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## Synergistic effect of alkali halide and Lewis base on the catalytic synthesis of cyclic carbonate from CO<sub>2</sub> and epoxide

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### ABSTRACT

The synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides catalyzed by alkali metal halides (MX) in combination with a Lewis base (LB) is reported here. The unique synergistic effect between MX and LB has been observed at an optimum mole ratio of 1:1. High turnover frequency (TOF, h<sup>-1</sup>) indicates that an increase in the reaction efficiency of up to 40 times is obtained by comparison with the reaction carried out using only MX. The activity of MX primarily falls in the order of alkali metal ion's Lewis acidity. The optimum conditions for this solventless reaction were 130 °C and 2 MPa of CO<sub>2</sub> pressure.

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### 1. Introduction

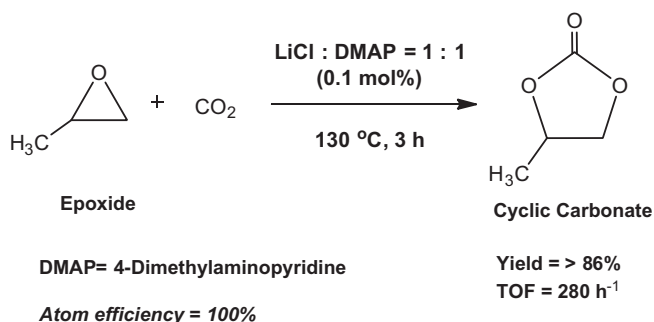
The activation of CO<sub>2</sub> is an important and challenging task. In this regard, synthesis of cyclic carbonate using epoxide has drawn significant attention [1–5]. The reason for using epoxide in cyclic carbonate synthesis is that epoxide, a reactive synthon, is generally obtained from the major petro- or fine chemical feedstocks such as olefins or diols. On the other hand, cyclic carbonate has a broad application domain that includes uses in high-boiling inert solvents for paints and coating formulations, electrolytes for lithium-batteries, precursors for important small molecules, and developing polymeric materials such as polycarbonates [6,7]. Furthermore, the synthesis of cyclic carbonates using CO<sub>2</sub> and epoxide meets 100% atom economy (Figure 1) [8], which is an important factor for sustainable development. As a result, extensive efforts have been made in order to develop and understand the viable synthesis of cyclic carbonate using CO<sub>2</sub> and epoxide [9]. Mechanistically, in the absence of any catalyst, the HOMO of epoxide interacts with the LUMO of CO<sub>2</sub> to produce the cyclic carbonate, but at subtle yield. Hence, in order to increase reaction yield and avoid harsh reaction conditions, the activation of CO<sub>2</sub> towards epoxide or *vice versa* has to be very strong and specific. This necessitates synthesizing cyclic carbonates using various well-defined catalysts. In this context, metal salen complexes [10–12] and metal porphyrin/phthalocyanine complexes [13,14] are noteworthy, and this method is one of the most attractive for synthesizing cyclic carbonates. In recent years use of dimeric metal

complexes has opened up further advancement in synthesizing cyclic carbonate under low pressure and temperature [12,15,16]. We have recently reported the use of Co(III)–tetraamidomacrocyclic complex for cyclic carbonate synthesis with high selectivity [17]. The catalyst showed 100% yield of cyclic carbonate production with TOF 350 h<sup>-1</sup> in 3 h at 120 °C for several aromatic and aliphatic epoxides in the presence of 4-dimethylaminopyridine (DMAP) as a co-catalyst. The catalyst used in this study was an anionic complex containing Li<sup>+</sup> counter-ion. We observed in our study on the influence of Li<sup>+</sup> on the activity of the Co(III)–tetraamidomacrocyclic that Lewis base and various alkali metal salts, particularly various Li-salts, have a combined influence in executing the reaction with high efficiency [17]. This particular observation led us to the present report on the synthesis of cyclic carbonate using a combination of alkali metal salt and Lewis base.

In addition to well-defined metal complexes, several organic and inorganic salts, especially alkali metal halide salts, are also known to catalyze the synthesis of cyclic carbonates using CO<sub>2</sub> and epoxides [18–20]. In fact, industrial synthesis of cyclic carbonates is catalyzed by using metal or organic halide salts, such as potassium iodide or tetraethylammonium bromide [21,22]. Ionic liquids are also important catalysts that belong to similar categories and have drawn much attention recently due to their benign nature and easy product separation [23]. Imidines, which form bicarbonate salt in the presence of trace water and CO<sub>2</sub>, are even more efficient catalysts for cyclic carbonate production [24]. Endo and co-workers have reported the catalytic synthesis of cyclic carbonates in dimethylformamide by incorporation of atmospheric CO<sub>2</sub> into oxiranes using a combination of NaI and triphenylphosphine (PPh<sub>3</sub>) as catalyst [25]. In this work, the authors reported

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**Figure 1.** Epoxide and carbon dioxide forming cyclic carbonate catalyzed by alkali halide and DMAP.

that the presence of both NaI and PPh<sub>3</sub> is essential for the successful incorporation of CO<sub>2</sub> into epoxides. Using NaI, PPh<sub>3</sub>, and phenol, Shi and co-workers reported an efficient synergistic catalytic system for chemical fixation of CO<sub>2</sub> without using any organic solvents [26]. In this reaction process, phenol acted as a Brønsted acid by accelerating the ring-opening reaction of epoxide through hydrogen bonding. The phosphonium salt formed as a result of the reaction of epoxide with NaI and PPh<sub>3</sub> acted as an active catalyst. In the context of alkali salt catalyzed reactions for the synthesis of cyclic carbonate, a study by Kihara et al. is note-worthy [27]. The authors reported synthesis of cyclic carbonate at 1 atm pressure of CO<sub>2</sub> using *N*-methylpyrrolidinone (NMP) as a solvent. Alkali metal salts, and particularly lithium salts, were found to be very reactive by these authors. Although low turnover frequency was obtained, their research accounts for an excellent detail of the kinetic study of CO<sub>2</sub> fixation into epoxides at 1 atm of CO<sub>2</sub> pressure. Most recently, Endo and co-workers reported use of *N*-methyltetrahydropyrimidine (MTHP) in combination with CO<sub>2</sub> and LiBr [28]. Their research indicates that substantial progress has been made toward finding a fruitful and cost-effective method of producing cyclic carbonate which is extremely important. In this study, too, the presence of both MTHP and LiBr is crucial for CO<sub>2</sub> fixation indicating the existence of possible synergism in their catalytic activity. Thus, from the above discussion, it is evident that, although certain research progress has been made, detailed research work to understand the synergistic effect of various Lewis bases in alkali metal halide catalyzed cyclic carbonate synthesis using CO<sub>2</sub> and epoxide has not yet been performed.

In the present work, we have explored the synergistic influence of various Lewis bases and alkali metal salts over a range of epoxides to their corresponding carbonate formation using CO<sub>2</sub>. A high TOF of 295 h<sup>-1</sup> and yield of 91.3% in 3 h at 2 MPa CO<sub>2</sub> was obtained with 4-dimethylaminopyridine (DMAP), which was used as a co-catalyst for lithium bromide catalyzed cycloaddition of CO<sub>2</sub> to propylene oxide (PO). Under similar conditions and in the absence of DMAP, TOF of only 8.2 h<sup>-1</sup> and 2.5% product yield were obtained. It is also noteworthy that the reactions were performed in the absence of any additional solvent.

## 2. Experimental

### 2.1. General

Chemicals were purchased from Aldrich Chemical Co., USA and Acros Chemical Co., USA are used without further purifications, unless otherwise mentioned. Propylene oxide and cyclohexene oxide were purified using calcium hydride [29] CO<sub>2</sub> was obtained from Airgas (99.9%). All high pressure reactions were carried out in a 100 mL Parr reactor connected to a 4842 controller. All of the high pressure reactions were run in triplicate. <sup>1</sup>H and <sup>13</sup>C NMR spectra

were obtained using a 600 MHz Bruker instrument equipped with a 5 mm triple resonance inverse probe. The spectra were collected at 25 °C, and chemical shifts were reported in ppm relative to TMS as external standard, unless otherwise stated. Infrared spectra were obtained using a Shimadzu FT-IR Affinity-1 spectrophotometer. Gas chromatography–mass spectra (GC/MS) were obtained using an Agilent technologies 6890 N network GC system equipped with an Agilent Technologies 5975 inert XL mass selective detector.

### 2.2. Synthesis of the cyclic carbonates

A representative method for the synthesis of cyclic carbonate (Propylene carbonate, PC) using propylene oxide (PO) and co-catalyst 4-dimethylaminopyridine (DMAP) is described below. PO (3.98 g, 0.068 mol), metal halide catalyst (lithium chloride, 3.0 mg, 0.07 mmol) and DMAP (8.6 mg, 0.07 mmol) were added in a 100 mL stainless steel Parr high-pressure reactor. The reactor was pressurized with CO<sub>2</sub> (purity 99.9%, Airgas) so that the final pressure reached 2 MPa at 130 °C. The reaction mixture was then allowed to stand with continuous stirring for 3 h. After 3 h, the reactor was cooled to room temperature, and pressure was released slowly. The reaction mixture was collected using dichloromethane and filtered to remove any insoluble reactants. The solvent and excess epoxide were removed under reduced pressure. The yield was estimated by external standard method. The isolated yield was also calculated by taking the weight of the isolated product. The reaction yield was calculated at different time intervals. The product was also characterized by GC/MS, IR, and <sup>1</sup>H and <sup>13</sup>C NMR.

In accordance with the above-mentioned procedure and conditions, desired reactions were conducted as required.

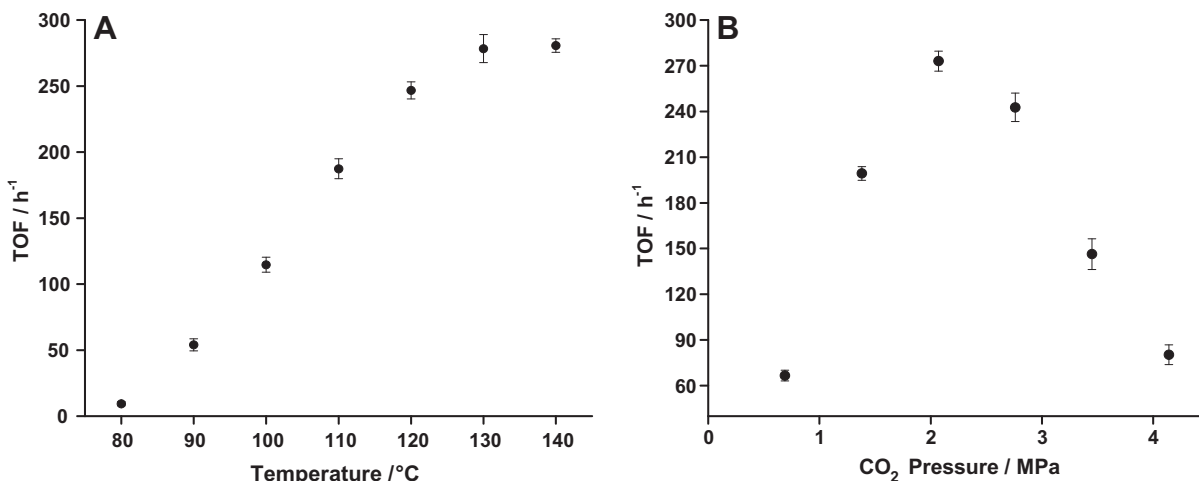
## 3. Results and discussion

### 3.1. Formation of carbonate from epoxide and CO<sub>2</sub>

The formation of cyclic carbonate was accomplished by reacting an alkali metal salt, DMAP, and epoxide with 1:1:1000 mol ratio using 2 MPa CO<sub>2</sub> at 130 °C in 3 h. Experiments with only epoxide and CO<sub>2</sub> executed little activity, showing the role of DMAP and metal salt. The products were confirmed by respective molecular ion peaks in GC/MS, as well as by the broad infrared peak at ~1800 cm<sup>-1</sup>, ν(-CO<sub>3</sub>, cyclic). The absence of other carbonate peaks in the IR spectra eliminates the possible formation of polycarbonate during the reaction, thus indicating high selectivity. Gas chromatography of the reaction mixture, obtained from the reaction of PO with CO<sub>2</sub> forming PC, showed the presence of the product (retention time, RT 6.6 min, PC) (Figure S1) as the sole component other than epoxide (RT 1.2 min, PO), suggesting a high reaction selectivity. The <sup>1</sup>H NMR of the product obtained from the reaction of *cis*-cyclohexene epoxide and CO<sub>2</sub> and catalyzed by LiBr and DMAP shows peaks at δ 4.67(m) and 1.85(m) ppm, 1.56(m) and 1.39(m) ppm, respectively (Figure S2). These values match well with the literature-reported values of cyclohexenecarbonate [16,30]. <sup>13</sup>C NMR spectrum of the product also replicates the literature values (Figure S2, inset).

Since there is a significant difference in the polarity between cyclic carbonate and epoxide, as demonstrated in the present case, distillation was chosen as a tool for their separation in large-scale synthesis [31]. Subsequent discussions, which are given below, involving reaction parameters and other critical factors, would further deepen our understanding of the reaction.

Reaction time, pressure, and temperature were considered from the point reaction yield reached at the optimum level. The TOF of



**Figure 2.** (A) Variation of TOF ( $\text{h}^{-1}$ ) of PC at different temperatures. PO 0.068 mol,  $\text{CO}_2$  2 MPa, 3 h, LiCl:DMAP = 1:1. (B) Variation of TOFs with  $\text{CO}_2$  pressure. 130 °C, 3 h, LiCl:DMAP = 1:1.

PC production increased with increasing temperature and reached saturation at  $273 \text{ h}^{-1}$  at 130 °C. The activity was found to increase with temperature reaching the maximum at 130 °C, Figure 2A. This finding has led us to optimize the temperature at 130 °C.

Results obtained at various pressures revealed that TOF increases with increasing pressure and reaches a maximum from which it drops gradually (Figure 2B). ~2 MPa is the pressure at which maximum efficiency can be observed. A decline in activity at higher pressure is however contrary to the effect of pressure reported previously [27], which indicated that pressure has no effect on yield.

We explored the ability of DMAP and a LiCl catalytic system for the synthesis of cyclic carbonates using various aromatic and aliphatic epoxides other than PO. Table 1 represents a summary of these experiments. The highest activity was recorded in the case of PO (84.2% yield). In addition to PO (entry 1), epichlorohydrin (entry 2) and epoxydodecane (entry 3) also showed significant activities. Some of the sterically-hindered epoxides, such as styrene oxide (entry 4), cyclohexene oxide (entry 5), and cyclooctene oxide (entry 6), were found to show no product formation when the reaction was run at 130 °C for 3 h. However, their corresponding carbonates were detected when the reaction was run at 180 °C for 8 h.

### 3.2. Role of LB and MX

We performed a set of experiments in order to understand the roles of LB and MX, and the results are listed in Table 2. The significance of MX and LB was tested separately when neither MX nor LB were used (entries 1–5 and 14). The results showed very inferior activity. Once MX and LB were added together, efficiency increased

**Table 2**

Effect of MX and LB in the formation of PC from PO and  $\text{CO}_2$ .<sup>a</sup>

Entry	MX	LB	Yield (%)	TOF ( $\text{h}^{-1}$ )
1	LiCl	No	$2.2 \pm 0.7$	$7 \pm 2.2$
2	LiBr	No	$2.5 \pm 0.5$	$8.2 \pm 1.8$
3	LiI	No	$2.6 \pm 0.7$	$8.4 \pm 2.2$
4	NaCl	No	$0.36 \pm 0.4$	$1 \pm 1.1$
5	KCl	No	0	0
6	LiCl	DMAP	$84.2 \pm 2.0$	$273 \pm 6.5$
7	LiI	DMAP	$88.7 \pm 3.1$	$287 \pm 10.2$
8	LiBr	DMAP	$91.3 \pm 2.0$	$295 \pm 6.6$
9	NaCl	DMAP	$78.3 \pm 2.6$	$253 \pm 8.5$
10	NaBr	DMAP	$55.5 \pm 2.2$	$180 \pm 7.2$
11	KCl	DMAP	$61.9 \pm 2.5$	$200 \pm 8.2$
12	KBr	DMAP	$68.5 \pm 1.9$	$222 \pm 6.3$
13	KI	DMAP	$73 \pm 3.4$	$236 \pm 11.1$
14	No	DMAP	$4 \pm 0.6$	$14 \pm 2.1$
15	LiCl	Triethylamine	$32.4 \pm 0.5$	$107 \pm 1.8$
16	LiCl	Pyridine	$24.9 \pm 1.0$	$81 \pm 3.4$
17	LiCl	NMP	$14.3 \pm 0.6$	$46 \pm 2.1$
18	LiCl	<i>N,N</i> -Dimethylaniline	$0.43 \pm 0.3$	$2.6 \pm 1.7$
19	LiCl	Tripropylamine	$0.38 \pm 0.3$	$2.3 \pm 1.6$
20	LiCl	Benzylidenemalononitrile	$0.37 \pm 0.3$	$2.3 \pm 1.7$

<sup>a</sup> PC = propylene carbonate, PO = propylene oxide 0.068 mol,  $\text{CO}_2$  2 MPa, 130 °C, 3 h, LiCl:organic base = 1:1 mol ratio.

dramatically to TOF  $295 \text{ h}^{-1}$  (entries 6–13 and 15–20). This clearly shows the importance of the presence of both MX and LB for carrying out the reaction.

It can be noticed that halides of the same metal ion have almost no effect on the catalytic production of cyclic carbonates [entries 6–8 (lithium salts), 9–10 (sodium salts), and 11–13 (potassium salts)]. On the other hand, efficiency is altered dramatically when metal ions are changed. This observation was supported by using DMAP as LB with different MXs, entries 6–13. Lithium salts showed highest activity on the reaction of PO with  $\text{CO}_2$  compared to other alkali halide salts, namely sodium and potassium halide salts. The results indicate that the size of the alkali metal ions ( $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ ) [32] is inversely related to the activity ( $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ ). The high activity of the lithium salts compared to other alkali metal salts, namely sodium and potassium, can be easily correlated with the higher ionic potential and higher Lewis acidity of  $\text{Li}^+$ , compared to  $\text{Na}^+$  and  $\text{K}^+$ . As will be discussed later, coordination of epoxide to the metal ion is necessary for facile ring cleavage of the epoxide and subsequent formation of the cyclic carbonate. Higher Lewis acidity in the case of lithium salts favors good coordination with the epoxide and the overall process. Another probable reason for

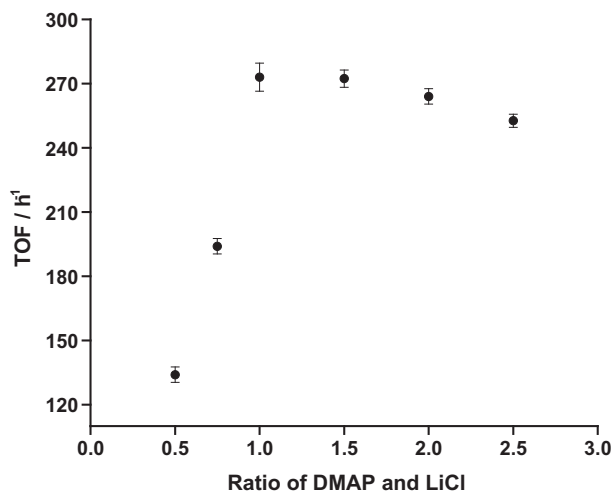
**Table 1**

MX and LB catalyzed formation of cyclic carbonates using various epoxides.<sup>a</sup>

Entry	Substrate	Yield (%)	TON	TOF ( $\text{h}^{-1}$ )
1	Propylene oxide	$86.4 \pm 2.0$	820	$273 \pm 6.5$
2	Epichlorohydrin	$77.4 \pm 2.0$	750	$250 \pm 6.4$
3	Epoxydodecane	$55.6 \pm 2.4$	266	$89 \pm 3.8$
4	Styrene oxide <sup>b</sup>	$53.4 \pm 1.9$	550	$67 \pm 2.4$
5	Cyclohexene oxide <sup>b</sup>	$29.4 \pm 1.2$	295	$37 \pm 1.8$
6	Cyclooctene oxide <sup>b</sup>	$2.13 \pm 2.5$	14	$1.7 \pm 1.8$

<sup>a</sup> Epoxide 0.068 mol, LiCl 0.07 mmol, DMAP 0.07 mmol,  $\text{CO}_2$  2 MPa, 3 h, 130 °C.

<sup>b</sup> 180 °C, 8 h.



**Figure 3.** Effect of ratio of DMAP and LiCl on TOF in PC synthesis. 130 °C, CO<sub>2</sub> 2 MPa, 3 h, PO 0.068 mol.

this trend can be attributed to the difference in the solubility of the salts. Generally, lithium salts are more soluble in weakly-coordinating solvents, like PO, compared to other alkali halide salts; thus, solubility can influence the reactivity, too. Furthermore, lithium bromide (entry 8) has a higher activity (91.3% yield, TOF 295 h<sup>-1</sup>), when compared with chloride and iodide salts of lithium. One possible reason for the higher activity of lithium bromide is the fact that bromide (Br<sup>-</sup>) acts both as a good nucleophile and a good leaving group [33].

We observed while using various LBs that a relatively stronger base (high pK<sub>a</sub>) acts as a better co-catalyst, namely DMAP (9.70) [34]. Thus, screening of seven different LBs, showed that LBs with low pK<sub>a</sub> values, namely pyridine (5.25, entry 16 [35], *N,N*-dimethylaniline (5.15, entry 18) [35], and benzyldienemalononitrile (4.68, entry 20) [36], are less efficient for cyclic carbonate synthesis. However, contrary to our assumption, some of the bases with higher pK<sub>a</sub>, such as triethylamine (11.01, entry 15) [35], NMP (10.46, entry 17) [37], and tripropylamine (10.66, entry 19) [37], also showed very poor activities. The values in parentheses indicate the pK<sub>a</sub> of LBs in water at 25 °C. The low activity in the case of NMP, *N,N*-dimethylaniline, and tripropylamine can be reasoned due to bulkiness of the nitrogen substituents, which lowers the accessibility of lone pairs of electrons for activity. This could also be correlated to their nucleophilicity [33].

### 3.3. Impact of catalyst and co-catalyst ratio

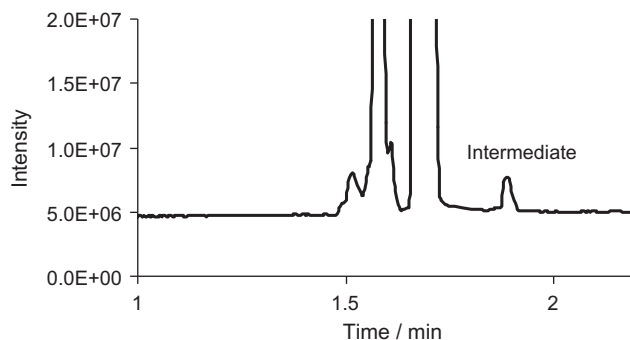
In addition to the significance that the presence of both LB and MX is necessary for optimum activity, we have also observed that the yield maximizes only at a particular ratio of LB to MX. Figure 3 shows that maximum efficiency is achieved when LiCl to DMAP mole ratio becomes 1:1. A slight but steady decrease in PC production was found with further increases in DMAP concentration. A possible explanation for this decrease is the saturation of Li<sup>+</sup> with DMAP, which is no longer available for binding and activating PO for PC synthesis. This finding led us to choose a 1:1 mol ratio of LiCl to DMAP for the remainder of the studies. This supports the afore-said observation that the presence of both alkali halide salts and co-catalysts or a Lewis base is necessary to obtain the optimum activity.

### 3.4. Mechanism

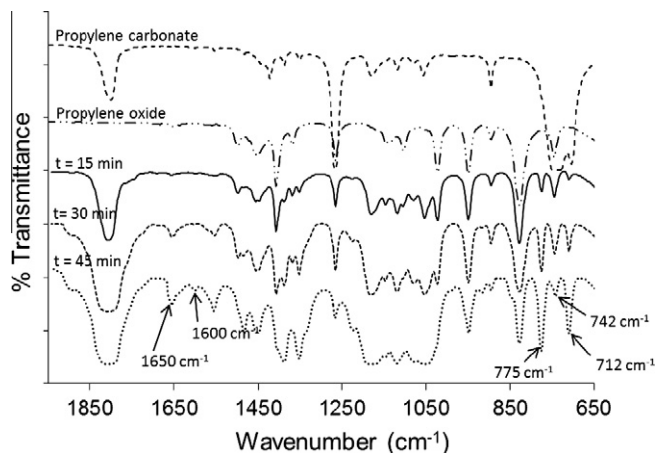
Interest in comprehending the mechanistic pathway caused us to carry out a reaction of PO (**1**), CO<sub>2</sub>, LiCl, and DMAP that was

prematurely stopped (after 30 min). GC/MS of this reaction mixture reveals a peak at 1.86 min, corresponding to 1-chloro-propan-2-ol (Figure 4). The likely origin of 1-chloro-propan-2-ol is the alkoxide intermediate, which transformed into the corresponding alcohol as the reaction mixture was dissolved in solution to record the spectrum (Figure 4). A similar intermediate was found when the reaction was carried out externally with **1** and LiI, supporting the common pathway of the formation of the intermediate, lithium 1-halo-2-propoxide (**2**). Figure 5 shows the FTIR spectra of the propylene oxide, propylene carbonate and reaction mixture at various time intervals: 15, 30, and 45 min. It shows much more information about the reaction pathway, as well. PO (**1**) ring vibrations appearing at 742 cm<sup>-1</sup> [38] slowly disappear, which indicates the transformation of epoxide to cyclic carbonate. The peak seen at 775 cm<sup>-1</sup> could be identified as C–Cl stretching [39]. Similar frequency was observed when **1** was treated with LiCl, separately. However, PC as examined shows an FTIR peak at ~1800 cm<sup>-1</sup> [17], which is due to carbonate-stretching frequency. Noticeably, another peak appears at 1650 cm<sup>-1</sup>, which is a characteristic stretching frequency of CO<sub>2</sub> activated DMAP (**5**) [40,41] that finally takes part in the catalytic cycle.

Taking into account all of the spectral data that are mentioned above, we propose a mechanism that is described in Figure 6, which eventually supports the previously proposed reaction pathway [27,28]. Initially, **1** coordinates with the metal ion, and either a halide or DMAP (or any co-catalyst) attacks the less-hindered site of **1** to open the ring to form a halo alkoxide intermediate (**2**).

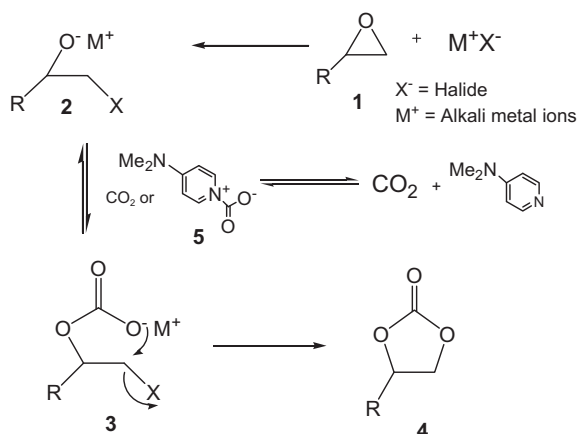


**Figure 4.** Gas chromatogram of the reaction of PO and CO<sub>2</sub> forming PC when stopped at 30 min indicating the presence of 1-chloro-propan-2-ol at 1.86 min. PO 0.068 mol, CO<sub>2</sub> 2 MPa, DMAP:LiCl 1:1 (0.07 mmol), 3 h, 130 °C.



**Figure 5.** FTIR spectra of propylene oxide, propylene carbonate and reaction mixture at different time intervals (15, 30, and 45 min). 1.86 min. PO 0.068 mol, CO<sub>2</sub> 2 MPa, DMAP:LiCl 1:1 (0.07 mmol), 130 °C.





**Figure 6.** Proposed mechanism of cyclic carbonate synthesis.

DMAP or any amines can react with  $\text{CO}_2$  to form **5**. Then, **5** reacts with **2** to form an uncyclized carbonate intermediate (**3**), which eventually cyclizes to form the desired cyclic carbonate product (**4**).

#### 4. Conclusions

In conclusion, we have demonstrated excellent synergism between MX and LB in the insertion of  $\text{CO}_2$  to epoxide, forming cyclic carbonate efficiently. The presence of both MX and LB in 1:1 mol ratio is necessary to obtain high catalytic activity, as either of them used separately under the reaction conditions produces significantly less product. Results revealed that less sterically-hindered epoxides are more efficient. LiBr was found to be the most reactive compared to Na, K, and to their other halide analogs. Based on the reaction studies using GC/MS and infrared spectroscopic studies with PO, we have proposed a possible reaction mechanism that describes the epoxide ring opening by MX forming metal haloalkoxide. This subsequently reacts with LB-activated  $\text{CO}_2$  to make a carbonate species that undergoes cyclization and produces the final product. The results described here indicate the viability of the present approach as one of the most efficient and economical methods for the carbonation of epoxides, which is important for sustainable development. At present we have little knowledge on the kinetic behavior of the reaction; definitely a challenge for the future study. Additionally, techno-economical evaluation of this valuable reaction using simple alkali salts as catalyst should also be the part of our forthcoming research in this arena.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2011.07.035](https://doi.org/10.1016/j.cplett.2011.07.035).

#### References

- [1] D.J. Darensbourg, *Inorg. Chem.* 49 (2010) 10765.
- [2] T. Sakakura, K. Kohno, *Chem. Commun.* (2009) 1312.
- [3] G.W. Coates, D.R. Moore, *Angew. Chem. Int. Ed. Engl.* 43 (2004) 6618.
- [4] M. North, R. Pasquale, *Green Chem.* 12 (2010) 1514.
- [5] A. Decortes, A.M. Castilla, A.W. Kleij, *Angew. Chem. Int. Ed. Engl.* 49 (2010) 9822.
- [6] J.H. Clements, *Ind. Eng. Chem. Res.* 42 (2003) 663.
- [7] A.-A.G. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [8] B.M. Trost, *Science* 254 (1991) 1471.
- [9] S. Inoue, *Organic and Bioorganic Chemistry of Carbon Dioxide*, Kodansha Ltd., Tokyo, 1982.
- [10] D.J. Darensbourg, P. Bottarelli, J.R. Andreatta, *Macromolecules* 40 (2007) 7727.
- [11] W. Clegg, R.W. Harrington, M. North, R. Pasquale, *Chem. Eur. J.* 16 (2010) 6828.
- [12] M. North, R. Pasquale, *Angew. Chem. Int. Ed. Engl.* 48 (2009) 2946.
- [13] T. Aida, S. Inoue, *J. Am. Chem. Soc.* 105 (1983) 1304.
- [14] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, *Tetrahedron Lett.* 45 (2004) 2023.
- [15] M. North, C. Young, *Catal. Sci. Technol.* (2011) 93.
- [16] A. Buchard, M.R. Kember, K. Sandeman, C.K. Williams, *Chem. Commun.* 47 (2011) 212.
- [17] A. Ghosh et al., *Catal. Lett.* 137 (2010) 1.
- [18] K. Kossev, N. Koseva, K. Troev, *J. Mol. Catal. A: Chem.* 194 (2003) 29.
- [19] F. Li, C. Xia, L. Xu, W. Sun, G. Chen, *Chem. Commun.* (2003) 2042.
- [20] J. Sun, S.-I. Fujita, F. Zhao, M. Arai, *Green Chem.* 6 (2004) 613.
- [21] B.C. Ream, US Patent 4877886, 1989.
- [22] C.H. McMullen, J.R. Nelson, B.C. Ream, J.R.J. Sims, US Patent 4314945, 1982.
- [23] J. Sun, S.I. Fujita, M. Arai, *J. Organomet. Chem.* 690 (2005) 3490.
- [24] Y. Kishimoto, I. Ogawa, *Ind. Eng. Chem. Res.* 43 (2004) 8155.
- [25] N. Kihara, T. Endo, *Macromolecules* 25 (1992) 4824.
- [26] J.W. Huang, M. Shi, *J. Org. Chem.* 68 (2003) 6705.
- [27] N. Kihara, N. Hara, T. Endo, *J. Org. Chem.* 58 (1993) 6198.
- [28] B. Barkakaty, K. Morino, A. Sudo, T. Endo, *Green Chem.* 12 (2010) 42.
- [29] D.D. Perrin, W.L.F. Armarego, *Purifications of Laboratory Chemicals*, Butterworth-Heinemann, Oxford, 2000.
- [30] F. Li, L. Xiao, C. Xia, B. Hu, *Tetrahedron Lett.* 45 (2004) 8307.
- [31] Y. Patel, J. George, S.M. Pillai, P. Munshi, *Green Chem.* 11 (2009) 1056.
- [32] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, 1999.
- [33] F.A. Carey, R.J. Sundberg, *Advanced Organic Chemistry: Structure and Mechanisms – Part A*, Springer, 2007.
- [34] H. Sakurai, N. Iwasawa, K. Narasaka, *Bull. Chem. Soc. Jpn.* 69 (1996) 2585.
- [35] J.A. Dean, *Leng's Handbook of Chemistry*, McGraw Hill Book Company, 1985.
- [36] H.A. Sober, *CRC Handbook of Biochemistry*, CRC Press, Cleveland, Ohio, 1968.
- [37] R.B. Pritchard, C.E. Lough, J.B. Reesor, H.L. Holmes, D.J. Currie, *Can. J. Chem.* 45 (1967) 775.
- [38] M.C. Tobin, *Spectrochim. Acta* 16 (1960) 1108.
- [39] N.B. Colthup, *Interpretation of Infrared Spectra*, The American Chemical Society, 1980.
- [40] D.J. Darensbourg, R.M. Mackiewicz, *J. Am. Chem. Soc.* 127 (2005) 14026.
- [41] D.J. Hildebrand, P.G. Jessop, C.A. Thomas, C.A. Eckert, C.L. Liotta, *J. Org. Chem.* 70 (2005) 5335.