

CYCLIC CARBONATE SYNTHESIS BY CARBON DIOXIDE FIXATION USING THE scCO₂-IONIC LIQUID REACTION SYSTEM

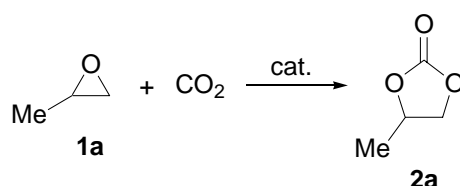
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INTRODUCTION

From the stand of the protection of the environment, the development of environmentally benign process using chemical fixation of CO₂, which is one of the greenhouse-effect gases, has been drawing much interest in industrial chemistry, because there are a lot of possibilities that carbon dioxide can be used as a safe and cheap C1 component to produce useful organic compounds. However, most of the chemical fixation have taken place at high temperatures and long reaction time is necessary, because of the low reactivity of CO₂. For carbon dioxide utilization, supercritical CO₂ (scCO₂) is attractive not only as a conventional organic solvent but also as a good substrate. Organic reactions under scCO₂ conditions are expected to be promoted even at rather milder conditions due to enhanced diffusivity and the disappearance of the gas-liquid phase boundary peculiar to the supercritical state. The chemical fixation of CO₂ has thus been attempted under supercritical conditions.

Cyclic carbonate synthesis from epoxide with CO₂ is well-known synthesis since 1967. This reaction looks environmentally benign process compared to that using poisonous phosgene,¹ and to synthesize the cyclic carbonates effectively, quite numerous homogeneous catalytic process have so far been reported.² However, this process has disadvantages such as long reaction time more than several hours and high reaction temperature more than 100 degree. Hence solid catalysts that possess high thermostability and easy catalyst-product separation leading to their recycling look promising, but the time taken to achieve the reactions in the presence of their catalysts was more than 6 h even at higher temperatures than 140 °C,² and so the activity was not so high.

Recently, we have demonstrated a remarkable promotion of the CO₂ chemical fixation in supercritical CO₂,^{3,4,5} especially at the near-critical pressure in the presence of small amount of DMF even without any catalysts.³ This is due to the function of DMF as a scCO₂ soluble acid-base catalyst. However, a reaction time longer than 12 hours was required for the CO₂ fixation to obtain cyclic carbonate, because of the poor catalytic activity of DMF. For the sake of further improvement in the activity and selectivity, we attempted to apply scCO₂-ionic liquid (IL) biphasic system⁶ to the CO₂ fixation, because IL can be used as a prominent acid-base catalyst^{7,8} as well as a suitable reaction media.⁹ Although in gaseous CO₂ below 5 MPa, the introduction of IL into propylene carbonate synthesis from propylene oxide led to high



Scheme The chemical fixation of carbon dioxide from propylene oxide to propylene carbonate.

yields, the reaction times longer than 6 hours were required for the complete fixation even at 110 °C (density; <0.08 gcm⁻³), and so the rate of reaction remains low.¹⁰ Such a low reaction rate might be attributable to the relatively lower density of gaseous CO₂, since this type of CO₂ fixation proceeds in S_N2 reaction.³ In addition, apolar organic compounds such as epoxides and carbonates are more highly soluble in higher density scCO₂ than in gaseous CO₂, whereas their solubilities in a polar IL are negligible small. Therefore we first demonstrate that the application of scCO₂ to this CO₂ fixation achieves nearly 100 % yield at reaction time shorter than 5 minutes even at the same temperature of 100 °C as that previously reported.¹⁰

I - MATERIALS AND METHODS

All materials are purchased from Sigma-Aldrich Ltd., and Wako Pure Chemical Industries, Ltd. All epoxides such as propylene oxide are purified by distillation before using.

The typical reaction experimental procedure is as follows: ionic liquid ([C₂-mim]⁺[BF₄]⁻, 0.51 mmol) was charged into a 50 cm³ reactor, and CO₂ was introduced into the reactor at desired temperatures. In the case of the scCO₂, liquid CO₂ was subsequently charged into the reactor using a high-pressure liquid pump and compressed to the desired pressures. Pressure control was achieved by a back-pressure regulator. Propylene oxide (2.0 mL, 3.0 mmol) is introduced by a high-pressure liquid pump, and the reaction in gaseous CO₂ or scCO₂ was started. After the reaction, the reactor was cooled to 0 °C with ice and pressure was released slowly. The crude product was analyzed compared with authentic samples by GC, and the yields were determined by GC using tridecane or tetradecane as an internal standard.

II - RESULTS AND DISCUSSION

The carboxylation of propylene oxide **1a** with CO₂ into propylene carbonate **2a** in the presence of the ionic liquid based on 1-methylimidazolium salt (Figure 1) was conducted in a batchwise operation under various conditions as shown in Table 1. Under supercritical conditions, NO₃⁻, CF₃SO₃⁻, BF₄⁻ and PF₆⁻ were examined as counter ions of the 1-ethyl-3-methylimidazolium ionic liquid ([C₂-mim]⁺[X]⁻ salt) for the synthesis of **1a** (runs 1 to 4). Of these, the BF₄⁻ was found to be the most effective at promoting the chemical fixation and to give an 87 % yield; however, the time taken to obtain the reasonable yield was as long as 2 h.

A series of the imidazolium ionic liquid with different alkyl chain length from C₂ to C₈ was further investigated. The yield of **2a** is increased with lengthening alkyl chain (runs 4 to 7). It is quite note worthy that the presence of [C₈-mim]⁺[BF₄]⁻ achieves nearly 100 % yield and 100 % selectivity for propylene carbonate production even at shorter reaction times around 5 minutes at the same temperature and pressure (runs 7 to 10), whose reaction rate is 77 times faster than that of previous reported.¹¹ This could be due to an increase in the solubilities of CO₂ and **1a** in IL phase with lengthening alkyl chain of IL.¹² To our surprise, lowering the temperature from 100 °C to 60 °C can also effect the 100 % yield though time-consuming for a period of 120 minutes (runs 7 and 11). However, further decrease in temperature to 40 °C was not allowed to proceed under the same pressure and time-consuming conditions (run 12). Furthermore, decreasing the pressure up to 6 MPa around a

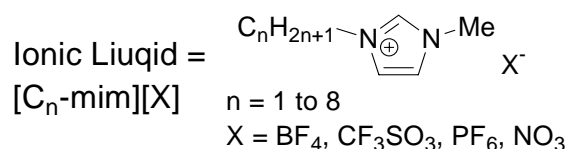


Fig. 1 Ionic liquid for the scCO₂-ionic liquid reaction system.

Table 1 Synthesis of propylene carbonate from propylene oxide with 3-methyl imidazolium based ionic liquid in supercritical carbon dioxide.

Run	Ionic Liquid	Pressure / MPa	Temp. / °C	Time / min	Yield ^a / %	Selectivity / %
1	[C ₂ -mim] ⁺ [NO ₃] ⁻	14	100	120	31	59
2	[C ₂ -mim] ⁺ [CF ₃ SO ₃] ⁻	14	100	120	25	45
3	[C ₂ -mim] ⁺ [PF ₆] ⁻	14	100	120	30	37
4	[C ₂ -mim] ⁺ [BF ₄] ⁻	14	100	120	61	87
5	[C ₄ -mim] ⁺ [BF ₄] ⁻	14	100	120	75	100
6	[C ₆ -mim] ⁺ [BF ₄] ⁻	14	100	120	95	100
7	[C ₈ -mim] ⁺ [BF ₄] ⁻	14	100	120	97	100
8	[C ₈ -mim] ⁺ [BF ₄] ⁻	14	100	30	99	100
9	[C ₈ -mim] ⁺ [BF ₄] ⁻	14	100	15	99	100
10	[C ₈ -mim] ⁺ [BF ₄] ⁻	14	100	5	98	100
11	[C ₈ -mim] ⁺ [BF ₄] ⁻	14	60	120	99	100
12	[C ₈ -mim] ⁺ [BF ₄] ⁻	14	40	120	- ^b	-
13	[C ₈ -mim] ⁺ [BF ₄] ⁻	6	100	120	71	78

^a Carbonate yields and selectivities were determined by GC using tridecane as an internal reference.

^b No reaction. Propylene oxide was recovered completely.

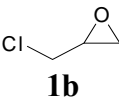
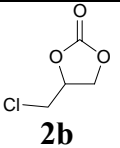
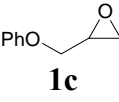
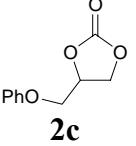

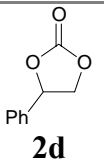

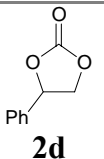
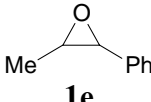
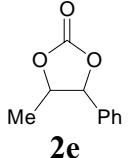
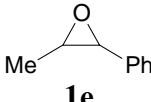
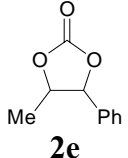
subcritical pressure of 6 MPa at a constant temperature of 100 °C led to a remarkable decrease in yield (run 13), and so this chemical fixation process was favored by the supercritical conditions. We thus demonstrate that the scCO₂-IL reaction system can synthesize propylene carbonates by chemical fixation of carbon dioxide in satisfactory yields even a lower temperature of 60 °C or shorter reaction time around 5 minutes.

A series of epoxide substrates was examined for the synthesis of the corresponding carbonates in the presence of [C₈-mim]⁺[BF₄]⁻ at 14 MPa and 100 °C (Table 2). Carbonates with alkyl side chain groups (runs 1, 2) were successfully synthesized from each epoxide in nearly 100 % yield and 100 % selectivity at reaction times shorter than 2 h, whereas the carbonates were obtained in approximately 100 % selectivity but low yields around 62% when the phenyl substituted epoxide were used. This is due to the low reactivity of β-carbon atom that would be activated by basic site of ionic liquid (BF₄⁻ anion). Moreover, the yields of carbonate **2d** and **2e** at a higher pressure of 14 MPa (runs 3, 5), are much higher than those at a lower pressure of 7 MPa (runs 4, 6) in the presence of the ionic liquid. This pressure dependence of the yield was found to be similar to that of propylene carbonate as shown in Table 1, in which the yield decreased with decreasing pressure. Consequently, there is a strong possibility that this reaction system composed of scCO₂-[C₆ or C₈-mim]⁺[BF₄]⁻ can be applied to the synthesis of various carbonates except for the phenyl substituted one.

CONCLUSION

We found that under supercritical CO₂, 1-methyl-3-octylimidazolium tetrafluoroborate ([C₈-mim]⁺[BF₄]⁻) that possesses long alkyl chain is the most effective for CO₂ fixation to carbonate. Particularly, this scCO₂-IL reaction media not only achieves nearly 100 % yield at 14MPa and at 100 °C for the propylene carbonate production at reaction times shorter than 5 minutes, leading to 77-fold rate of reaction that so far reported, but also can be applied to the synthesis of various carbonates in satisfactory yields.

Table 2 Synthesis of various carbonate in the presence of [C₈-min]⁺[BF₄]⁻ at 100 °C in CO₂.^a

Run	Epoxide	Carbonate	Pressure / MPa	Yield / %	Selectivity / %
1	 1b	 2b	14	90	99
2	 1c	 2c	14	100	100
3	 1d	 2d	14	61	97
4	 1d	 2d	7	28	98
5	 1e	 2e	14	62	98
6	 1e	 2e	7	39	99

^a Reaction time; 2h. Carbonate yields were determined by GC using tridecane as an internal standard.

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