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SHORT COMMUNICATION

Chemical fixation of carbon dioxide to dimethyl carbonate from propylene carbonate and methanol using ionic liquid catalysts

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Abstract−The synthesis of dimethyl carbonate (DMC) through the transesterification of propylene carbonate (PC) with methanol was investigated by using imidazolium salt ionic liquid catalysts. 1-alkyl-3-methyl imidazolium salts of different alkyl group (C_2, C_4, C_6, C_8) and anions (Cl^-, Br^-, BF_4^-, PF_6^-) were used for catalysts. The reaction was carried out in an autoclave at 140-180 °C under carbon dioxide pressure of 1.48-5.61 MPa. The imidazolium salts of shorter alkyl group, and more nucleophilic counter anion exhibited higher catalytic activity. The conversion of PC increased as CO_2 pressure and reaction temperature increased. Kinetic studies were also performed to better understand the reaction mechanism.

Key words: Dimethyl Carbonate, Transesterification, Propylene Carbonate, Methanol, Ionic Liquid

INTRODUCTION

Using CO_2 as an environmentally benign, safe, and cheap C_1 building block in synthetic chemistry is a great challenge in "green chemistry" [1]. CO_2 is a promising alternative to toxic substances, such as CO and phosgene [2]. One of the most successful processes utilizing CO_2 is the synthesis of cyclic carbonate. The synthesis is based on cycloaddition of carbon dioxide to epoxides instead of conventional synthesis using phosgene as a starting material [3-6].

Recently, the use of ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted due to their particular properties, especially with the emergence of the *N,N*-dialkylimidazolium cation derivatives [7]. Both the cationic and the anionic partners can be easily varied, so that these ionic liquid solvents can be designed for particular applications or for particular sets of properties [8]. 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 [9-11]. Especially, cyclic carbonate like propylene carbonate (PC), has been synthesized from CO_2 and epoxide with 1-alkyl-3-methylimidazolium salts ionic liquids [12].

Nowadays, dimethyl carbonate (DMC) has become a new basic material in the organic synthesis field. DMC can be synthesized from transesterification of methanol and cyclic carbonate like ethylene carbonate or propylene carbonate [13]. Several researchers report the synthesis of DMC from ethylene carbonate and methanol [14-18]. In these studies, alkali metals [14], zeolite [15,16], basic metal oxides [13,17], and hydrotalcite [18] are used as catalysts. In our previous work [19], we reported the synthesis of DMC from propylene carbonate and methanol using quaternary ammonium salt catalysts.

The aim of this study was to investigate the effects of structure of ionic liquids, reaction temperature, and pressure for the synthesis of dimethyl carbonate from propylene carbonate and methanol without using any solvent in the presence of ionic liquid as a catalyst. Kinetic studies were also performed to better understand the role of ionic liquid and reaction mechanism.

EXPERIMENTAL

Propylene carbonate (PC) was supplied by Aldrich Co. and used without further purification. Ionic liquids based on 1-ethyl-3-methylimidazolium (EMIm), 1-n-butyl-3-methylimidazolium (BMIm), 1-n-hexyl-3-methylimidazolium (HMIm) or 1-n-octyl-3-methylimidazolium (OMIm) with different anions such as Cl^-, BF_4^-, PF_6^- were prepared according to the procedures reported previously [20]. The ionic liquids were dried and degassed under vacuum at 100 °C for 4 h prior to use.

The synthesis of DMC from propylene carbonate and methanol by using ionic liquid was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, ionic liquid (2 mmol) and PC (25 mmol) and methanol (200 mmol) were charged into the reactor without solvent, and then CO_2 was introduced at room temperature to a preset pressure. The reaction was run by stirring when the desired temperature and pressure were attained. The products were analyzed by gas chromatograph.

RESULTS AND DISCUSSION

The synthesis of DMC from PC and methanol was carried out using various 1-alkyl-3-methyl imidazolium salt catalysts under a certain carbon dioxide pressure. The main reaction is shown in Scheme 1.

The conversions of PC with different ionic liquids consisting of cations of $EMIm^+$, $BMIm^+$, $HMIm^+$, $OMIm^+$ and anions of Cl^-, BF_4^-, PF_6^- are summarized in Table 1. The conversion of PC decreased as the chain length of alkyl substituent of the imidazolium salt ionic liquid increased from $EMIm^+$ to $OMIm^+$. The variation of the length

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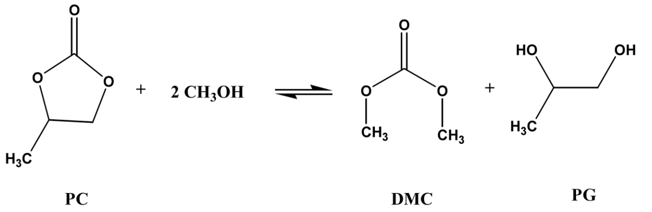
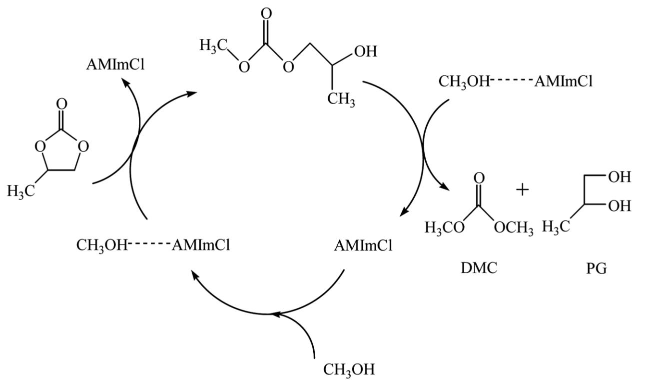


Scheme 1. Synthesis of DMC from PC and methanol.

Table 1. Conversion of PC and selectivity to DMC and PG with imidazolium salt ionic liquid catalysts of different anions and cations

Run	Catalyst	PC conversion (%)	Selectivity (%)	
			DMC	PG
1	EMImCl	35.7	43.2	40.5
2	BMImCl	26.7	67.0	58.6
3	HMImCl	22.1	33.4	20.4
4	OMImCl	20.8	25.6	14.3
5	$EMImBF_4$	25.2	31.9	20.0
6	$EMImPF_6$	22.7	21.4	11.4

Reaction condition: MeOH/PC=8/1, catalyst=2 mmol, P=3.55 MPa, T=140 °C, time=6 h.



Scheme 2. Plausible mechanism for the synthesis of DMC using alkylmethyl imidazolium chloride (AMImCl).

of the second carbon chain in the imidazolium salt ionic liquid alters the physical characteristics of the substances used [20]. For a series of 1-alkyl-3-methylimidazolium cations, Huddleston et al. [21] reported that increasing the alkyl chain length decreased hydrophilicity of the ionic liquid. Therefore, increasing the alkyl chain length from ethyl to octyl might decrease the solubility of the ionic liquid in methanol.

The role of ionic liquid catalyst in the synthesis of DMC may be proposed as shown in Scheme 2 [22]. The initial step is the activation of methanol by the ionic liquid to form a complex ($CH_3OH \cdot$ AMImCl) followed by the reaction with propylene carbonate to form an intermediate which reacts again with the complex to produce DMC. Bulky imidazolium salt, having longer distance between cation and anion, is generally known to exhibit higher ability in activating anions [8]. However, this controversial effect of alkyl chain length seems to be less important compared to the decrease of solubility for bulky ionic liquid.

Table 2. Conversion of PC and selectivity to DMC and PG at different reactor pressures

Run	Pressure (MPa)	PC conversion (%)	Selectivity (%)	
			DMC	PG
7	1.48	20.3	21.7	4.9
1	3.55	35.7	43.2	40.5
8	5.61	36.6	45.7	43.3

Reaction condition: MeOH/PC=8/1, catalyst=EMImCl (2 mmol), T=140 °C, time=6 h.

Table 3. Conversion of PC and selectivity to DMC and PG at different reaction temperatures

Run	Temperature (°C)	PC conversion (%)	Selectivity (%)	
			DMC	PG
1	140	32.7	46.1	48.5
9	160	55.4	70.1	97.7
10	180	75.1	80.4	90.7

Reaction condition: MeOH/PC=8/1, catalyst=EMImCl (2 mmol), P=3.55 MPa, time=6 h.

The effects of anions in the reaction of PC and methanol are compared in Run 1, 5 and 6. The conversion of PC increased in the order of $PF_6^- < BF_4^- < Cl^-$, which is consistent with the order of the nucleophilicity of anions. The imidazolium salt with more nucleophilic anion might be more active to form a complex with methanol as shown in Scheme 2.

The effect of pressure on the synthesis of DMC was studied using EMImCl at 140 °C. Table 2 shows the conversion of PC and the selectivity to DMC and PG. The conversion of PC increased as the initial pressure of the reactor increased from 1.48 to 3.55 MPa. Then it did not vary significantly from 3.55 to 5.61 MPa. CO_2 did not involve in the transestrification of PC and methanol. However, a high pressure of CO_2 is considered to be favorable for the inhibition of PC decomposition to propylene oxide and CO_2.

Table 3 summarizes the conversion of PC and DMC selectivity at different temperatures using EMImCl catalyst. The increase of reaction temperature from 140 °C to 180 °C greatly increased the conversion from 32.7 to 75.1%. High operation temperature is one of the advantages of this ionic liquid compared to other solvents. Quaternary ammonium salt catalyst used in our previous study [19] is known to be degraded over 150 °C [23].

The transesterification of propylene carbonate and methanol shown in Scheme 1 was carried out with excess amount of methanol. Therefore, the rate equation can be written as pseudo first order with respect to the concentration of PC.

$$-r_{PC}=k\,[PC]\,[MeOH]^2=k'\,[PC]$$
$$\text{where } k'=k\,[MeOH]^2$$

Fig. 1 shows the plots of $\ln[1/(1-X)]$ vs. time, where X is conversion of PC. One can see that the experimental data fit well to the first order rate equation. The pseudo first order reaction rate constant was determined as 0.0801, 0.2789 and 0.4051 h^{-1} for 140, 160,

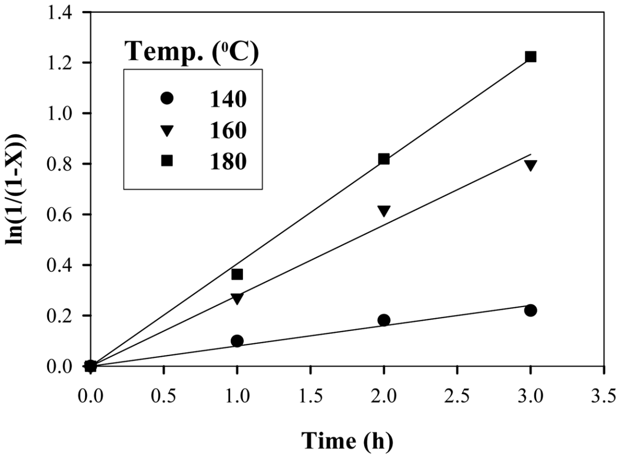


Fig. 1. Plots of ln[1/(1−X)] vs. time.

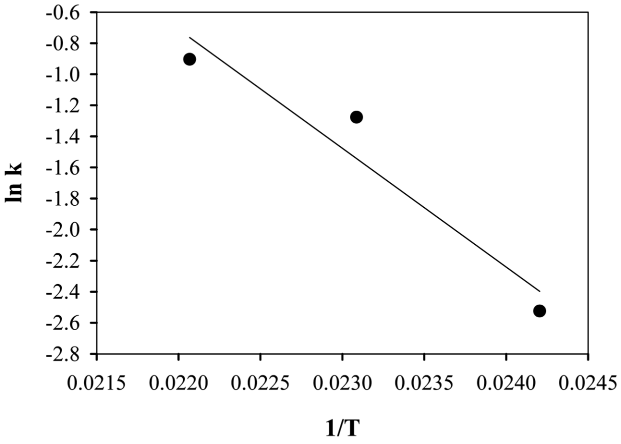


Fig. 2. Arrhenius plot.

and 180 °C, respectively. From the Arrhenius plot (Fig. 2), the activation energy was estimated as 63.6 kJ/mol.

CONCLUSION

Imidazolium salt ionic liquids of shorter alkyl chain length and more nucleophilic anion exhibited higher reactivity in the synthesis of DMC from PC and methanol. The conversion of PC increased with the increase of reaction temperature and carbon dioxide pressure. The transesterification of PC with methanol by using ionic liquid catalyst can be considered as pseudo-first order with respect to PC concentration and its activation energy was estimated as 63.6 kJ/mol.

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REFERENCES

1. A. Behr, *Angew. Chem., Int. Ed.*, **27**, 661 (1988).
2. M. Aresta and E. Quaranta, *Chem. Tech.*, **27**, 32 (1997).
3. B. M. Trost, *Science*, **254**, 1471 (1991).
4. S. Fujita, B. M. Bhanage, Y. Ikushima, M. Shirai, K. Torii and M. Arai, *Catal. Lett.*, **79**, 95 (2002).
5. M. Aresta and A. Dibenedetto, *J. Mol. Catal. A Chem.*, **182**, 399 (2002).
6. M. Aresta, A. Dibenedetto and I. Tommasi, *Appl. Organomet. Chem.*, **14**, 799 (2000).
7. I. Billard, G. Moutiers, A. Labet, A. E. Azzi, C. Gaillard, C. Mariet and K. Lutzenkirchen, *Inorg. Chem.*, **42**(5), 1726 (2003).
8. H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A. Chem.*, **182**, 419 (2002).
9. D. S. Kim and W. S. Ahn, *Korean J. Chem. Eng.*, **20**, 39 (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. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
13. B. M. Bhanage, S. Fujita, Y. Ikushima and M. Arai, *Appl. Catal. A. Gen.*, **219**, 259 (2001).
14. H. J. Buysch, H. Krimm and H. Rudolph, *US Patent* 4, 181, 676 (1980).
15. T. Kondoh, Y. Okada, F. Tanaka, S. Asaoka and S. Yamamoto, *US Patent* 5, 436, 362 (1995).
16. T. Tatsumi, Y. Watanake and K. A. Koyano, *Chem. Commun.*, 2281 (1996).
17. H. Abimanyu, K. S. Yoo, D. J. Moon, B. S. Ahn and J. W. Song, *J. Ind. Eng. Chem.*, **11**, 502 (2005).
18. Y. Watanabe and T. Tatsumi, *Micropor. Mesopor. Mater.*, **22**, 399 (1998).
19. E. S. Jeong, K. H. Kim, D. W. Park, S. W. Park and J. W. Lee, *React. Kinet. Catal. Lett.*, **86(2)**, 241 (2005).
20. P. Bonhote, A. P. Dias, N. Papgeorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, **35**, 1168 (1996).
21. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, **3**, 156 (2001).
22. J. S. Tian, J. Q. Wang, J. Y. Chen, J. G. Fan, F. Lai and L. N. He, *Appl. Catal. A. Gen.*, **301**, 215 (2006).
23. C. M. Starks, C. L. Littoa and M. Halpern, *Phase transfer catalysis*, Chapman and Hall, New York, 1994.