USE OF IMIDAZOLIUM TRANSITION METAL HALIDES IN THE SYNTHESIS OF CYCLIC CARBONATES FROM THE COUPLING REACTION OF EPOXIDE AND CO_2

Hoon Sik Kim, O-Sung Kwon, Hyunjoo Lee and Jelliarko Palgunadi

Reaction Media Research Center
Korea Institute of Science and Technology
39-1, Hawolgokdong, Seongbukgu,
Seoul, 136-791, Korea

Introduction

The synthesis of cyclic carbonates by the coupling reactions of epoxides with carbon dioxide has attracted much attention with regard to the utilization of CO_2, which is a responsible for global warming.[1] The importance of cyclic carbonates is increased due to their versatile utilization in many application areas. For instance, they can be used as aprotic polar solvents, electrolytes in secondary and fuel-cell batteries, and valuable raw materials in a wide range of chemical reactions.[2, 3] Accordingly, much efforts have been made on the catalyst development for the synthesis of cyclic carbonates *via* coupling reactions has been reported.[4] While the advances have been significant, there still remain many subjects to be improved in terms of catalytic activity, stability, and recovery of catalyst.

Recently, there have been a considerable number of articles regarding the use of ionic liquids as environmentally benign media in separation, extractions, electrochemistry, and immobilization of homogeneous catalysts.[5] Imidazolium-based ionic liquids have also been introduced as effective catalysts for the synthesis of propylene carbonate from the coupling reaction of propylene oxide and CO_2, but their catalytic activities were not high enough for the industrial purpose.[6]

With a hope to develop highly active catalysts for the coupling reactions, we have imidazolium metal halide complexes and tested their activities for the production of cyclic carbonates from the coupling reactions of epoxides and CO_2. Herein, we report the synthesis and reactivity of a series of ionic liquid-derived imidazolium metal halide complexes consisting of 1-alkyl-3-methylimidazolium cations and metal halide anion.

Experimental

Synthesis of (1,3-dimethylimidazolium)$_2$ZnBr$_2$Cl$_2$. A solution of (1,3-dimethylimidazolium)Cl[7] (2.10 g, 15.83 mmol) in methylene chloride (25 mL) was mixed with a solution of $ZnBr_2$ (1.78 g, 7.90 mmol) in tetrahydrofurane (25 mL) and heated to reflux for 3 h. After cooling to room temperature, the white precipitate was collected by filtration. Yield: 93.9 %; elemental analysis cald.(%) for $C_{10}H_{18}Br_2Cl_2N_4Zn$: C 24.49, H 3.70, Br 32.59, Cl 14.46, N 11.43, Zn 13.33; found: C 24.23, H 3.75, Br 31.83, Cl 14.18, N 11.18, Zn 13.43;

All other imidazolium metal halides were similarly prepared.

Coupling reactions of epoxide and CO_2. The coupling reactions were conducted in a 200 mL stainless-steel bomb reactor equipped with a magnetic stir bar and an electrical heater. The reactor was charged with an appropriate catalyst and an epoxide and pressurized with CO_2. The bomb was then heated to a specified reaction temperature with the addition of CO_2 from a reservoir tank to maintain a constant pressure. After the reaction, the bomb was cooled down to room temperature, and the product mixture was analyzed by Hewlett Packard 6890 gas chromatography equipped with a flame ionized detector and a DB-wax column, and Hewlett Packard 6890-5973 MSD GC-mass spectrometry.

Results and Discussion

As shown in equation (1), a series of imidazolium metal halides, (1-R-3-methylimidazolium)$_b$MX$_a$Y$_b$ (M = Zn, Fe, Mn, In; R = CH_3, C_2H_5, *n*-C_4H_9, $CH_2C_6H_5$; X, Y = Cl, Br; a, b = 2, 3) were prepared by reacting MX$_a$ (X = Cl, Br) with (1-R-3-methylimidazolium)Y (R = CH_3, C_2H_5, *n*-C_4H_9, $CH_2C_6H_5$; Y = Cl, Br) at an ambient temperature or at reflux depending on the nature of halide groups.

R = CH_3, C_2H_5, *n*-C_4H_9, $CH_2C_6H_5$; X, Y = Cl, Br; a, b = 2, 3
M = Zn, Fe, Mn, In

Interestingly, (1-R-3-methylimidazolium)$_b$MX$_a$Y$_b$ was also obtained when MX$_a$ and (1-R-3-methylimidazolium)X were reacted. For example, (1-butyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$, can be obtained either from the reaction of $ZnCl_2$ and (1-butyl-3-methylimidazolium)Br or from the reaction of $ZnBr_2$ and (1-butyl-3-methylimidazolium)Cl.

The catalytic activities of various imidazolium metal halides were evaluated for the coupling reactions of CO_2 and ethylene oxide (EO) or propylene oxide (PO) at 100 ℃ for 1 h.

As shown in Table 1, imidazolium halides and metal halides were hardly able to catalyze the coupling reactions when they were used alone. However, the combination of metal halide with imidazolium halide exhibited much higher activity for the coupling reactions (entry 1-3). Among (1-R-3-methylimidazolium)$_b$MX$_a$Y$_b$ tested, imidazolium zinc tetrahalide exhibited the highest activities. Such enhanced activities are most likely to be attributed to the in situ formation of new active complexes, bis(1-butyl-3-methylimidazolium) zinc tetrahalides from 1-butyl-3-methylimidazolium halide and $ZnBr_2$. This is supported by the fact that (1-butyl-3-methylimidazolium)$_2$ZnBr$_2$Cl$_2$ and (1-butyl-3-methylimidazolium)$_2$ZnBr$_4$ show similar activities to the corresponding catalytic systems of 1-butyl-3-methylimidazolium chloride-$ZnBr_2$ and 1-butyl-3-methylimidazolium bromide-$ZnBr_2$ (entry 9-10). By-products such as polyalkylene oxides and halogenated compounds were not detected by GC and GPC analysis.

The catalytic activities of imidazolium metal halides were greatly influenced by the nature of halide ions bonded to metal atom. The order of reactivity was found to be in the following order: $[ZnBr_4]^{2-}$ > $[ZnBr_2Cl_2]^{2-}$ >> $[ZnCl_4]^{2-}$, suggesting the importance of the nucleophilicity of halide ions. The nucleophilicity of halide ions is likely to be enhanced by the presence of imidazolium cations.

The dissociation of a halide ion and the following attack of the dissociated halide ion on the carbon atom of the coordinated ethylene oxide would take place more easily for more nucleophilic bromide ion.[8] Interestingly, the effect of the alkyl groups on the imidazolium cations is relatively small and can be negligible.

Table 1. Catalytic activities of imidazolium metal halides for the coupling reactions of CO_2 and epoxides[a]

Entry	Catalyst	TOF(h^{-1})[b]	
		EO	PO
1	(1-butyl-3-methylimidazolium)Br	78	37
2[c]	MX_a	n.r.[d]	n.r.[d]
3	(1-butyl-3-methylimidazolium)$_2$ $ZnBr_2Cl_2$	2112	1295
4	(1,3-dimethylimidazolium)$_2ZnBr_2Cl_2$	2697	1001
5	(1-ethyl-3-methylimidazolium)$_2ZnBr_2Cl_2$	2137	1335
6	(1-ethyl-3-methylimidazolium)$_2ZnBr_4$	3588	1617
7	(1-ethyl-3-methylimidazolium)$_2ZnCl_4$	2538	1352
8	(1-ethyl-3-methylimidazolium)$_2MnBr_2Cl_2$	210	79
9	(1-benzyl-3-methylimidazolium)$_2MnBr_4$	2527	1201
10[e]	(1-butyl-3-methylimidazolium)$_3FeBr_3Cl_3$	697	410
11[e]	(1-ethyl-3-methylimidazolium)$_2FeBr_4$	923	439
12[e]	(1-benzyl-3-methylimidazolium)$_3InBr_3Cl_3$	790	359

[a] Reactions were carried out at 100 ℃ and 3.5 MPa of CO_2 for 1 h. Molar ratios of epoxide to imidazolium metal halide complex were set at EO/catalyst = 5,000 and PO/catalyst = 2,000. [b] TOF(h^{-1}): moles of alkylene carbonate/moles of catalyst/hour. [c] MX_a = $ZnBr_2$, $FeBr_3$, $InBr_3$. [d] No reaction. [e] Molar ratios of EO/catalyst = 1,000, PO/catalyst = 500.

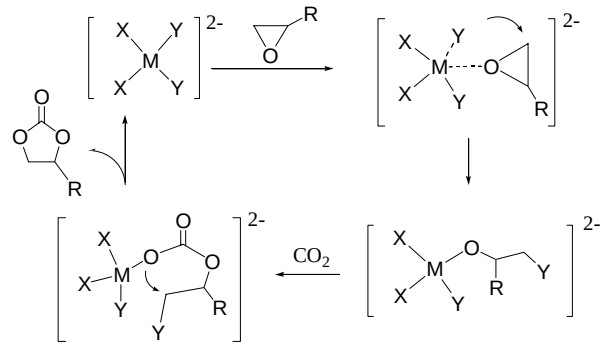
The coupling reactions of various epoxides with CO_2 were also conducted in the presence of a imidazolium metal halide, (1-ethyl-3-methylimidazolium)$_2ZnBr_2Cl_2$. As shown in Table 2, corresponding carbonates were produced in high yields and selectivities except for tert-butyl glycidyl ether and glycidyl isopropyl ether. The lower reactivity of tert-butyl glycidyl ether and glycidyl isopropyl ether is likely due to the crowdness around epoxide, which might prevent the attack of CO_2 on the coordinated epoxide.[9] In fact, the yields of cyclic carbonates decreased with increasing bulkiness of the substituent on the epoxide group (entry 1, 2 and 4).

Table 2. Results of catalytic formations of alkylene carbonates from various epoxides by (1-ethyl-3-methylimidazolium)$_2$-$ZnBr_2Cl_2$[a]

Entry	Substrate	yield(%)	Selectivity(%)	TOF(h^{-1})
1	1,2-epoxybutane	98	100	490
2	Tert-butyl glycidyl ether	11	97	55
3	Epichlorohydrin	77	100	385
4	Glycidyl isopropyl ether	23	98	115
5	Styrene oxide	77	99	385
6	Glycidyl methacrylate	98	100	490

[a] Reactions were carried out at 100°C and 500 psig of CO_2 for 1 h. Molar ratio of epoxide to zinc was set at 500. [b] TOF(h^{-1}): moles of cyclic carbonate/moles of catalyst/hour.

Previous reports by Kisch on the synthesis of cyclic carbonates from CO_2 and epoxide suggested the parallel requirement of both Lewis acid-activation of epoxide and Lewis base-activation of CO_2.[9] In the case of imidazolium metal halide-catalyzed reaction, metal center is expected to act as a Lewis acid for the coordination of an epoxide and halide ion is expected to act as a Lewis base to ring-open the coordinated epoxide. The plausible mechanism for the coupling reaction catalyzed by an imidazolium metal halide [MX_2Y_2] is depicted in scheme 1.



Scheme 1. Proposed reaction mechanism for the coupling reaction of ethylene oxide with CO_2 catalyzed by (1-R-3-ethylimidazolium)$_2$- MX_2Y_2.

Conclusions

A series of ionic liquid-based imidazolium metal halide, (1-R-3-methylimidazolium)$_b$$MX_aY_b$ (M = Zn, Fe, Mn, In; R = CH_3, C_2H_5, *n*-C_4H_9, $CH_2C_6H_5$; X, Y = Cl, Br; a, b = 2, 3), prepared from the reaction of MX_a with (1-R-3-methylimidazolium)Y were effective for the coupling reaction of epoxides and CO_2. The catalytic activity of (1-R-3-methylimidazolium)$_b$$MX_aY_b$ was found to increase with increasing nucleophilicity of halide ion. But, the substitution on the imidazolium cation showed a negligible effect on the catalytic activity.

Acknowledgement

This work was financially supported by the Ministry of Environment of Korea and Honam Petrochemical Co.

References

(1) Darensberg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996,** *153*, 155.
(2) Shaikh, S. *Chem. Rev.* **1996**, *96*, 951.
(3) Inaba, M.; Siroma, Z.; Funabiki, A.; Asano, M. *Langmuir* **1996,** *12*, 1535.
(4) (a) Kim, H. S.; Kim, J. J.; Kwon, H. N.; Chung, M. J.; Lee, B. G. Jang, H. G. J. Catal. **2002**, *205*, 226. (b) Paddock, R.; Nguyen, S. *J. Am. Chem. Soc*. **2001**, *123*, 11498. (c) Kim, H. S.; Kim, J. J.; Lee, B. G.; Jung, O. S.; Jang, H. G. Jang, Kang, S. O. *Angew. Chem. Int. Ed.*, **2002**, *39*, 4096. (d) Yamaguchi, K.; Ebitani, K.; Yoshida, T,; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526.
(5) Rogers, R. D.; Seddon, K. R. "Ionic liquid: Industrial Applications to Green Chemistry", ACS symposium series 818, American Chemical Society, Washington DC, **2002**.
(6) Peng, J.; Deng, Y. *New J. Chem.* **2001,** *25*, 639.
(7) Hasan, M.; Kozhevnikov, I. V.; Siddiqui, M. R. H.; Steiner, A.; Winterton, N. *Inorg. Chem.* **1999**, *38*, 5637.
(8) Calo, V.; Nacci, A.; Monopoli, A.; Fanizzi A. *Org. Lett*. **2002**, *4*, 2561.
(9) Kim, M. R.; Jeon, S. R.; Park, D. W.; Lee, J. K. *J. Ind. Eng. Chem*. **1998**, *4*, 122.
(10) (a) Dümler, W.; Kisch, H. *Chem. Ber*. **1990**, *123*, 277. (b) Kisch, H.; Millini, R.; Wang, I. J. *Chem. Ber*. **1986**, *119*, 1090. (c) Ratzenhofer, M.; Kisch, H. *Angew. Chem. Int. Ed. Engl.*, **1980**, *19*, 317.