

이온성 액체를 이용한 프로필렌과 메탄올로 부터
디메틸 카보네이트의 합성

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**Synthesis of Dimethyl Carbonate from Propylene Carbonate and Methanol
Using Imidazolium Salt Catalysts**

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INTRODUCTION

Dimethyl carbonate (DMC) has been considered as a green chemical raw material of the 21st century and registers as an innocuous chemical in the world [1,2]. DMC represents a viable alternative to acetate esters and ketones in most applications, from paints to adhesives, taking advantage of its good solvency power. Nowadays, DMC has become a new basic material in the organic synthesis field.

Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted. Especially cyclic carbonate like PC, has been synthesized from CO₂ and epoxide with 1-alkyl-3-methylimidazolium salts ionic liquids [3]. Many reactions catalyzed with ionic liquids and showing high performance have been reported [4].

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

MATERIALS

Propylene carbonate (PC) was supplied by Aldrich Co. without further purification. Room temperature ionic liquids based on 1-n-ethyl-3-methylimidazolium (EMIm), 1-n-butyl-3-methylimidazolium (BMIm), 1-n-hexyl-3-methylimidazolium (HMIm) or 1-n-otyl-3-methylimidazolium (OMIm) with different anions such as Cl⁻, BF₄⁻, PF₆⁻ were prepared according to

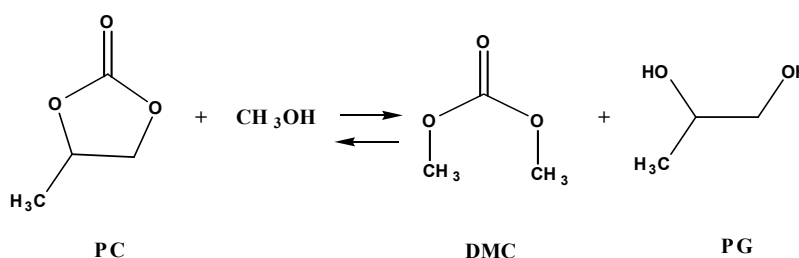
the procedures reported previously [5]. The ionic liquids were dried and degassed under vacuum at 100 °C for 4 h prior to use.

EXPERIMENTAL

The synthesis of DMC from propylene carbonate and methanol 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 the CO₂ was introduced at room temperature to a preset pressure. The reaction was started by stirring when the desired temperature and pressure were attained. The product was analyzed by gas chromatograph.

RESULTS AND DISCUSSION

The synthesis of DMC from PC and methanol was carried out using various quaternary ammonium salt catalysts under carbon dioxide pressure. The synthesis of DMC from PC and methanol shown in Scheme 1 was carried out using ionic liquid catalysts.



Scheme 1.

The conversions of PC with different ionic liquids consisting of cations of EMIm⁺, BMIm⁺, HMIm⁺, OMIm⁺ and anions of Cl⁻, BF₄⁻, PF₆⁻ are summarized in Table 1. The order of the PC conversion decreased as the size of the cation of the imidazolium salt ionic liquids increased from EMIm⁺ > BMIm⁺ > HMIm⁺ > OMIm⁺, probably due to the increase of steric hindrance.

The effects of anions in the reaction of EC and methanol are compared in Run 1, 5 and 6. The conversion of PC increased in the order of PF₆⁻ < BF₄⁻ < 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 intermediate with methanol.

Table 2 is showed that the effect of pressure was studied using EMImCl. The conversion of PC increased as the pressure increased from 200 psig to 800 psig. But, the conversion of PC decreased as the high pressure like 1000 psig.

Table 3 summarizes the conversions of PC with different temperature. The reaction temperature strongly affected the conversion; the increase of temperature from 140 °C to 180 °C increased the conversion.

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

Run	Catalyst	PC conversion (%)	Selectivity (%)	
			DMC	PG
1	EMImCl	35.72	43.17	40.49
2	BMImCl	26.69	66.96	58.61
3	HMImCl	22.05	33.42	20.39
4	OMImCl	20.75	25.55	14.27
5	EMImBF ₄	25.19	31.93	19.97
6	EMImPF ₆	22.72	21.41	11.35

Reaction condition : MeOH/PC = 8/1, catalyst = 2 mmol, P = 500 psig, T = 140 °C, time = 6 h.

Table 2. Conversion of PC and selectivity to DMC and PG with ionic liquid catalysts of different pressure.

Run	Pressure (psig)	PC conversion (%)	Selectivity (%)	
			DMC	PG
7	200	20.29	21.68	4.86
1	500	35.72	43.17	40.49
8	800	36.58	15.70	13.27
9	1000	21.26	17.13	4.27

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, PG with ionic liquid catalysts of different temperature.

Run	Temperature (°C)	PC conversion (%)	Selectivity (%)	
			DMC	PG
1	140	32.71	46.06	48.51
10	160	55.42	80.11	97.74
11	180	75.12	80.44	90.67

Reaction condition : MeOH/PC = 8/1, catalyst = EMImCl (2 mmol), P = 500 psig, time = 6 h.

The transesterification of ethylene 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. 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 fitted well to the first order rate equation. The pseudo first order reaction rate constant was determined as 0.0467, 0.3209 and 0.4051 h⁻¹ for 140, 160, and 180 °C, respectively. From the Arrhenius plot, the activation energy was estimated as 85.0 kJ/mol.

CONCLUSIONS

Ionic liquid of more nucleophilic anion exhibited higher reactivity. The conversion of PC increased with the increase of reaction temperature and carbon dioxide pressure. The transesterification of PC to methanol can be considered as first order with respect to PC concentration and its activation energy

was estimated as 85.0 kJ/mol.

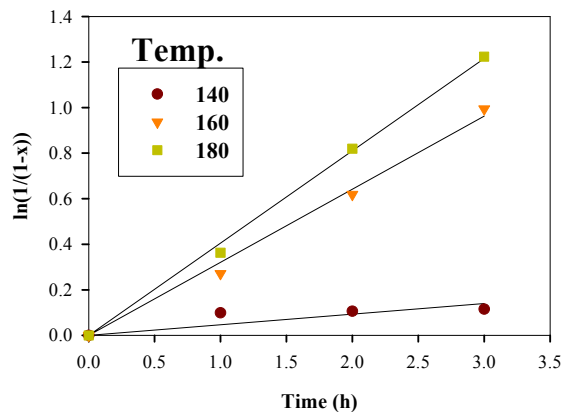


Fig. 1. Plots of $\ln[1/(1-X)]$ vs. time

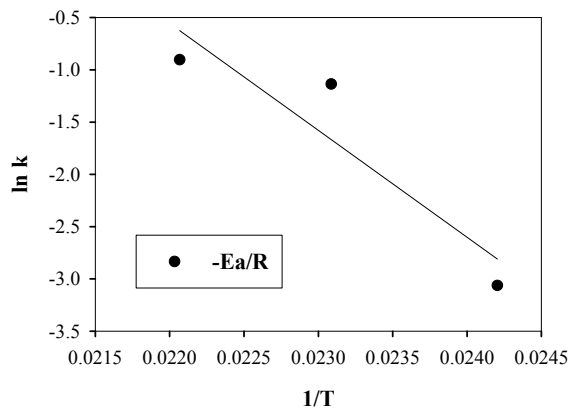


Fig. 2. Arrhenius plot.

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