

# Carbon dioxide chemistry: Examples and challenges in chemical utilization of carbon dioxide\*

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*Abstract:* The development of catalytic methods for chemical transformation of CO<sub>2</sub> into useful compounds is of paramount importance from a standpoint of C1 chemistry and so-called green chemistry. The kinetic and thermodynamic stability of CO<sub>2</sub> molecule presents significant challenges in designing efficient chemical transformations based on this potential feedstock. In this context, efforts to convert CO<sub>2</sub> to useful chemicals will inevitably rely on its activation through molecular catalysts, particularly transition-metal catalysts. Two preparative processes employing solid catalyst or CO<sub>2</sub>-philic homogeneous catalyst were devised for environmentally benign synthesis of organic carbonates and oxazolidinones under solvent-free conditions. Those processes represent pathways for greener chemical fixations of CO<sub>2</sub> to afford industrial useful materials such as organic carbonates and oxazolidinones with great potential applications.

*Keywords:* carbon dioxide; heterogeneous catalysis; homogeneous catalysis; molecular activation; organic carbonate; oxazolidinone.

## INTRODUCTION

The development of catalytic methods for chemical transformation of CO<sub>2</sub> into useful compounds is of paramount importance not only from a standpoint of C1 chemistry and so-called green chemistry, but also from that of simulating photosynthesis and enzyme-catalyzed reactions in the laboratory for understanding the photosynthetic process in nature and in utilizing enzyme-analogous reactions for chemical syntheses [1]. However, CO<sub>2</sub>'s inherent thermodynamic stability and kinetic inertness hinder the development of metal catalysts that achieve CO<sub>2</sub> activation and functionalization. Accordingly, efforts to convert CO<sub>2</sub> to useful chemicals will inevitably rely on its activation via either metal coordination or weak interaction between active species and CO<sub>2</sub> molecule. In this context, metal complexes with CO<sub>2</sub> may offer both structural and functional models for surface-bound intermediates in catalytic conversion processes [2].

Currently, organic carbonates and oxazolidinones are both valuable products, and the carboxylation of epoxides/aziridines with CO<sub>2</sub> is one of the most promising and eco-friendly methods for chemical conversion of CO<sub>2</sub> into cyclic carbonates and/or polycarbonates or oxazolidinones. Organic carbonates have come to occupy an important position as excellent solvents and useful intermediates [3]. In particular, dimethyl carbonate (DMC) has been drawing much attention as a safe, non-

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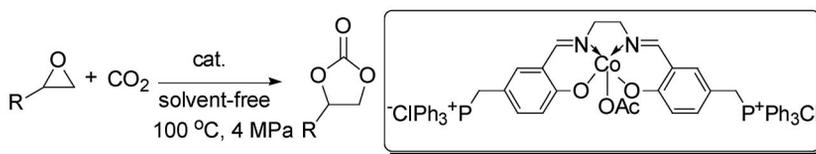
corrosive, and environmentally friendly building block for the production of polycarbonate and other chemicals [4]. Also, DMC is of interest as an additive to fuel oil owing to the high octane number, reducing particulate emission from diesel engines. In addition, oxazolidinones are important heterocyclic compounds showing a large application as intermediates and chiral auxiliaries in organic synthesis [5]. Cyclic carbamates like 5-substituted oxazolidinones are often employed as fragments in biologically active materials for pharmaceutical and agricultural uses.

## RECYCLABLE HOMOGENEOUS CATALYSIS FOR CYCLIC CARBONATE SYNTHESIS

The reaction of CO<sub>2</sub> with oxiranes to produce cyclic carbonates has been of interest as a useful method for its fixation by a chemical process. Homogeneous catalysts generally show higher catalytic activity and selectivity, so many catalytic systems have been developed for cyclic carbonate synthesis, mainly including onium salts or metal halide, ionic liquids, multicomponent bifunctional catalysts, polyoxometalates, and others. As catalyst recycling is often a vital problem in homogeneous catalysis, efficient recycling concepts have to be developed. To preserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst, an appealing methodology would employ a CO<sub>2</sub>-philic support for the reaction such that the supported catalyst dissolves during the reaction and can be precipitate quantitatively at the separation stage. The most commonly used parameters to induce the precipitation are temperature, solvent, polarity, and pH of the solution [6].

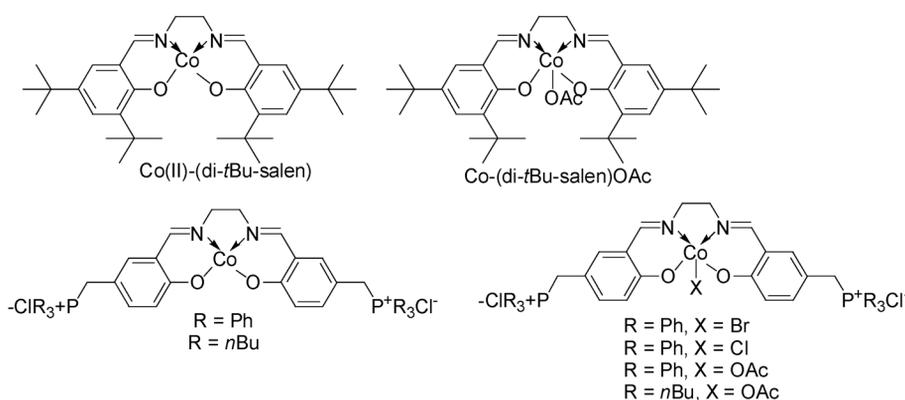
### Bifunctional metal-salen complexes: Efficient and recyclable homogeneous catalyst

A bifunctional cobalt-salen complex containing a Lewis acidic metal center and a quaternary phosphonium salt unit anchored on the ligand effectively catalyzes the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides under mild conditions without the utilization of additional organic solvents or co-catalysts (Scheme 1) [7]. The effects of various reaction variables on the catalytic performance were studied in detail and indicate an optimized reaction temperature of about 100 °C and CO<sub>2</sub> pressure of around 4 MPa, although the reaction proceeds smoothly even at pressures as low as 2 MPa. In order to compare the activity of the catalysts, we also synthesized the simple salen complexes besides the bifunctional complexes (Scheme 2). The catalyst is applicable to a variety of epoxides, producing the corresponding cyclic carbonates in good yields in most cases. Furthermore, the catalyst can be easily recovered and reused several times without significant loss of its catalytic activity. This process thus represents a greener pathway for the environmentally benign chemical fixation of CO<sub>2</sub> to produce cyclic carbonates.



**Scheme 1** Co-catalyst with no co-catalyst for the cycloaddition of CO<sub>2</sub> with epoxides.

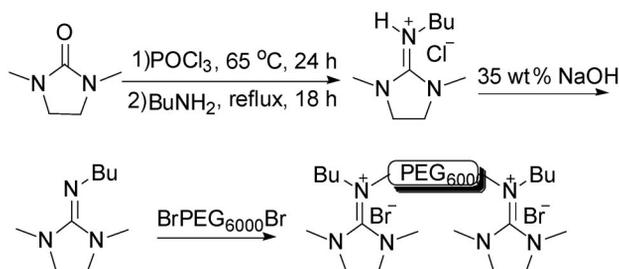
A possible mechanism for the single-component bifunctional metal-salen complex-catalyzed coupling of epoxides and CO<sub>2</sub> is proposed. This mechanism is closely related to that of the corresponding two-component metal-salen complex-catalyzed reaction. Accordingly, the enhancement of catalytic performance is presumably attributed to a synergistic effect of the two functional groups, with Lewis acidic centers (i.e., Co center) activating propylene oxide (PO) and Lewis basic species (chloride anion) attacking an activated epoxide coordinated to another Co-salen molecule. On the other hand, poor catalytic activity is putatively attributed to the lack of such a cooperative effect in the catalyst systems.



**Scheme 2** Co<sup>II/III</sup>-salen catalyst used in this study.

### Guanidinium salt-functionalized polyethylene glycol

A guanidinium bromide covalently bound to CO<sub>2</sub>-philic polyethylene glycol (PEG) is proved to be a highly effective homogeneous catalyst for the eco-friendly synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides under mild conditions (Scheme 3), which requires no additional organic solvents or co-catalyst [8]. Notably, it has been found that there is a pronouncedly cooperative effect between the catalyst part and the support part. Moreover, the catalyst is able to be reused with retention of high catalytic activity and selectivity. This process looks promising as a strategy for homogeneous catalyst recycling.

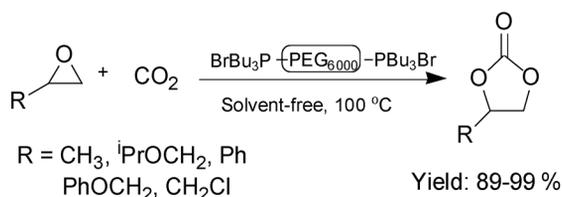


**Scheme 3** Synthesis of PEG<sub>6000</sub>-supported guanidinium bromide.

A series of catalytic cycles were subsequently examined to test the catalyst recycling. The work-up of the reaction was performed by extraction with ethyl ether. The recovered catalyst was then subjected to a second run of the reaction without replenishment of fresh catalyst by charging with the same substrate. The yield of product achieved over 90 % after the fourth recycling process. It has been demonstrated that the catalyst is able to be reused with retention of high catalytic activity. The leaching of the active ingredient of the catalyst was also tested. The solidified catalyst was thoroughly filtered from the product solution, and the content of bromide ion in the resulting filtrate was measured by ion chromatography with a DIONEX DX-120 ion chromatographic instrument. The content of bromide ion was at the level of 60 ppm, demonstrating the thermal stability of the catalyst. Conclusively, the recyclability of the catalyst makes the reaction economically and potentially viable for commercial applications.

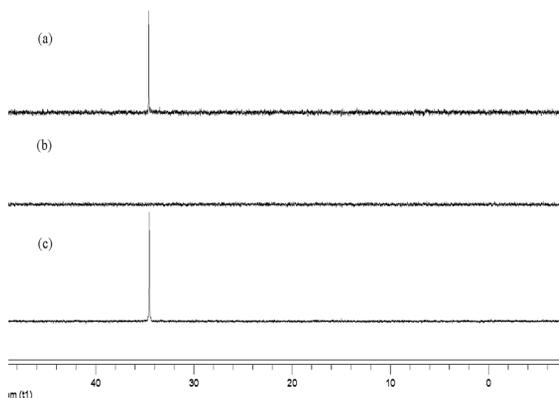
### Phosphonium salt-functionalized polyethylene glycol

The  $\text{BrBu}_3\text{PPEG}_{6000}\text{PBu}_3\text{Br}$  displayed higher catalytic activity than the unsupported one ( $n\text{-Bu}_4\text{PBr}$ , TBAB), even more effective than the simple physical mixture of  $n\text{-Bu}_4\text{PBr}$  and  $\text{PEG}_{6000}$  under the same conditions (Scheme 4). The enhancement of catalyst performance by supporting  $n\text{-Bu}_4\text{PBr}$  on soluble PEG is presumably attributed to the benefits from changes in the physical properties [9] of the reaction mixture, such as lower melting points, lower viscosity, high diffusion rates, and increased solubility for PO and  $\text{CO}_2$  through “ $\text{CO}_2$ -expansion of a liquid” effect [10]. Indeed, as judged by visual inspection through a window-equipped high-pressure reactor, we found that PEG and its derivatives are expandable with  $\text{CO}_2$ .



**Scheme 4** Synthesis of various carbonates catalyzed by  $\text{BrBu}_3\text{PPEG}_{6000}\text{PBu}_3\text{Br}$ .

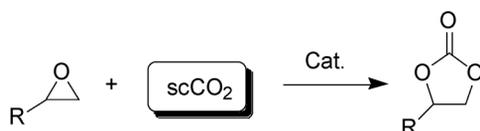
A series of catalytic cycles were examined to test the catalyst recycling. In each cycle, the catalyst ( $\text{BrBu}_3\text{PPEG}_{6000}\text{PBu}_3\text{Br}$ ) was solidified by adding ether and cooling after the reaction, and recovered by a simple filtration without catalyst leaching detected by  $^{31}\text{P}$  NMR (Fig. 1), and then subjected to a second run of the reaction by charging with the same substrates [11]. The five runs are almost consistent in yield and selectivity. Moreover, a high purity (>99 %) of the product was obtained in each cycle without any additional purification process. Hence, immobilization of a phosphonium salt on a soluble polymer (e.g., PEG) provides an alternative pathway for realizing homogeneous catalyst recycling.



**Fig. 1**  $^{31}\text{P}$  NMR (161.7 MHz,  $\text{CDCl}_3$ ): (a) the fresh  $\text{BrBu}_3\text{PPEG}_{6000}\text{PBu}_3\text{Br}$ ; (b) the filtrate after reaction; (c) the separated catalyst after the third run.

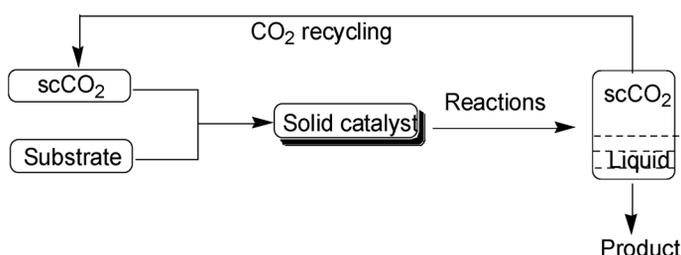
## HETEROGENEOUS CATALYSIS FOR CYCLIC CARBONATE SYNTHESIS

In current processes employed by industry and research activities on chemical synthesis, homogeneous catalyst is undesirably dissolved in a phase containing cyclic carbonate. Thus, it is required to separate the catalyst from the product through a purification process such as distillation after completion of the reaction, resulting in complicated production processes, and decomposition of the catalyst or formation of by-products during the separation step. In order to facilitate the separation of the catalyst, a preparative process employing solid catalyst was devised for environmentally benign synthesis of cyclic carbonates under supercritical CO<sub>2</sub> without any organic solvent, as shown in Schemes 5 and 6 [12].



Cat.: R<sub>4</sub>NX/SiO<sub>2</sub>; ILs/SiO<sub>2</sub>; R<sub>3</sub>N<sup>+</sup>X<sup>-</sup>-polystyrene

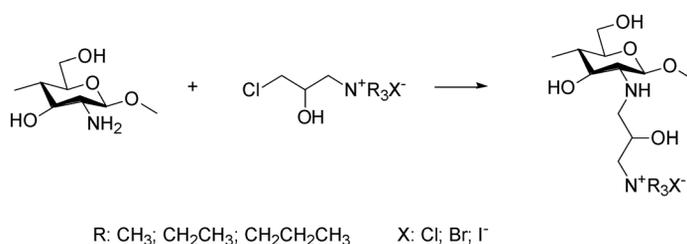
**Scheme 5** Cyclic carbonate synthesis from CO<sub>2</sub> and epoxide.



**Scheme 6** Heterogeneous catalysis in supercritical CO<sub>2</sub>.

To preserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst, one strategy is to graft the active species onto an insoluble support, whereby the catalyst can be readily separated from the reaction mixture by filtration. One type of polystyryl-supported catalyst containing ammonium salt or amino group, and the polar macroporous adsorption resin, and silica-supported ammonium salt as well as silica-supported imidazoline-based ionic liquids, are efficient and reusable heterogeneous basic catalysts under supercritical CO<sub>2</sub> conditions without any additional organic solvent for the synthesis of propylene carbonate (PC) from PO and CO<sub>2</sub>. The almost quantitative yield together with excellent selectivity was obtained. The purity of product directly separated out by filtration from the reaction mixture in a batch reactor reached more than 99.3%. The catalyst was then recovered and reused in subsequent cycles. The process represents a simple, ecologically safer, cost-effective route to cyclic carbonates from the reactions of epoxides with CO<sub>2</sub>.

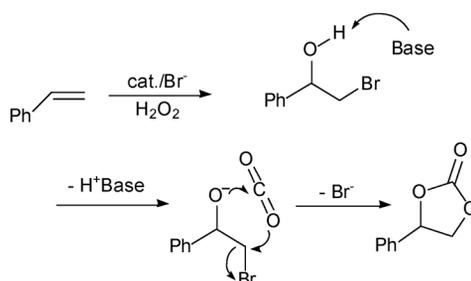
A functionalized biopolymer-chitosan-supported quaternary ammonium salt (abbreviated as CS-N<sup>+</sup>R<sub>3</sub>X<sup>-</sup>, Scheme 7) was also shown to be a single-component active catalyst for the cycloaddition reaction of epoxides and CO<sub>2</sub> [13]. This organic solvent-free process presented here could show much potential application in industry due to its simplicity, easy product separation, using a biopolymer as a support, and ease of catalyst recycling.



**Scheme 7** Ammonium salt-functionalized chitosan.

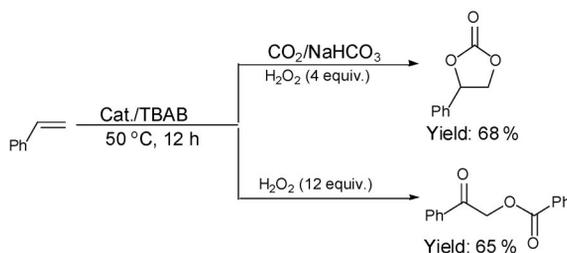
## DIRECT CONVERSION OF OLEFIN INTO CYCLIC CARBONATE

One of the most promising methodologies of chemical fixation CO<sub>2</sub> is the synthesis of five-membered cyclic carbonates via the cycloaddition of epoxide to CO<sub>2</sub>. However, such a cycloaddition generally requires the initial synthesis of epoxides, which involves toxic or costly reagents and requires tedious work-up for separation. Therefore, a promising approach would be direct synthesis of cyclic carbonates from olefins instead of epoxides [14], a so-called one-pot “oxidative carboxylation” of olefin utilizing CO<sub>2</sub> as a building block (Scheme 8).



**Scheme 8** Direct synthesis of styrene carbonate from styrene and CO<sub>2</sub> through “oxybromination” in situ generated.

Inspired by the biomimetic oxybromination, a binary catalyst system composed of sodium phosphotungstate and TBAB was developed for facile synthesis of styrene carbonate in a single operation from styrene and CO<sub>2</sub> using 30 % H<sub>2</sub>O<sub>2</sub> as an oxidant with an aid of an inorganic base as a “CO<sub>2</sub>-activator” or “deprotonation reagent” (Scheme 8) [14]. Notably, the presence of a base like NaHCO<sub>3</sub> markedly improved the formation of styrene carbonate. Interestingly, an oxidized product (i.e., phenacyl benzoate) could be obtained exclusively in good yield directly from styrene in the absence of CO<sub>2</sub> under the appropriate reaction conditions (Scheme 9).

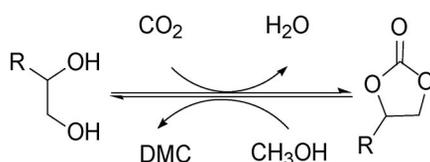


**Scheme 9** CO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>-tunable reaction: direct conversion of styrene into styrene carbonate or phenacyl benzoate.

This methodology is easily found to be applicable to several styrene derivatives, producing the corresponding cyclic carbonates. It is worth mentioning that the catalyst system can be recovered and reused with excellent activity. On the other hand, this finding represents a simpler and cost-effective pathway for the environmentally benign chemical fixation of CO<sub>2</sub> to produce cyclic carbonates and also offers a practical methodology to the synthesis of benzoate derivatives.

### CYCLIC CARBONATE FROM 1,2-DIOLS AND CO<sub>2</sub>

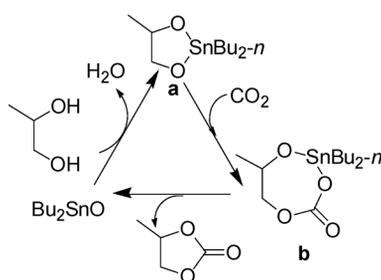
The process of DMC synthesis is composed of two steps: the carboxylation of PO with CO<sub>2</sub> to give PC, and PC is converted to DMC in the second step. In this procedure, propylene glycol (PG) is always a co-product with DMC. If PC can be synthesized from PG and CO<sub>2</sub> (Scheme 10), the process becomes more valuable since PG can be recycled. Overall, the reaction can be regarded as DMC synthesis from CO<sub>2</sub> and methanol. In this context, the synthesis of PC from PG and CO<sub>2</sub> could be more promising. The Sn compounds have been found to be active for synthesis PC from PG and CO<sub>2</sub> [15]. Currently, a great deal of interest has focused on the role of metal as the active centers in the fixation of CO<sub>2</sub>.



**Scheme 10** Green access to DMC from methanol and CO<sub>2</sub>.

Low-toxic magnesium and its oxide are proved to be a catalyst for highly selective synthesis of PC through the carbonylation of PG with CO<sub>2</sub> without any organic solvents or additives. Interestingly, the catalyst was demonstrated to be applicable to a variety of 1,2-diols such as glycol, phenyl glycol, and methanol, forming the corresponding carbonates in 100 % selectivity. As a result, employing a low-toxic and cheap catalyst could make PC synthesis much environmentally friendlier.

As for mechanistic consideration, CO<sub>2</sub> is likely to insert into the metal-oxygen. As shown in Scheme 11, the possible mechanism for Bu<sub>2</sub>SnO-catalyzed PC synthesis from PG and CO<sub>2</sub> was proposed [15]. The key intermediates **a**, **b**, or analog of **b** in the catalytic cycle were successfully characterized by IR and NMR (Figs. 2 and 3).



**Scheme 11** Postulated mechanism for the Bu<sub>2</sub>SnO-catalyzed reaction.

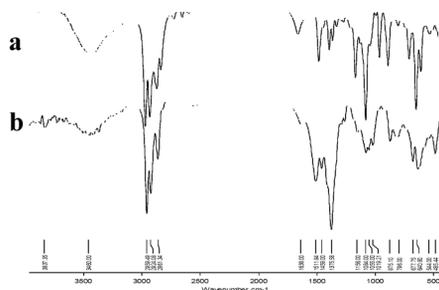


Fig. 2 FT-IR spectra.

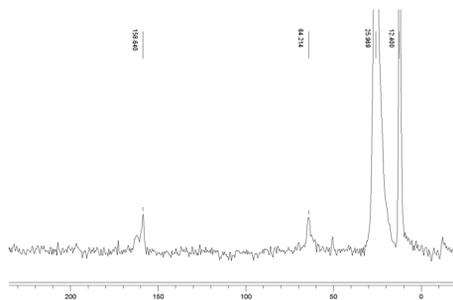
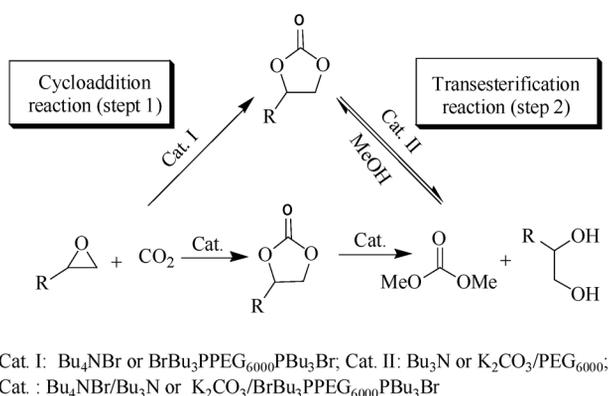


Fig. 3 CP-MAS  $^{13}\text{C}$  NMR of intermediate **b**.

Dioxastannolane **a** [16] was obtained in almost quantitative yield by stirring a mixture of 10 mmol of  $\text{Bu}_2\text{SnO}$  and 100 mmol of PG at 50 °C for 30 min [m.p. 192–194 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.89 (t,  $^3J = 7.2$  Hz, 6H) 1.10 (d,  $^3J = 5.6$  Hz, 3H), 1.62–1.26 (m, 12H), 2.98 (m, 1H), 3.69 (s, 2H);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.2, 20.5, 22.1, 26.6, 26.7, 27.1, 27.2, 68.1, 68.9]. Then dry  $\text{CO}_2$  (gas) was bubbled through 6 ml,  $\text{CHCl}_3$  solution of **a** (1.2280 g, 3 mmol) for 10 min. The solution turned turbid, and a cyclic tin carbonate **b** (white powder, m.p. >300 °C) was isolated by filtration. The spectral evidences includes the signature of 158.6 ppm corresponding to “ $\text{CO}_3$ ” in the solid state (cross-polarization magic angle spinning, CP-MAS)  $^{13}\text{C}$  NMR spectrum (Fig. 3), and the IR absorption bands (Fig. 2) assigned to carbonyl [1511(s), vas ( $\text{CO}_3$ ) and 1375 (vs), vs ( $\text{CO}_3$ )] support the presence of the carbonyl group in the intermediate **b**, indicating the  $\text{CO}_2$  insertion to the intermediate **a**.

### ONE-POT SYNTHESIS OF DMC FROM EPOXIDE, $\text{CO}_2$ , AND METHANOL

To simplify the preparative procedure for DMC synthesis based on the two-step process from  $\text{CO}_2$ , namely, to eliminate the separation of the cyclic carbonate and realize catalyst recycling, we separately explored in detail the cycloaddition of PO and  $\text{CO}_2$  to form PC (step 1, Scheme 12) and the transesterification reaction of PC with methanol to DMC (step 2). The coexistence of all reactants (epoxide, methanol, and  $\text{CO}_2$ ) could cause several side reactions, such as methanolysis of epoxide, and optimal reaction conditions for steps 1 and 2 are not always compatible with each other. Accordingly, developing efficient catalysts for both steps and the optimization of reaction conditions are crucial to the one-pot synthesis of DMC. Our strategy is such a so-called “monophase reaction, two-phase separation” that supports active homogenous catalyst, e.g., phosphonium halide, which could be easily detected by  $^{31}\text{P}$  NMR, onto  $\text{CO}_2$ -philic polymer PEG is expected to enhance the catalytic activity and recover the catalyst. It was found that the recyclable binary catalyst system or single catalyst displayed highly actively for this process under mild reaction conditions.

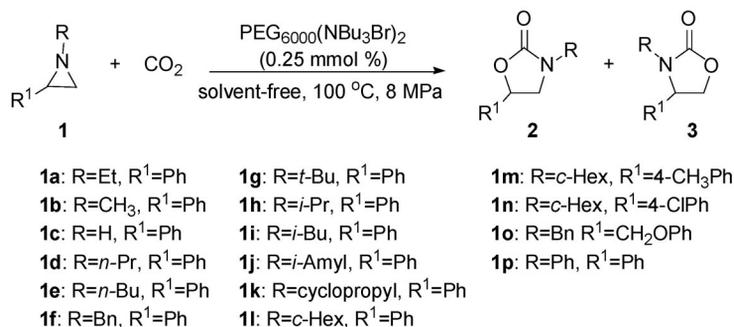


**Scheme 12** Synthesis of DMC from methanol, epoxides, and  $\text{CO}_2$ .

A homogeneous binary catalyst system in Scheme 12,  $n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N}$ , was found to be active for the synthesis of DMC from styrene oxide (SO), methanol, and supercritical  $\text{CO}_2$  [17]. Under the optimized conditions, the DMC yield could reach 84 % at SO conversion of 98 %. The designing of effective binary catalysts for two steps and judicious choice of reaction conditions are keys to the highly efficient one-pot synthesis of DMC.

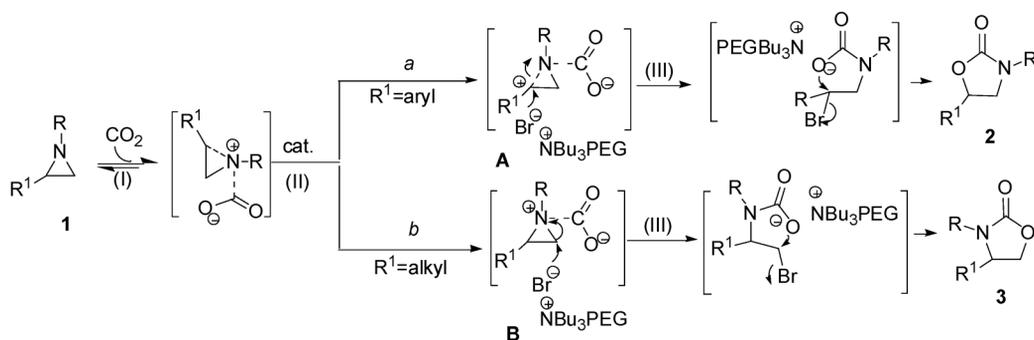
### RECYCLABLE HOMOGENEOUS CATALYSIS FOR SELECTIVE SYNTHESIS OF 5-ARYL-2-OXAZOLIDINONES

A quaternary ammonium bromide covalently bound to PEG ( $M_w = 6000$ ), i.e.,  $\text{PEG}_{6000}(\text{NBu}_3\text{Br})_2$  was found to be an efficient and recyclable catalyst for the cycloaddition reaction of aziridines to  $\text{CO}_2$  under mild conditions without utilization of additional organic solvents or co-catalysts in Scheme 13. As a result, 5-aryl-2-oxazolidinone was obtained in high yield with excellent chemo- and regioselectivity. The catalyst worked well for a wide variety of 1-alkyl-2-arylaziridines [18]. Besides, the catalyst could be recovered by centrifugation and reused without significant loss of catalytic activity and selectivity.



**Scheme 13** Carboxylation of aziridine into oxazolidinone.

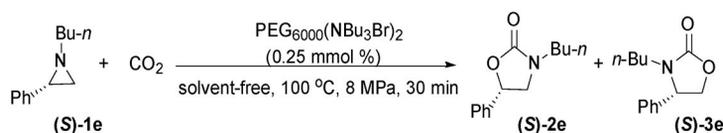
Based on the experiment results, a possible mechanism for the  $\text{PEG}_{6000}(\text{NBu}_3\text{Br})_2$ -catalyzed cycloaddition of  $\text{CO}_2$  with aziridine was proposed as shown in Scheme 14. This proposal is analogous to that of LiI-catalyzed version for the same reaction. The mechanism involves three steps: coordination of  $\text{CO}_2$  to aziridine (step I), then ring-opening of the aziridine through two different pathways as represented by paths a and b mainly depending on the nature of R<sup>1</sup> group when alkyl substitution at the



**Scheme 14** Putative mechanism.

N-position (step II), and subsequent cyclization via an intramolecular nucleophilic attack leading to oxazolidinones and regeneration of the catalyst (step III). In this respect, the following observation supports our hypothesis. The rate dependence on the steric effect of the R group on the nitrogen atom implies that the coordination of CO<sub>2</sub> to the aziridine (I) is a reversible step in the catalytic cycle. This proposed mechanism could also account for the effect of the R<sup>1</sup> substituent on the selective formation of **2** or **3**. As deduced from Scheme 14, it is reasonable that if R<sup>1</sup> is an aryl group, intermediate **A** would be more stable than **B**, accordingly leading to predominant-forming **2**; whereas, if R<sup>1</sup> is an alkyl group, **B** would be favored, thus resulting in dominant-producing **3**.

Furthermore, the reaction of (*S*)-1-butyl-2-phenylaziridine (**S-1e**) with CO<sub>2</sub> in the presence of 0.25 mol % PEG<sub>6000</sub>(NBu<sub>3</sub>Br)<sub>2</sub> affords **S-2e** in 91.4 % yield and **S-3e** in 8.6 % yield with retention of stereochemistry (Scheme 15) [18], further supporting the above mechanism; where there is a double inversion of stereochemistry at the chiral carbon center, which is attacked, to produce **S-2e** or the reaction does not involve the chiral carbon center to generate **S-3e**.



**Scheme 15** Carboxylation of (*S*)-1-butyl-2-phenylaziridine into oxazolidinone.

We developed an efficient and recyclable catalyst for high selective synthesis of 5-substituted oxazolidinones from CO<sub>2</sub> and various aziridines without any added organic solvents or co-catalysts. It is also found that selective formation of 5-substituted oxazolidinone or 4-substituted isomer relies on substituents at the carbon of the substrate. One of the salient features of this protocol would be that the catalyst can be readily recovered by centrifugation and reused with retention of high catalytic activity and both chemo- and regioselectivities.

## CONCLUSIONS

CO<sub>2</sub> can be regarded as an abundant and readily accessed atmospheric gas that could, in principle, be a useful synthon for organic compounds. However, its inherent thermodynamic stability and kinetic inertness hinder the development of metal catalysts that achieve CO<sub>2</sub> activation and functionalization. In this regard, the formation of a transition-metal CO<sub>2</sub> complex via direct coordination is one of the most powerful ways to induce the inert CO<sub>2</sub> molecule to undergo chemical reactions. However, only weak inter-

actions between CO<sub>2</sub> and the active catalytic center in specific cases are sufficient to bring about catalytic reactions involving the insertion of CO<sub>2</sub> [2]. Accordingly, only if we understand the underlying principles of CO<sub>2</sub> activation can the goal of using CO<sub>2</sub> as an environmentally friendly and economically feasible source of carbon be achieved. Those findings summarized here would open synthetic pathways for the selective synthesis of organic carbonates and oxazolidinones as well as their derivatives from an abundant chemical feedstock and demonstrate that such CO<sub>2</sub> functionalization with high-energy starting material like epoxides is easily operative. We hope this presentation will stimulate further interest in research that may lead to the development of CO<sub>2</sub> as a new source for fuels and fine chemicals.

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