

Carboxylation Using Supercritical Fluid and Ionic Liquid

Loan Thi To Vo¹, Jong Won Kim¹, Hong Bum Lee², Choon Sup Ra², and Jae-Jin Shim*¹

¹ School of Display and Chemical Engineering, Yeungnam University, Korea

²Department of Chemistry, Yeungnam University, Korea

Corresponding author: jjshim@yu.ac.kr, Fax: +82-53-810-4711

ABSTRACT

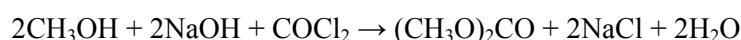
In the presence of ionic liquid and supercritical fluid, organic compounds can be made environmentally friendly without harmful organic solvents. In this study we synthesized dimethyl carbonate from carbon dioxide and methanol, and ethylphenyl carbonate from styrene oxide and carbon dioxide. Ionic liquids such as [bmim][BF₄] and [bmim][PF₆] have been used as polar solvents. The yield was measured as a function of the amount of reactants, reaction time, the amount of catalyst, the amount of ionic liquid, and types of ionic liquid as well as temperature and pressure.

INTRODUCTION

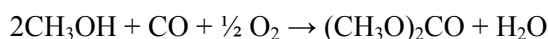
Polycarbonate that has excellent physical properties, excellent toughness and good transparency is used in making bullet-proof windows, exterior automotive components, outdoor lighting fixtures, plastic lenses, medical supply components, and equipment housings. However, since polycarbonate has been made via the toxic phosgene and carbon monoxide processes, attention has been focused on making polycarbonate from DMC made without using phosgene or carbon monoxide. DMC is been widely used in many areas such as high performance resins, solvents, dye intermediates, drugs, perfumes, antiseptics, lubricating oil additives and a useful organic intermediate that can react with alcohols, phenols, amines, aminoalcohols to manufacture various products such as polycarbonate, isocyanate, carbamate, and malonate [1]. Due to high solubility in gasoline and high oxygen content as well as nontoxicity, it is considered as a potential alternative to the toxic conventional octane number booster, methyl tert-butyl ether (MTBE) produced from butane, for internal combustion engine [2].

The conventional process used in DMC synthesis is as follows:

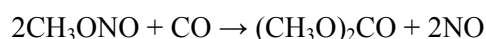
(a) Phosgene Process



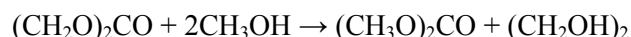
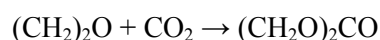
(b) ENIChem Process(Cu catalysts) (MeOH Oxidation Process)



(c) Ube Process (Methylnitrite Process)

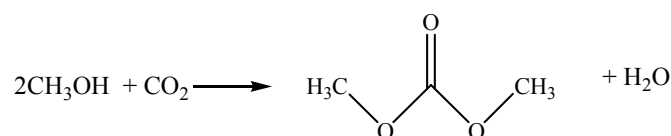


(d) Esterification Process



Though the phosgene process (a) is the first process in manufacturing DMC, there have been many problems throughout the entire process due to its toxicity. ENIChem process (b) and Ube process (c) have been studied commercialized as alternatives to the phosgene process (a) [2,3].

However, these processes also have critical problems of using toxic carbon monoxide. To avoid these problems, Texaco has developed process (d) for manufacturing DMC from ethylene oxide, carbon dioxide and methanol using basic catalysts. In addition, several processes using epoxides, ammonia, alkyl chlorides, trimethyl orthoacetate or tert-amines and acetylene have been reported [2]. A direct method of synthesizing DMC from CO₂ and methanol has been studied by some research groups [4,5].



This process is simple and environmentally friendly and does not require toxic phosgene or carbon monoxide. Although this process has a very low yield of DMC as it is strongly limited by the thermodynamic equilibrium, however, due to the recent activities of United Nations such as Rio Agreement (Brazil, 1992) and Kyoto Protocol (1997), people are interested in consuming CO₂, a greenhouse gas, as a raw material.

Moreover, the carboxylation of epoxides affording the cyclic carbonates *via* the cyclo-addition of CO₂ with epoxides has emerged as one of the promising methods in the green processes. Five-membered cyclic carbonates are valuable as monomers, polar aprotic solvents and intermediates for the synthesis of pharmaceuticals and fine chemicals.

Recently, ionic liquids (ILs) (Figure 1) are getting attention in synthesis of organic compounds due to its special characteristics. The ionic salts that exist as liquid below 373.15 K is called as ionic liquid. The ionic liquids that exist as a liquid below room temperature is called room temperature ionic liquid (RTIL) [6]. ILs are nonvolatile, nontoxic, nonflammable, exist as liquid over a wide temperature range and have good thermal stability and ionic conductivity. They also dissolve inorganic and organic metal compounds due to their high polarity. Some people call ILs “designer solvents” as their melting points, densities, viscosities, and hydrophilic- and hydrophobic characteristics can be adjusted by properly choosing cations and anions [7]. Therefore, ILs can be applied to variety of areas such as catalysis, separation and electrochemistry.

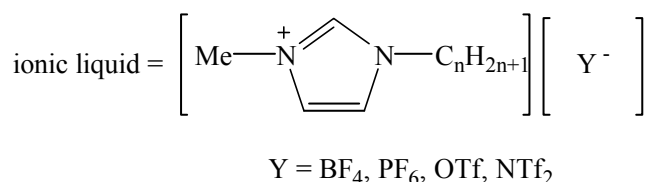
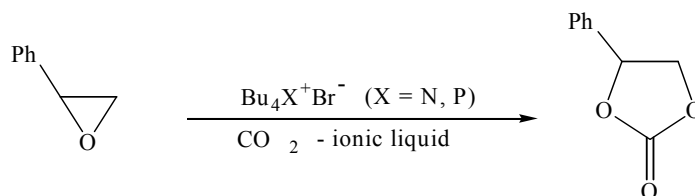


Figure 1: The structures of ionic liquids

To use the advantages of supercritical fluids and ionic liquids, we have studied the direct method for DMC synthesis from methanol and CO₂ and the solvent-free carboxylation of styrene oxide (Scheme 1) in ionic liquid using some catalysts.



Scheme 1: The solvent-free carboxylation of styrene oxide

EXPERIMENTAL

Materials

High purity CO₂ (99.995%) was purchased from Korea Industrial Gases and used without further purification. Two ionic liquids, [bmim][PF₆] (> 99 %, moisture content = 1,200 ppm, chloride content = 79 ppm) and [bmim][BF₄] (> 99 %, moisture content = 5,900 ppm, chloride content = 520 ppm), were purchased from C-Tri. The moisture content was reduced to about 700 ppm by evacuating the vessel containing ionic liquid. Other chemicals were purchased from Aldrich Chemical and used without any further purification.

Experimental Apparatus and Procedure

The experimental apparatus used in this research is shown in Figure 2. The reactor is a variable-volume view cell with 26 ml in volume that can maintain the pressure constant during the reaction and that the reaction progress inside it can be seen through the sapphire window. Firstly, a known amount of reactants and catalyst was placed in the front chamber of the cell. After capping the cell, a fixed amount of carbon dioxide was introduced into the same chamber, while stirring. The cell was heated to the desired reaction temperature and maintained during reaction time. After a certain reaction time, the cell was put into an ice bath to stop the reaction. When the temperature in the cell was dropped to about 275.15 K, the vapor space was vented slowly to a cold trap. After the entire vapor passed the cold trap, the remaining liquid in the cell was collected in a vial by dissolving it appropriate solvent. The sample from the gas phase (collected in the cold trap) was analyzed by gas chromatography (GC) and the sample from the liquid phase, by 300 MHz NMR (Bruker, Model DPX 300). The GC (Donam Instruments, DS6200) was equipped with a 3 m column (1/8 inch OD) packed with Carbowax 20M. The GC analysis conditions are as follows: (a) injector temperature 453.15 K, (b) detector type: TCD, (c) detector temperature: 473.15 K, (d) oven temperature: initially at 343.15 K, programmed at a rate of 5 K/min to 373.15 K, then, programmed at a rate of 10 K/min until it reaches 443.15 K.

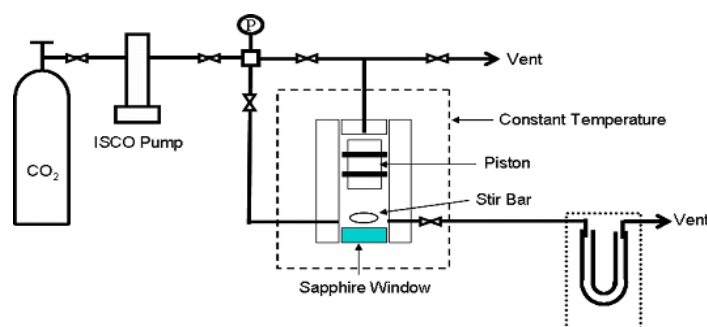


Figure 2: Schematic diagram of the experimental equipment.

RESULTS AND DISCUSSION

Synthesis of DMC with Methanol

The reaction at 373.15 K and 10 MPa for 5 hours were performed to examine the effect of catalyst on the yield of DMC. The amount of [bmim][PF₆] was 4 mmol and the amounts of reactants were 90 mmol, 220 mmol, and 0.4 mmol for CH₃OH, CO₂ and CH₃I, respectively. Figure 3 shows the variation in the DMC yield due to the change in the amount of catalyst (K₂CO₃). Up to 0.3 mmol of catalyst, the yield of DMC remained nearly the same (about 1 mol%), but thereafter, increased linearly so that it reached 3 mol% at 0.8 mmol.

The reactions at 373.15 K for 5 hours were done to investigate the effect of pressure on the yield of DMC. The amounts of [bmim][PF₆] and K₂CO₃ were 4 mmol and 0.6 mmol, respectively, and the amounts of reactants were 90 mmol, 220 mmol, and 0.4 mmol for CH₃OH, CO₂ and CH₃I, respectively. The DMC yield was plotted versus the reaction pressure in Figure 4. As the yield of DMC was defined as the mole ratio of DMC and methanol, the DMC yield will be affected by the

amount of methanol. As Fujita et al.[8] proposed the reaction mechanism, one mole of methanol will react with one mole of base catalyst to form one mole of methoxy ion, while one mole of catalyst are oxidized. At low pressure, the yield of DMC was much smaller than that at high pressure. As the reaction temperature is higher than the boiling point of methanol, at low pressure almost all the methanol is at the fluid and not much methanol exist in the ionic liquid phase to react with K_2CO_3 but at high pressure some of the methanol dissolves into the ionic liquid and the reaction with K_2CO_3 proceeds as Fujita et al. proposed.

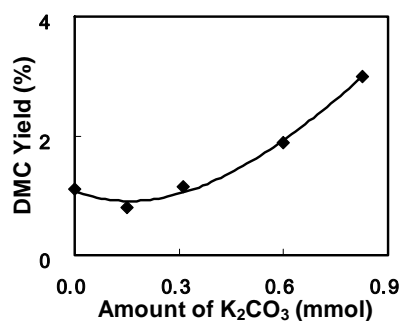


Figure 3: Effect of catalyst on the yield of DMC. Reaction conditions: $T = 373.15$ K, $P = 10$ MPa, time = 5 h, $[bmim][PF_6] = 4$ mmol. $CH_3OH = 90$ mmol, $CO_2 = 220$ mmol, $CH_3I = 0.4$ mmol.

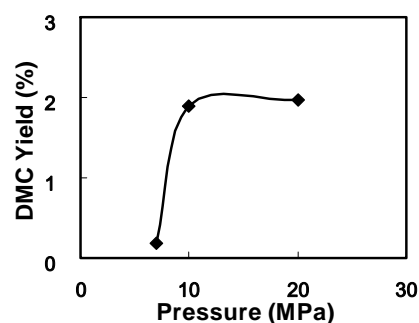


Figure 4: Effect of pressure on the yield of DMC. Reaction conditions: $T = 373.15$ K, time = 5 h, $[bmim][PF_6] = 4$ mmol. $CH_3OH = 90$ mmol, $CO_2 = 220$ mmol, $K_2CO_3 = 0.6$ mmol, $CH_3I = 0.4$ mmol.

The reactions at the same condition using the different IL, $[bmim][BF_4]$ were done. The yield of DMC when $[bmim][PF_6]$ was used appeared smaller than that when $[bmim][BF_4]$ was used. Therefore, $[bmim][BF_4]$ is about 20% better in the synthesis of DMC (Figure 5). As the polarity of $[bmim][BF_4]$ is much larger than that of $[bmim][PF_6]$, the former IL will influence the reaction more than the latter, by making more methoxy ions and thus making more DMC.

The influence of the concentration of methanol on the yield of DMC was also determined. The amount of $[bmim][BF_4]$, CO_2 , K_2CO_3 and CH_3I were 4, 220, 0.6, and 0.4 mmol, respectively. The variation of the DMC yield is shown in Figure 6. The DMC yield decreased as increasing the amount of methanol. If the reaction mechanism follows Fujita's, the number of methoxy ions does not change with the amount of methanol and thus the amount of DMC formed is not changed. Therefore, the DMC yield should be inversely proportional to the amount of methanol.

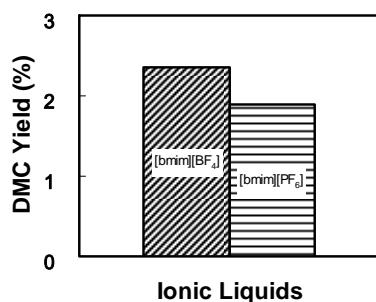


Figure 5: Effect of ionic liquids on the yield of DMC. Reaction conditions: $T = 373.15$ K, $P = 10$ MPa, time = 5 h, ionic liquids = 4 mmol, $CH_3OH = 90$ mmol, $CO_2 = 220$ mmol, $K_2CO_3 = 0.6$ mmol, $CH_3I = 0.4$ mmol.

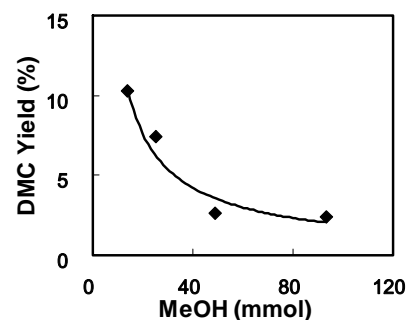


Figure 6: Effect of methanol on the yield of DMC. Reaction conditions: $T = 373.15$ K, $P = 10$ MPa, time = 5 h, $[bmim][BF_4] = 4$ mmol, $CO_2 = 220$ mmol, $K_2CO_3 = 0.6$ mmol, $CH_3I = 0.4$ mmol.

Synthesis of Ethylphenyl Carbonate from Styrene Oxide and Carbon Dioxide

Table 1 shows the results of the experiments performed to optimize the conditions for the carboxylation of styrene oxide in the presence of catal amounts of several quaternary ammonium salts (2 mol%) under 560 psi of CO₂ and at 120°C. The reaction catalyzed by tetrabutylammonium bromide gave the highest yield of styrene carbonate, while the reaction favored a longer alkyl chain length (entry 1, 2, 4, 7, 12). The activities of Bu₄NX (X = halogen) decreased as the following orders: Br>Cl>I (entry 9, 10, 12). The reaction temperature was found to be crucial to the progress of the carboxylation of styrene oxide using quaternary ammonium salts. The reactions of CO₂ with styrene oxide gave a higher yield of the carbonate at 120°C for 2 hours than that at 80°C for a longer time (entry 3, 6, 11). For tetrabutylammonium bromide-catalyzed reaction, the optimized yield as achieved with the reaction time of 4 hours (entry 13)

Table 1: Effect of tetraalkylammonium halides on the carboxylation of styrene oxide under 560 psi of CO₂ pressure

| Entry | Catalyst | Temp (°C) | Time (h) | Yield (%) ^a |
|-------|--|-----------|----------|------------------------|
| 1 | (CH ₃) ₄ N(Br) | 120 | 2 | trace |
| 2 | (CH ₃ CH ₂) ₄ N(Br) | 120 | 2 | trace |
| 3 | [CH ₃ (CH ₂) ₇] ₄ N(Br) | 80 | 4 | 32 |
| 4 | [CH ₃ (CH ₂) ₇] ₄ N(Br) | 120 | 2 | 42 |
| 5 | [CH ₃ (CH ₂) ₇] ₄ N(Br) | 120 | 4 | 48 |
| 6 | C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃ | 80 | 4 | 30 |
| 7 | C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃ | 120 | 2 | 39 |
| 8 | C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃ | 120 | 4 | 55 |
| 9 | (CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Cl) | 120 | 2 | 60 |
| 10 | (CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(I) | 120 | 2 | 56 |
| 11 | (CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br) | 80 | 4 | 34 |
| 12 | (CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br) | 120 | 2 | 81 |
| 13 | (CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br) | 120 | 4 | 96 |

^aIsolated yields.

Table 2: Effect of reaction temperature on the carboxylation of styrene oxide

| Entry | Ionic liquid (mol %) | Onium salt (2 mol %) | Temperature (°C) | CO ₂ Pressure (psi) | Time(h) | Yield(%) ^a |
|-------|------------------------------|----------------------|------------------|--------------------------------|---------|-----------------------|
| 1 | [bmim][BF ₄](20) | Bu ₄ PBr | 80 | 560 | 2 | 12.5 |
| 2 | [bmim][BF ₄](20) | Bu ₄ PBr | 80 | 560 | 4 | 30.8 |
| 3 | [bmim][BF ₄](40) | Bu ₄ PBr | 80 | 560 | 4 | 30.0 |
| 4 | [bmim][BF ₄](60) | Bu ₄ PBr | 80 | 560 | 4 | 28.7 |
| 5 | [bmim][BF ₄](20) | Bu ₄ PBr | 80 | 2030 | 2 | 8.2 |
| 6 | [bmim][BF ₄](20) | Bu ₄ PBr | 120 | 560 | 2 | 70.2 |
| 7 | [bmim][BF ₄](20) | Bu ₄ NBr | 80 | 560 | 4 | 33.0 |
| 8 | [bmim][BF ₄](20) | Bu ₄ NBr | 120 | 560 | 2 | 71.1 |
| 9 | [bmim][BF ₄](20) | Bu ₄ NBr | 120 | 2030 | 2 | 99.2 |

^aisolated yield

As shown in Table 2, the yield of the styrene carbonate was strongly affected by the reaction temperature. The yield of the styrene carbonate reached up to 99% with [bmim][BF₄] under supercritical condition (2,030 psi) at 120 °C (entry 9). However, the reaction as a lower reaction temperature (80°C) usually gave a poor conversion, irrespective of varying the concentration of ionic liquids (entry 1-4), reaction time (entry 2-4,7) and CO₂ pressure (entry 5,6). Moderate yields were obtained at elevated temperature under low CO₂ pressure (560 psi) (entry 6,8).

CONCLUSIONS

The yield of DMC was higher as the ionized portion of the reactant increased when the amount of IL or the amount of catalyst increased. It is important to make more methoxy ions and to force them to react with CO₂ in the synthesis of DMC. The ratio of reactant and CO₂ has influenced on the DMC synthesis. For a fixed amounts of catalysts and ionic liquids, the increase in the amount of reactant results in lowering the concentration of CO₂, leading to the decrease in the probability that methoxy ions see CO₂ molecules, lowering the DMC yield. The DMC yield does not change much even when the reaction pressure gets larger, indicating that the CO₂ density does not have a large effect on DMC synthesis.

The carboxylation of styrene oxide was catalyzed by some onium salts such as quaternary ammonium and phosphonium salts to produce styrene carbonate in an efficient and environmentally benign fashion. The reactions depends on greatly on the alkyl chain length of the substituents of the salts and the reaction using catalysts with an optimum chain length give a high yield of the cyclic carbonate. The formation of styrene carbonate increased with the concentration of ionic liquids, CO₂ pressure and temperature.

ACKNOWLEDGMENT

This research was supported by the grant (RTI04-01-04) from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE).

REFERENCES

- [1] ONO, Y., *Appl. Catal. A: General*, Vol. 155, **1997**, p. 133
- [2] PACHECO, M., A., MARSHALL C., L., *Energy and Fuels*, Vol. 11(1), **1997**, p. 2
- [3] TUNDO, P., *Pure Appl. Chem.*, Vol. 73(7), **2001**, p. 1117
- [4] JIANG, C., GUO, Y., WANG, C., HUA, C., WU, Y., WANG E. *Appl. Catal. A: General*, Vol. 256, **2003**, p. 203
- [5] LEE, Y., S., GO, J., C., KIM, B., S., KIM, G., J., GU, G., G., *J. Korean Ind. Eng. Chem.*, Vol. 14(7), **2003**, p. 885
- [6] FREDLAKE, C., P., CROSTHWAITE, J., M., HERT, D., G., Hert, AKI, S., N. V. K., BRENNECKE J. F., *J. Chem. Eng. Data*, Vol. 49, **2004**, p. 954
- [7] KIM, D., B., WON, J., O., KIM, H., S., *Polym. Sci. Technol.*, Vol. 15(4), **2004**, p. 449
- [8] FUJITA, S. I., BHANAGE, B. M., IKUSHIMA, Y., ARAI, M., *Green Chem.*, Vol. 3, **2001**, p. 87.