BGE concentration and its activation energy was estimated as 15.4 kJ/mol.

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