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Chemical fixation of CO_2 with highly efficient $ZnCl_2$/[BMIm]Br catalyst system

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Abstract—The chemical fixation of CO_2 with mono-substituted terminal epoxides or cyclohexene oxide to form cyclic carbonates under the $ZnCl_2$/[BMIm]Br catalyst system without using additional organic solvents was achieved in excellent selectivity (>98%) and TOF ($5410\,h^{-1}$) and the catalyst could be used six times almost without losing its catalytic activity and selectivity. Besides, the pure *cis*-cyclic carbonate of cyclohexene oxide was obtained in this catalyst system.

The search for environmentally benign and economic process has been the impetus for much of the research involving epoxide and carbon dioxide coupling in view of the so called 'green chemistry' and 'atom economy', since CO_2 is a renewable resource and can be used as a safe and cheap C1 building block to synthesize useful organic compounds without producing any co-products.[1,2]

One of the most attractive synthetic goals starting from carbon dioxide is the chemical fixation of CO_2 onto epoxide to afford the five-membered cyclic carbonates, which are excellent aprotic polar solvents and are used extensively as intermediates in the production of pharmaceuticals and fine chemicals.[3] In the last decades of the 20th century numerous catalytic systems have been developed for this transformation. While some advances have been obtained, all suffer from either low catalyst stability/reactivity, the need for co-solvent, or the requirement for high pressure and/or catalyst costing expensive.[4] Therefore, to find an effective, not expensive, environmentally benign and economic catalyst system is urgent.

Herein we wish to report an extremely simple, not expensive, highly efficient and environmentally benign route to cyclic carbonate from the reactions of epoxide with carbon dioxide under mild reaction conditions.

Kim and co-workers reported a zinc pyridine complex for the coupling reactions of carbon dioxide and epoxides, but the catalytic reactivity is not too high.[5] Enlightened by these reports, we firstly investigated the zinc imidazolium complex (MIm_2ZnCl_2) in the cycloaddition between carbon dioxide and propylene oxide (**1a**), only trace propylene carbonate (**2a**) was obtained (Table 1, entry 1). But we delightfully found that the corresponding cyclic carbonate could be formed with 37% yield in the presence of $ZnCl_2$, 3-methylimidazole, and 1-bromobutane (Table 1, entry 2). This drastically different result caused us to believe that the additional 1-bromobutane played a crucial role in this catalyst system, since the zinc imidazolium complex has no reaction activity in this reaction. So we think that the [BMIm]Br transformed in situ from 3-methyl-imidazole and 1-bromobutane with $ZnCl_2$ efficiently co-catalyzed this reaction. When the synthesized [BMIm]Br (1-butyl-3-methylimidazolium bromine salt) was utilized as co-catalyst with $ZnCl_2$ in the system, the cyclic carbonate was formed in extremely excellent yield (95%) and moles of propylene carbonate produced per mole of catalyst ($TOF = 5410\,h^{-1}$) under mild conditions (1.5 MPa CO_2, 100 °C, 1 h) (Table 1, entry 6). It is important to note that the [BMIm]Br by itself only shows very low catalytic activity (8% yield) (Table 1, entry 3). These result led us to believe that the combination of $ZnCl_2$ and [BMIm]Br could highly efficient co-catalyzed this

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Keywords: Chemical fixation of CO_2; Epoxide; $ZnCl_2$/[BMIm]Br; Catalyst reused; Pure *cis*-cyclic carbonate of cyclohexene oxide.

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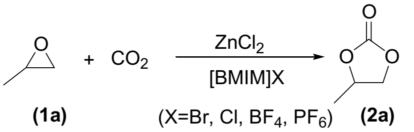
Table 1. Effect of reaction parameters on the coupling of carbon dioxide and propylene oxide[9,a]



Entry	Catalyst	Temperature (°C)	Yield (%)[b]	TOF
1	$[MIm_2ZnCl_2]$	100	Tr[c]	—
2	$ZnCl_2$/MIm/*n*-BuBr[d]	100	37	2111
3	[BMIm]Br[e]	100	8	456
4	$ZnCl_2$/[BMIm]Br[f]	100	60	3417
5	$ZnCl_2$/[BMIm]Br[g]	100	79	4500
6	$ZnCl_2$/[BMIm]Br	100	95	5410
7	$ZnCl_2$/[BMIm]Cl	100	38	1564
8	$ZnCl_2$/$[BMIm]BF_4$	100	Tr	—
9	$ZnCl_2$/$[BMIm]PF_6$	100	Tr	—
10	$ZnCl_2$/[BMIm]Br	80	50	2848
11	$ZnCl_2$/[BMIm]Br	60	7	392
12	$ZnBr_2$/[BMIm]Br	100	98	5580
13	$Zn(OAc)_2$/[BMIm]Br	100	64	3636

[a] Reaction conditions: $ZnCl_2$ (6.8 mg, 0.05 mmol), [BMIm]X (0.30 mmol), propylene oxide (20 mL, 0.285 mol), CO_2 reaction pressure 1.5 MPa, reaction time 1 h.

[b] Isolated yield.

[c] Tr = trace.

[d] MIm (0.10 mmol), *n*-BuBr (0.12 mmol).

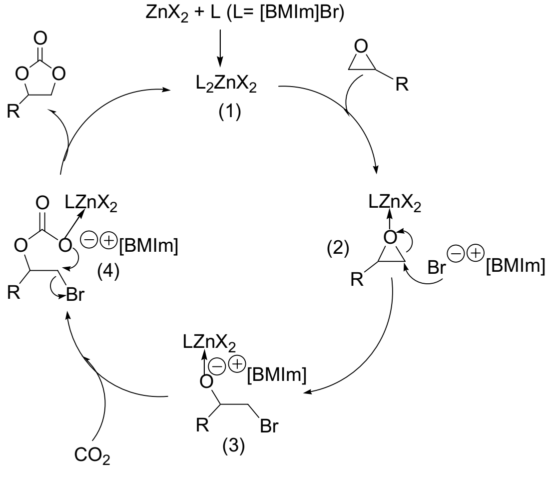
[e] [BMIm]Br (0.30 mmol).

[f] [BMIm]Br (0.10 mmol).

[g] [BMIm]Br (0.20 mmol).

reaction. To the best of our knowledge, this result is the highest reported in the chemical fixation of carbon dioxide onto epoxide.

The scope and limitations of catalysts and the various reaction parameters have been carefully examined. Under the same reaction conditions, the ratio of [BMIm]Br to $ZnCl_2$ had a pronounced positive effect on the TOF, which increased as the number of equiv of [BMIm]Br increased (Table 1, entries 4–6). A series of 1-butyl-3-methylimidazolium salts with different counter ions were investigated for the synthesis of **2a** (Table 1, entries 6–9). There are only trace reactions in $[BMIm]BF_4$ and $[BMIm]PF_6$. The [BMIm]Cl shows low reaction activity too, and only 38% yield of **2a** was obtained. These results illuminate that the counter ions play an important role in the catalytic activity and the Br^- is the most effective of these negative ions.

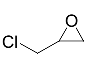
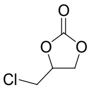
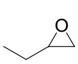
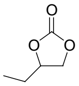
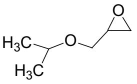
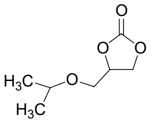
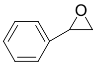
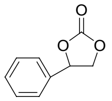
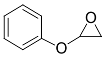
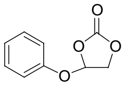
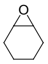
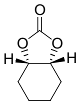


Scheme 1. Proposed mechanism for the reaction.

We are delighted to find that our catalyst system can operate very efficiently at low CO_2 pressure and temperature. The highest catalytic activity could be attained at 100 °C, 1.5 MPa. The reaction temperature has significant effect on the yield of **2a**. Using the same catalyst system, the reaction of CO_2 with propylene oxide gave a higher yield of **2a** at 100 °C than 80 °C or 60 °C (Table 1, entries 10 and 11). When $ZnBr_2$ and $Zn(OAc)_2$ were utilized as the zinc salt, 98% and 64% yield of **2a** were obtained, respectively (Table 1, entries 12 and 13). These two results also show that the halogen ion is crucial for this catalyst system. The catalyst system exhibits remarkable constancy. When 1.1 mol propylene oxide was used, the activity does not deteriorate over a period of 10 h, attaining 20,000 turnovers. The reusability of the catalyst was also investigated. It retained almost the same catalytic activity (yield = 95%) even after being reused five times.

Under the optimized reaction conditions, we examined the reactions of other terminal epoxides (**1b–f**) and cyclohexene oxide (**1g**) with CO_2. The results are summarized in Table 2. The catalyst system was found to be applicable to a variety of terminal epoxides, forming the corresponding cyclic carbonates (**2b–f**) in very high

Table 2. Coupling of CO_2 and various epoxides catalyzed by $ZnCl_2$ and [BMIm]Br[a]

Substrate	Product	Yield (%)	TOF (h^{-1})
 **1b**	 **2b**	89	4578
 **1c**	 **2c**	95	4369
 **1d**	 **2d**	100	3165
 **1e**	 **2e**	86	3015
 **1f**	 **2f**	99	2919
 **1g**	 **2g**	34	1206

[a] Reaction conditions: $ZnCl_2$ (0.05 mmol), [BMIm]Br (0.30 mmol), epoxides (20 mL), CO_2 pressure 1.5 MPa, temperature 100 °C, time 1 h, based on the GC–MS, and NMR. The selectivity to carbonate is >98%.

TOF and more than 98% selectivity. Besides terminal epoxides constantly adopted, we also examined the cyclohexene oxide (**1g**) in this reaction under the same reaction conditions, providing corresponding cyclic carbonate (cyclohexyl-[1,3]-dioxolan-2-one **2g**) in 1206 h^{-1} TOF. Interestingly, the cyclic carbonate produced from cyclohexene oxide was exclusively of *cis*-stereochemistry according to the ^1H, ^{13}C, and NOESY of NMR spectra of **2g**.[6] In related other studies involving zinc catalysts, which are quite active for polycarbonate production during the coupling of cyclohexene oxide and carbon dioxide, only the small quantity of cyclic cyclohexene carbonate was formed.[7] Otherwise, absolute *cis*-cyclic carbonate of cyclohexene oxide was obtained in our catalyst system.

Considering the reaction mechanism, Kim and co-workers showed zinc complex could efficiently activated the epoxy ring of epoxide.[5] The ^1H NMR spectrum of [BMIm]Br in D_2O shows no signal of 2-H of the imidazolium ring because it is replaced by the deuteron atom, however, its signal appeared after reaction with 0.5 equiv of $ZnCl_2$. This drastically different result caused us to believe that the $ZnCl_2$ has coordinated with the 2-H of the imidazolium ring by the hydrogen-bond forming the zinc 1-butyl-3-methylimidazolium complex L_2ZnX_2 (L = [BMIm]Br).[8] This coordination type probably activated zinc complex and improved the catalytic activity of this catalyst system.

Based on the above results, we propose the plausible mechanism for this chemical fixation reaction of CO_2 (Scheme 1). $ZnCl_2$ and [BMIm]Br reacted to synthesize the zinc imidazolium complex (**1**), which coordinated the epoxide by replacing one of the 1-butyl-3-methylimidazole first. On the same time, nucleophilic attack of the dissociated [BMIm]Br on the less sterically hindered carbon atom of the coordinated epoxide occurred (**2**) to form the active species (**3**). The insertion of CO_2 into the Zn–O bond of **3** would give a zinc carbonate active species (**4**), which eventually provided the cyclic carbonate.

In summary, $ZnCl_2$ and [BMIm]Br is a extremely simple, highly efficient and environmentally benign catalyst system in the chemical fixation of CO_2 with epoxides at mild temperature and pressure. It is an air stable, easily synthesized, cheap, extremely robust, and environmentally benign catalyst system, which is free of co-solvent and tolerates various substrates. It is also important to note that this catalytic system could be used six times almost without losing its catalytic activity and selectivity.[6] These characteristics make it an ideal catalyst system in terms of potential industrial application in chemical carbon dioxide fixation.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.09.074.

References and notes

1. Leitner, W. *Coord. Chem. Rev.* **1996**, *155*, 257.
2. Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155.
3. Shaikh; Sivaram, S.. *Chem. Rev.* **1996**, *96*, 951.
4. (a) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304; (b) Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198; (c) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725; (d) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526; (e) Kawanami, H.; Ikushima, Y. *Chem. Commun.* **2000**, 2089; (f) Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498; (g) Peng, J. J.; Deng, Y. Q. *New J. Chem.* **2001**, *25*, 639; (h) Caió, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561; (i) Shen, Y. M.; Duan, W. L.; Shi, M. *J. Org. Chem.* **2003**, *68*, 1559; (j) Li, F. W.; Xia, C. G.; Xu, L. W.; Sun, W.; Chen, G. X. *Chem. Commun.* **2003**, 2042; (k) Huang, J. W.; Shi, M. *J. Org. Chem.* **2003**, *68*, 6705.
5. (a) Kim, H. S.; Kim, J. J.; Lee, B. G.; Jung, Q. S.; Jang, H. G.; Kang, S. O. *Angew. Chem., Int. Ed.* **2000**, *39*, 4096; (b) Kim, H. S.; Kim, J. J.; Kwon, H. N.; Chung, M. J.; Lee, B. G.; Jang, H. G. *J. Catal.* **2002**, *205*, 226.
6. ^{13}C NMR, ^1H NMR, and NOSEY spectrum of **2g** reusability result of the catalyst can be seen in Supplementary data.
7. Darensbourg, D. J.; Yarbrough, J. C.; Oritiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586.

8. Hitchcock, P. B.; Seddon, L. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2639.
9. Representative procedure for the reaction of propylene oxide with CO_2: A 100 mL stainless pressure reactor was charged with propylene oxide (20 mL, 16.6 g, 0.285 mol), $ZnCl_2$ (6.8 mg, 0.05 mmol), [BMIm]Br (65 mg, 0.3 mmol). The reaction vessel was then heated to 100 °C for 1 h under a constant pressure (1.5 MPa) of carbon dioxide. Once the reaction is completed, the vessel was cooled to ambient temperature and the pressure released, then the contents were transferred to a round-bottom flask. Unreacted substrate was removed in a vacuum first, then the product was obtained. When about 1 ml of the reaction mixture was left, the distillation was stopped and the last mixture was used as a catalyst to begin the fresh reaction. The catalyst could be reused five times almost without losing its catalytic activity. According to the GC–MS and NMR, the selectivity to the cyclic carbonates are >98%.