

## 4급 암모늄염 촉매를 이용한 프로필렌카보네이트와 메탄올로부터 디메틸카보네이트의 합성

문나영, 주혜영, 이은하, 김경훈, 박대원\*  
부산대학교 화학공학과  
(dwpark@pusan.ac.kr\*)

### Synthesis of Dimethyl Carbonate from Propylene Carbonate and Methanol Using Quaternary Ammonium Salt

Na-Young Mun, Hye-Young Ju, Eun-Ha Lee, Kyung-Hoon Kim, Dae-Won Park\*  
Division of Chemical Engineering, Pusan National University  
(dwpark@pusan.ac.kr\*)

#### Introduction

Dimethyl carbonate (Mw. 90.08, b.p. 90.3 °C) is attracting much attention in recent years due to its versatile usage. In many aspects, DMC has attracted worldwide attention as an environmentally nontoxic material. DMC can be variously applied as a solvent in carbonylation and methylation agent owing to the presence of a carbonyl group and two methoxy groups in its molecule[1-3]. In addition, due to its high oxygen content, a lot of research on the possibility of DMC as a gasoline fuel additive is being conducted. DMC has about three times higher oxygen content than MTBE (methyl tert-butyl ether)[4]. Also DMC is a safe substitute for phosgene, dimethyl sulfate and methyl halides[5]. Mostly, DMC has been synthesized by using these conventional toxic and corrosive methylating agents and there are stoichiometric amount of by-products. Therefore a number of nontoxic DMC synthetic processes have been suggested and some processes have already been commercialized[6-7].

The characteristic of the transesterification method is that propylene glycol (PG) is simultaneously produced in equimolar ratio with DMC as shown is scheme 1. Since PC can be produced from carbon dioxide and propylene oxide, the transesterification method is believed to be more beneficial in terms of the decrease of green house effect than other reaction routes.

In this study, we investigated the synthesis of DMC through the transesterification of propylene carbonate (PC) with methanol using quaternary ammonium salt catalysts. Fundamental aspects of reaction characteristics have been investigated using a stainless steel autoclave. Special focus of the study was placed on the effects of quaternary ammonium salt catalyst structure on the yield of DMC.

#### Experimental

Quaternary ammonium salt catalysts based on different alkyl cations such as

tetrapropylammonium (TPA<sup>+</sup>), tetrabutylammonium (TBA<sup>+</sup>), tetrahexylammonium (THA<sup>+</sup>), tetraoctylammonium (TOA<sup>+</sup>), tetradodecylammonium (TDodA<sup>+</sup>), and those with different anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> were used. The transesterification reaction was carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, quaternary ammonium salt (2 mmol), propylene carbonate (25 mmol) and excess methanol (200 mmol) were charged into the reactor, and the CO<sub>2</sub> was introduced at room temperature to a prest pressure. The reaction was started by stirring when the desired temperature and pressure were attained. The analysis of the products and reactants was performed by using a gas chromatograph (HP 6890N) equipped with a FID and a capillary column (HP-5, 5% phenyl methyl siloxane). DMC yield was calculated on the basis of PC as a limited reactant.

### **Result and Discussion**

The synthesis of DMC from PC and methanol was carried out using various quaternary ammonium salt catalysts with different cations of TPA<sup>+</sup>, TBA<sup>+</sup>, THA<sup>+</sup>, TOA<sup>+</sup>, TDodA<sup>+</sup> and anions of Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>. The conversions of PC and selectivities to DMC are summarized in Table 1. The catalytic activity of quaternary ammonium salt usually depends on the corresponding catalyst cation and anion. The activity increased in the order of TPA<sup>+</sup> < TBA<sup>+</sup> < THA<sup>+</sup> < TOA<sup>+</sup> < TDodA<sup>+</sup>. Bulky quaternary salts, having longer distances between cations and anions, are generally known to exhibit higher activity due to higher capacity in activating anions. The effects of anions in the transesterification of PC and methanol are compared in Run 2, 6, 7 and 8. When the quaternary ammonium salts of different anions were used, the conversion of PC increased in the order of HSO<sub>4</sub><sup>-</sup> < I<sup>-</sup> < Br<sup>-</sup> < Cl<sup>-</sup>, which is consistent with the order of the nucleophilicity of anions.

The catalytic activity of a quaternary ammonium salt usually depends on the corresponding catalyst cation and counter anion [8,9]. In order to understand the effects of the cation structure in the transesterification between methanol and PC, quaternary ammonium chloride catalysts of different alkyl cations, TPAC, TBAC, THAC, TOAC, and TDodAC were used at 140 °C. The conversion of PC and selectivities to DMC and PG are summarized in Table 1.

The conversion of PC increased with the increase of alkyl chain length of the cation of quaternary ammonium chloride salts. Bulky quaternary salt, having longer distances between cation and anion, is generally known to exhibit higher activity in activating anions [15]. The mechanism of DMC synthesis has been reported to consist the formation of an intermediate from the reaction of PC and CH<sub>3</sub>O<sup>-</sup> [17]. Quaternary salt (QX) reacts with methanol to form CH<sub>3</sub>O<sup>-</sup>Q<sup>+</sup>, which in turn participates to the reaction with PC. Therefore, bulky quaternary salts are effective for the production of DMC.

In order to understand the effects of quaternary salt anions in the reaction of PC and methanol, tetrabutyl ammonium salts of different anions (TBAC, TBAB, TBAI) are used at 140 °C. Table 1 also shows that the PC conversion increased in the order of I<sup>-</sup> < Br<sup>-</sup> < Cl<sup>-</sup>, which agrees with the order of

nucleophilicity of the anions.

Fig. 1 demonstrates time variant conversion of PC and selectivities to DMC and PG with TBAC at 140 °C. It can be seen that PC conversion and selectivities to DMC and PG increased quite rapidly up to 3 h of reaction, and then they maintained at nearly constant values or increased a little over 3 h of reaction. Therefore, the kinetic studies were performed for the reaction time up to 2 h.

The transesterification reaction between PC and MeOH is expressed as  $PC + 2 M \rightarrow D + G$  ; where M, D, and G represent MeOH, DMC, and PG, respectively. If the reaction is assumed elementary, the reaction rate can be expressed

$$-r_{PC} = -[dC_{PC}/dt] = kC_{PC}C_M^2$$

Since MeOH is used in excess compared to PC,  $C_M$  can be assumed constant during the reaction.

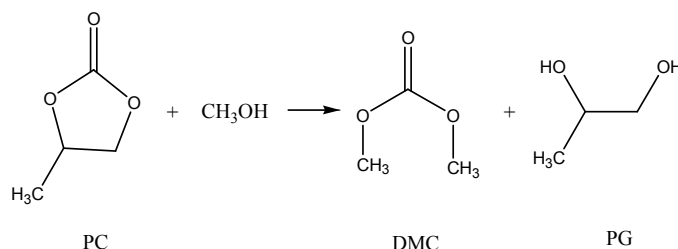
Therefore, the reaction rate equation can be written as a pseudo first order with respect to the concentration of PC.

$$-r_{PC} = k'C_{PC}$$

$$\text{Where } k' = kC_M^2$$

Fig. 2 shows the plot of  $\ln[(C_{PC})_0/C_{PC}]$  vs. time during first 2 h. Quite good straight lines were obtained, and the pseudo first-order reaction rate constants for 120, 130 and 140 °C were 0.0908, 0.1167 and 0.1563 h<sup>-1</sup>, respectively. From the Arrhenius plot of the first order reaction rate, one can estimate the activation energy as 37.7 kJ/mol.

Table 2 shows the effect of reaction temperature on the PC conversion and the DMC and PG selectivities. As the reaction temperature increased, the PC conversion and the selectivities to DMC and PG increased.



Scheme 1.

Table 1. Effect of catalyst structure on PC conversion and selectivities to DMC and PG

CO <sub>2</sub> pressure (psig)	PC conversion (%)	Selectivity (%)	
		DMC	PG
TPAC	48.9	68.3	77.4
TBAC	58.8	81.0	70.5
THAC	59.0	67.0	75.6
TOAC	60.2	68.5	84.8
TDodAC	61.6	67.6	72.6
TBAB	43.2	77.0	98.0
TBAI	37.6	74.4	93.2

PC = 25 mmol, MeOH = 200 mmol, catalyst = 2 mmol, temp. = 140 °C, time = 6 h

Table 2 Effect of temperature on PC conversion and selectivities to DMC and PG

Temperature (°C)	PC conversion (%)	Selectivity (%)	
		DMC	PG
120	20.4	64.9	5.2
130	31.3	67.1	22.0
140	58.8	80.8	70.4

PC = 25 mmol, MeOH = 200 mmol, TBAC = 2 mmol,

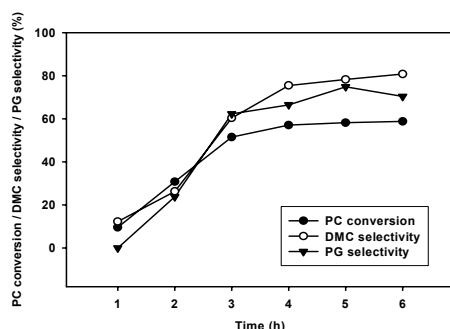


Fig. 1. Time variant conversion of PC and selectivity to DMC and PG.

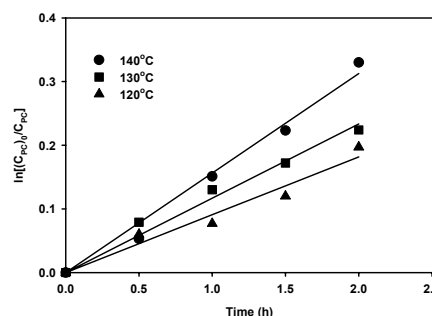


Fig. 2. Pseudo first-order plots of  $\ln[(C_{PC})_0/C_{PC}]$  vs. time for TOAC catalyst

### Acknowledgments

This work was supported by the KOSEF (R01-2003-000-10020-0), and Brain Korea 21 and Brain Busan 21 program.

### Reference

- [1] K. Tomishige, K. Kunimori, *Appl. Catal. A: Gen.* 237 (2002) 103-109.
- [2] M. Aresta, E. Quaranta, *CHEMTECH*, (1997) 32.
- [3] A. A. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [4] M. A. Pacheco, C. L. Marshall, *Energy & Fuels*, 11 (1997) 2.
- [5] Y. Ono, *Appl. Catal. A: Gen.* 155 (1997) 133.
- [6] F. Rivetti, *Chemistry*, 3 (2000) 497-503.
- [7] D. Delledonne, F. Rivetti, U. Romano, *Appl. Catal. A: Gen.* 221 (2001) 241-251.
- [8] A. A. Shaikh, S. Sivaram: *Chem. Rev.*, 96, 951 (1996).
- [9] T. Wei, M. Wang, W. Wei, Y. Sun, B. Zhong: *Fuel Process. Technol.*, 83, 175 (2003).