

이온성 액체를 촉매로한 Epichlorohydrin 과 CO₂로부터 Cyclic carbonate 의 합성

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Synthesis of Cyclic Carbonate from Epichlorohydrin and CO₂ using Ionic Liquid as Catalyst

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INTRODUCTION

Carbon dioxide (CO₂) is the most abundant waste produced by human activities and one of the greenhouse gases. In order to prevent the risky reinforcement of the greenhouse effect, the accumulation of CO₂ in the atmosphere should be controlled by removing it from industrial emissions. On the other hand, CO₂ is recognized to be a naturally abundant, cheap, recyclable and non-toxic carbon source that can sometimes replace toxic chemicals such as phosgene, isocyanates or carbon monoxide [1-4]. Under these circumstances, chemical fixation of CO₂ becomes more and more important from the ecological and economic points of view. The synthesis of cyclic carbonate via cycloaddition of CO₂ to epoxide is one of effective routes of CO₂ chemical fixation. Cyclic carbonates have found extensive use as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc. [5,6].

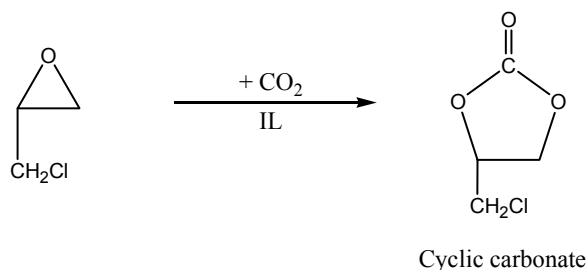
The synthesis of cyclic carbonates from CO₂ and epoxides has been applied in industrial scales and a number of works as above-cited on the catalyst development and the reaction mechanisms were reported in the literature. However, activity, stability and recovery of catalysts still remain to be improved. In the present work, the effects of structure of ionic liquids, temperature, and carbon dioxide pressure were studied for the cycloaddition of carbon dioxide to epichlorohydrin

EXPERIMENTAL

Ionic liquids based on 1-n-ethyl-3-methylimidazolium (EMIm), 1-n-butyl-3-methylimidazolium (BMIm), 1-n-hexyl-3-methylimidazolium (HMIm), 1-n-octyl-3-methylimidazolium (OMIm) with different anions such as Cl^- , BF_4^- , Br^- , PF_6^- were prepared according to the procedures reported previously [7]. All of ionic liquids and epichlorohydrin were used without further purification. The addition reaction was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, ionic liquid (2 mmol) and epichlorohydrin (5 mL) were charged into the reactor without solvent, and the CO_2 was introduced at room temperature to a preset pressure. The reaction was started by stirring when the desired temperature and pressure were attained. The pressure was maintained constant using a back-pressure regulator during the experiments.

RESULTS AND DISCUSSION

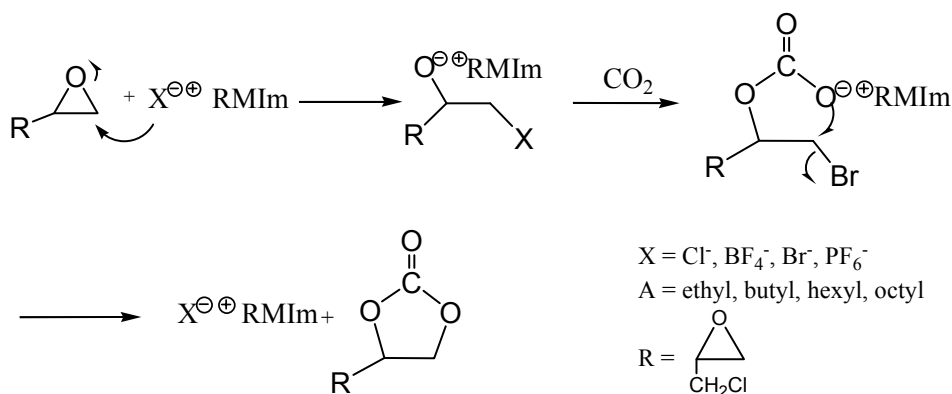
The cyclic carbonate was synthesized from epichlorohydrin and carbon dioxide using various ionic liquid catalysts under carbon dioxide pressure.



The conversions of epichlorohydrin to the cyclic carbonate with different ionic liquids consisting of cations of EMIm⁺, BMIm⁺, HMIm⁺, OMIm⁺ and anions of Cl^- , BF_4^- , Br^- , PF_6^- are summarized in Table 1. The order of the epichlorohydrin conversion increased as the size of the cation of ionic liquid increased from EMIm⁺ < BMIm⁺ < HMIm⁺ < OMIm⁺. Bulky imidazolium salts having longer distances between cations and anions, seem to exhibit higher activity in activating anions. The increase in the solubilities of CO_2 and epichlorohydrin in ionic liquid with lengthening alkyl chain of ionic liquid could also be a reason of the increase of epichlorohydrin conversion [8]. Kawanami et al. [8] also reported the increase of reactivity when the length of alkyl chain increased from C₂ to C₈ in 1-alkyl-3-methylimidazolium chloride [C_xMIm]⁺[Cl]⁻ for the synthesis of epichlorohydrin carbonate using CO_2 -ionic liquid system.

The effect of anions in the addition of CO_2 to epichlorohydrin are compared in Run 2, 5, 12 and 13. The conversion of epichlorohydrin increased in the order of $\text{PF}_6^- < \text{BF}_4^- < \text{Br}^- < \text{Cl}^-$, which is consistent

with the order of nucleophilicity of anions. The mechanism for the cycloaddition of epoxide and carbon dioxide with ionic liquid catalyst can be suggested as follows [9] :



Therefore, the ionic liquid with bulkier cation having more anion activating ability and that with more nucleophilic anion would exhibit better reactivity.

Table 1. Catalytic activities of ionic liquid in the cyclic reactions of CO₂ with epichlorohydrin

Run	Ionic liquid	Temp (°C)	Time (h)	Pressure (psi)	Conversion (%)
1	EMImCl	80	6	120	32.6
2	BMImCl	80	6	120	33.6
3	HMImCl	80	6	120	41.3
4	OMImCl	80	6	120	42.5
5	BMImBr	80	6	120	21.8
6	HMImCl	60	6	120	31.7
7	HMImCl	100	6	120	52.7
8	HMImCl	120	6	120	61.4
9	BMImCl	80	12	120	31.0
10	BMImCl	80	24	120	54.8
11	BMImCl	80	48	120	64.4
12	BMImPF ₆	80	6	120	8.0
13	BMImBF ₄	80	6	120	9.2
14	BMImCl	80	6	60	18.3

The conversion increased as the temperature increased from 60 °C to 120 °C. It means that there is no severe decomposition of the cyclic carbonate to epichlorohydrin and CO₂ even at 120 °C. Table 1 shows that the conversion of epichlorohydrin with BMImCl ionic liquid increased from 33.6% (Run 2, after 6 h) up to 64.4% (Run 11, after 48 h) at 80 °C. The conversion also increased as the pressure increased from 60psi (Run 14) to 120psi (Run 2). High pressure generally increases the absorption of carbon dioxide into the solution of epichlorohydrin and ionic liquid.

CONCLUSION

In the synthesis of cyclic carbonate from epichlorohydrin and carbon dioxide, ionic liquids showed good catalytic activity without using any solvent. The ionic liquid of larger alkyl chain structure and more nucleophilic anion exhibited better reactivity for the cycloaddition of carbon dioxide and epichlorohydrin. High temperature, long reaction time and high CO₂ pressure also increased the conversion of epichlorohydrin.

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