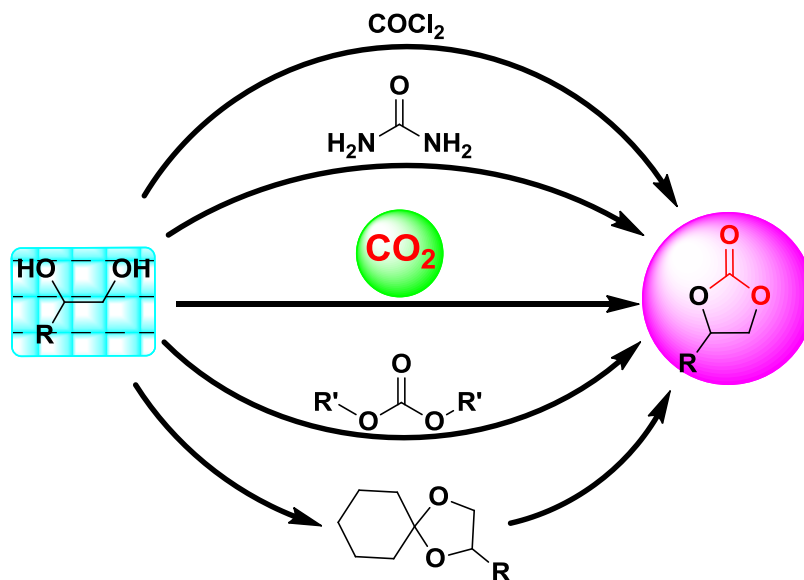


Metal-promoted Synthesis of Cyclic Carbonates from 1,2-diols and Carbon Dioxide

Chun-Xiang Guo, Ran Ma and Liang-Nian He*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, People's Republic of China

Abstract: Chemical fixation of CO₂ to value-added products/materials/fuel has attracted more and more attention from both academia and governmental agencies all over the world since CO₂ is an easily available and sustainable C₁ resource with the advantage of being abundant, nontoxic, nonflammable and renewable. Synthesis of organic carbonates starting from CO₂ is one of the most promising methodologies and has been widely investigated. The use of CO₂ and 1,2-diols can bring many advantages, such as reusing the byproducts generated in the industrial dimethyl carbonate (DMC) process and simplifying the post purification process. In this paper, synthetic methods with reaction mechanism of ethylene carbonate (EC), propylene carbonate (PC) and glycerol carbonate from CO₂ and ethylene glycol (EG), or propylene glycol (PG) or glycerol are systematically discussed.



Keywords: Carbon dioxide, catalysis, cyclic carbonate, glycerol, glycol.

1. INTRODUCTION

Carbon dioxide as one of the main greenhouse gases has badly endangered the environment in association with global warming, sea-level-rise and species extinction [1]. The concentration of CO₂ in the atmosphere has risen up speedily from 280 ppm to 380 ppm in the past 200 years and this trend will be maintained for a long term [2]. On the other side of the coin, CO₂ is a safe, cheap and abundant C₁

building block in organic synthesis with enormous potential applications [3, 4]. Chemical fixation of CO₂ into value-added products has attracted more and more attention from both the scientific communities and governmental agencies. Generous efforts have been devoted to the development of various efficient chemical approaches for the utilization of CO₂, in which the production of cyclic carbonate is an effective route [4-6].

Organic carbonates, which have favorable properties with high boiling/flash points, low odor levels, low evaporation rates and low toxicities, have been used in various domains such as solvents, detergents, monomers for polycarbonates and polyurethanes, electrolytes liquid carrier in lithium and lithium-ion batteries, and so on [7, 8].

*Address correspondence to this author at the State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, People's Republic of China; Tel.: (+86) 22-23503878; Fax: (+86) 22-23503878; E-mail: heln@nankai.edu.cn

Linear carbonates, for example, dimethyl carbonate (DMC) are widely used as raw materials for the production of polycarbonates in chemical industry. The traditional synthetic method commonly uses toxic and corrosive phosgene as a carbonylating reagent (Scheme 1). In view of green chemistry, indirect utilization of CO₂ and 1,2-diols to form DMC may avoid facility corrosion and reduce the environmental burden [9, 10]. DMC synthesis directly from methanol and CO₂ is one of the most anticipated routes. Several transition metals have been developed to promote this process, whereas productivity is far from being applied to industrial exploitation due to the thermodynamic limitation [11-13]. One strategy is to go through the transesterification of methanol with cyclic carbonate e.g. PC or EC to afford DMC. But some shortcomings still exist: (1) epoxy compounds are expensive and toxic; (2) the co-product i.e. 1,2-diol is an oversupplied; (3) separation of DMC from 1,2-diol is an energy-extensive process.

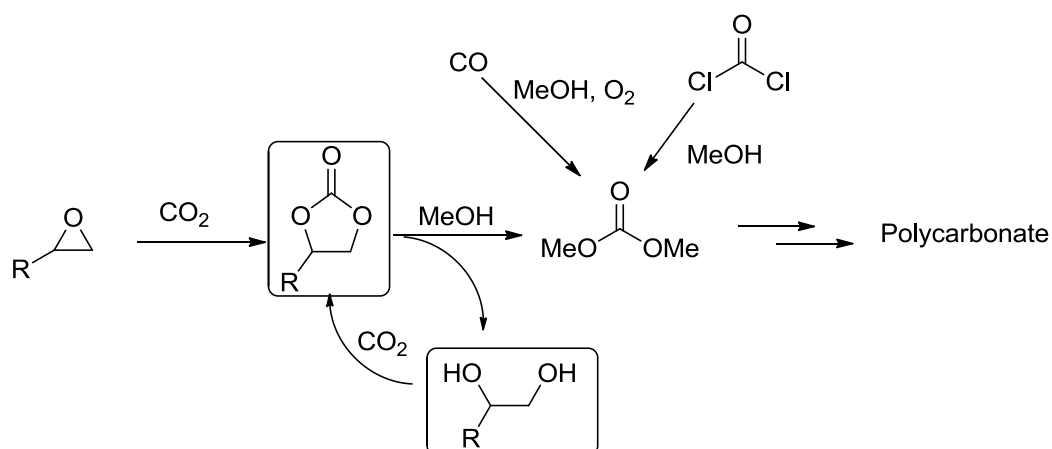
If cyclic carbonate (PC or EC) could be synthesized from the corresponding 1,2-diol and CO₂, the process would be more valuable since the 1,2-diol can be recycled, the overall reaction can be regarded as DMC production from CH₃OH and CO₂.

There are two routes to synthesize cyclic carbonates from 1,2-diols and CO₂. One is direct dehydration of 1,2-diols and CO₂ promoted by metallic oxides, metal carbonates, organic bases and transition metal complexes with the aid of physical or chemical dehydrating agent. Another is an indirect method by using derivatives of 1,2-diols to overcome the thermodynamic limitation. In this paper, we attempt to feature the advances in the field of cyclic carbonate synthesis from 1,2-diols and CO₂ except electrochemical routes.

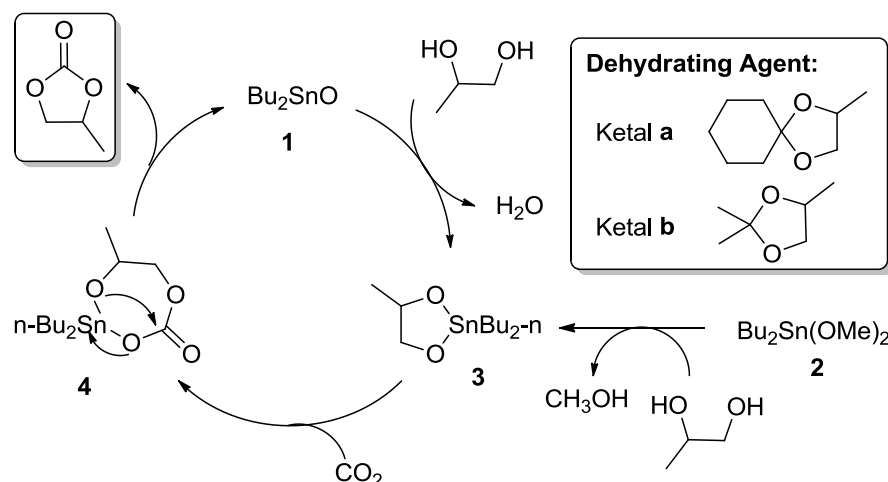
2. DIRECT COUPLING OF 1,2-DIOL AND CO₂

2.1. Metallic Oxide/Acetate-catalyzed Cyclic Carbonate Synthesis

Tomishige [14, 15] and co-workers have reported that the CeO₂-ZrO₂ mixed oxide by calcining hydroxides in air can catalyze the synthesis of cyclic carbonate from CO₂ and 1,2-diol with high activity and selectivity. The catalytic activity depends on the molar ratio of Ce to Zr and preparative temperature. The highest activity is reached when Ce/(Ce+Zr)= 0.33 is used and calcined at 1273 K. No carbonate is detected when ZrO₂ is used alone, suggesting



Scheme 1. Synthetic methods for DMC production.



Scheme 2. The proposed reaction mechanism for the Bu₂SnO-catalyzed PC synthesis from CO₂ and PG.

that CeO_2 could be a real active species and the role of ZrO_2 is to maintain sufficient surface area.

Sn-complexes e.g. Bu_2SnO and $\text{Bu}_2\text{Sn}(\text{OMe})_2$, known as efficient catalysts for DMC preparation from CH_3OH and CO_2 [16-18], have been successfully applied to cyclic carbonate synthesis with 99.9% selectivity and the highest TON (Turnover number) of 68 [19]. The conversion of PG is notably improved when *N,N*-dimethylformamide (DMF) is added as co-solvent. But no reaction occurs when DMF alone is used. Less toxic $\text{Ti}(\text{OPr})_4$ also exhibits good activity for the reaction of PG and CO_2 to form PC under similar conditions.

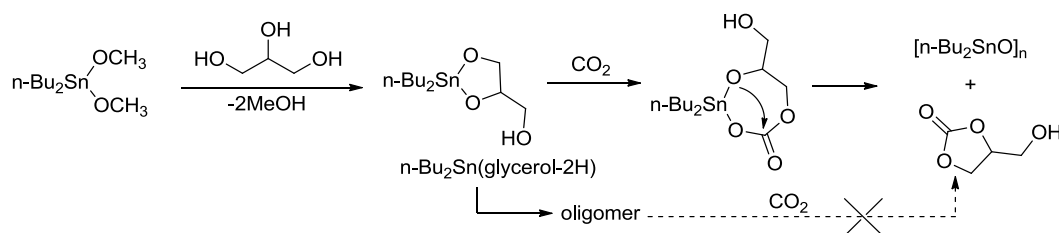
Though the perfect selectivity could be attained under the optimal reaction conditions, the PC yield is unsatisfactory. This is probably because the reaction is controlled by thermodynamic equilibrium. Therefore, it is necessary to remove water in situ generated during the reaction. Furthermore, when a ketal (cyclohexanone cyclic propylene ketal, ketal **a** or 2,2,4-trimethyl-1,3-dioxolane, ketal **b**) is used as a dehydrating agent, the PC yield is greatly enhanced [19].

A plausible mechanism for the Bu_2SnO -catalyzed synthesis of cyclic carbonate from PG and CO_2 has been proposed as illustrated in Scheme 2: At first, *n*- Bu_2SnO reacts with PG to give 2,2-dibutyl-1,3,2-dioxastannolan **3**;

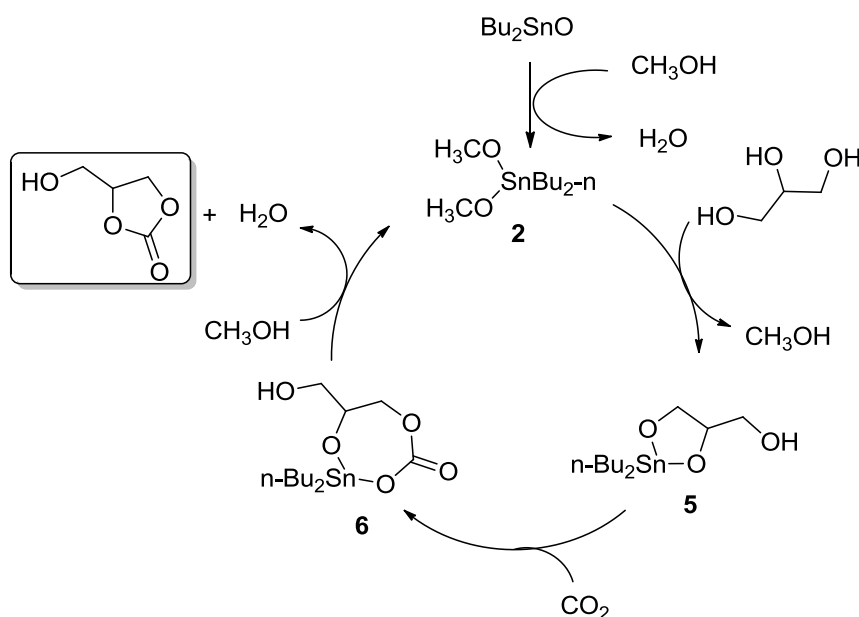
since Sn-O bond is prone to CO_2 insertion, the cyclic tin carbonate **4** then is generated from complex **3**; finally, intramolecular nucleophilic attack of alkoxy group at the carbonyl carbon atom results in PC formation with regeneration of dibutyltin oxide. In addition, $\text{Bu}_2\text{Sn}(\text{OMe})_2$ gave comparable catalytic activity with Bu_2SnO [20].

The transesterification of EC/PC with glycerol is found to be only one method for glycerol carbonate synthesis until Angela [21] and coworkers have reported glycerol carbonate synthesis directly from glycerol and CO_2 (5 MPa) at 450 K in the presence of the tin-catalyst. In particular, *n*- $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$ displays relatively higher activity than *n*- Bu_2SnO , while $\text{Sn}(\text{OMe})_2$ reacts with CO_2 to afford $[(\text{MeO})\text{Sn}[\text{OC}(\text{O})\text{OMe}]]_n$ and thus is inactive for glycerol carbonate synthesis. *n*- $\text{Bu}_2\text{Sn}(\text{OMe})_2$ initially reacts with glycerol to afford *n*- $\text{Bu}_2\text{Sn}(\text{glycerol-2H})$, which then could either oligomerize or incorporate with CO_2 to generate glycerol carbonate. The oligomer precipitates from the reaction mixture and can not further react with CO_2 , leading to decrease in the catalytic activity as shown in Scheme 3 [22].

In George's report, catalytic amount of *n*- Bu_2SnO (1mol%) is used to prepare glycerol carbonate from glycerol and CO_2 in CH_3OH [23]. CH_3OH plays vital role in promoting the reaction. CH_3OH not only works as a solvent, but also facilitates the reaction. At least 25–30 mol%



Scheme 3. Synthesis of glycerol carbonate from CO_2 and glycerol promoted by *n*- $\text{Bu}_2\text{Sn}(\text{OMe})_2$.



Scheme 4. $\text{Bu}_2\text{Sn}(\text{OMe})_2$ -catalyzed PC synthesis from CO_2 and PG.

methanol (relative to glycerol) is required for performing the reaction smoothly. Although *n*-Bu₂SnO is known as the catalyst for DMC formation, no DMC is detected in this reaction system. The yield of glycerol carbonate can reach as high as 35% when 13X (soda) zeolite is introduced as a dehydrating reagent under optimal conditions. The possible mechanism is proposed as shown in Scheme 4: Bu₂SnO is activated by methanol to give the active species **2**, which is quite different from previous reports; **2** is then converted into **5** with the formation of glycerol carbonate [21].

Low toxic magnesium and its oxide have been developed for the synthesis of PC from PG and CO₂ without any solvent or additive [24]. PC is detected as the sole product and a variety of alcohols such as glycol, phenyl glycol, and even CH₃OH work well. Other metal oxides such as ZnO, MgO and Al₂O₃ are also found to be active and the activity is higher than that of the two-component CeO₂-ZrO₂ and the homogeneous tin catalysts.

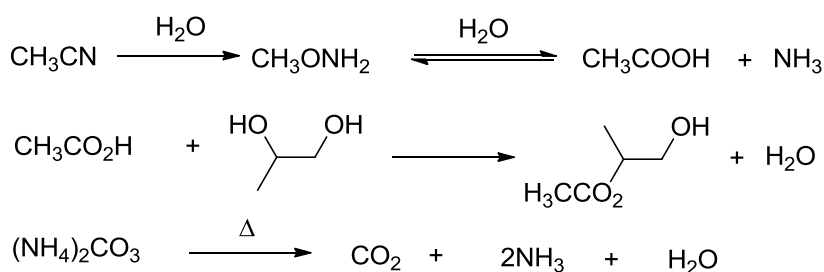
Potassium salt-modified ZnO catalyst developed by Sun *et al.* [25] displays excellent activity for the synthesis of PC. ZnO modified with KI (4 mmol/g) performs the highest activity. However, superfluous KI content leads to a decrease in activity, presumably due to that plethoric KI makes uneven dispersion of KI on ZnO. The activity can be further improved by calcination [26].

In this system, CH₃CN is used as not only a solvent but also a dehydrating reagent to remove water as shown in

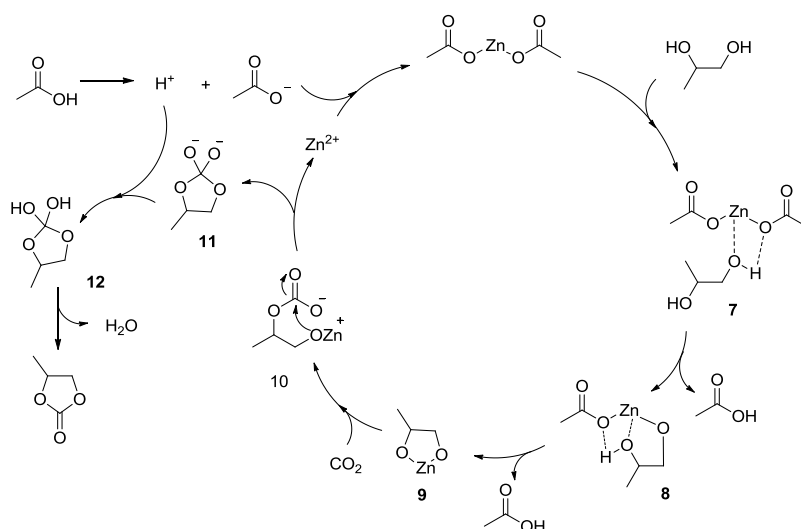
Scheme 5. The acetamide generated from the reaction of CH₃CN and H₂O can further react with H₂O to form acetic acid, which then undergoes the esterification with PG to produce propylene glycol-2-acetate. Although the PC yield achieves 12.6%, the selectivity is only 53%. To improve the selectivity, ammonium carbonate [(NH₄)₂CO₃] is employed [27]. It is well known that (NH₄)₂CO₃ can be easily degraded to produce NH₃. As a result, the addition of NH₃ prevents from further hydrolysis of acetamide and thereby improves PC selectivity up to 100%.

La-Zn mixed oxides have been utilized for the glycerol carbonate formation from CO₂ and glycerol [28]. Three kinds of La oxide are evaluated. La₂O₂CO₃ shows the best performance compared with La(OH)₃ and La₂O₃. A series of La₂O₂CO₃-ZnO oxides with various molar ratios are prepared at specific calcining temperature. The catalyst with molar ratio of La: Zn = 1:4 and calcining at 773 K displays the highest activity.

The reason why La-doped catalysts enhance the activity can be explained as follows: on one hand, addition of La increases the specific surface area and the exposed basic sites. On the other hand, introduction of La₂O₂CO₃ significantly increases the amount of lattice oxygen (La-O pairs) on the surface which leads to an increase in moderately basic sites. In addition, electron transfer from the Zn to the La or O improves the binding energy of Zn 2p_{3/2} and makes La-Zn catalyst more favorable to interact with glycerol [29, 30].



Scheme 5. CH₃CN with (NH₄)₂CO₃-promoted PC formation.



Scheme 6. Zn(OAc)₂-catalyzed mechanism for PC synthesis.

Different metallic acetates (*e.g.* Zn(OAc)₂) are used as catalysts for the synthesis of cyclic carbonates from CO₂ and 1,2-diols with CH₃CN as solvent [31]. Under optimal conditions, the yield of 1,2-propylene carbonate reaches 24.2% with 38.9% conversion of 1,2-propylene glycol. A possible mechanism is proposed as below: firstly, anhydrous Zn(OAc)₂ interacts with PG to form the complex **7**. Secondly, **7** eliminates two molecules of acetic acid to form **9**. Then, **9** can attack at CO₂ to afford the intermediate **11** and releases Zn²⁺. At last, **11** combines with H⁺ to form PC with the regeneration of the catalyst (Scheme 6) [32].

2.2. Organic/Inorganic Base-catalyzed Carbonate Synthesis

Alkali carbonates have also been found to be catalysts for PC synthesis from PG and CO₂ [33]. A series of alkali carbonates are examined systematically and potassium carbonate shows the highest catalytic activity. On the other hand, benzonitrile can be used as an excellent dehydrating reagent in place of CH₃CN to overcome some drawbacks such as low boiling point, toxicity and high polarity [34].

Apart from inorganic base, organic base can also promote the synthesis of cyclic carbonates from 1,2-diols and CO₂ [35, 36]. 15.3% yield and 100% selectivity can be attained when 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is used as a catalyst under the optimal conditions. In addition, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylamine (TEA) have also been active for the carboxylative cyclization of 1,2-diols with CO₂.

Through analyzing the optimized structures and energy of different probable routes by density functional theory (DFT) calculation, the dehydration step of the secondary hydroxyl in the PG-activated mechanism is identified as the most possible reaction pathway with the lowest energy barrier of 56.96 kcal/mol. TBD can be considered as a proton bridge activated by the synergistic effect of the N atoms. The proton transfer activity makes the deprotonated species more susceptible to be attacked by CO₂ [37]. The possible

mechanism has been proposed as follows: the secondary hydroxyl of PG is captured by TBD, followed by the attack of CO₂ at the O atom of hydroxyl resulting in the formation of the "ion-pair" (TBDH⁺ and RCO₃⁻) [38]. Finally, the proton migrates from TBDH⁺ to the other hydroxyl group to form water with the regeneration of TBD. Simultaneously, intramolecular nucleophilic substitution affords PC as depicted in Scheme 7.

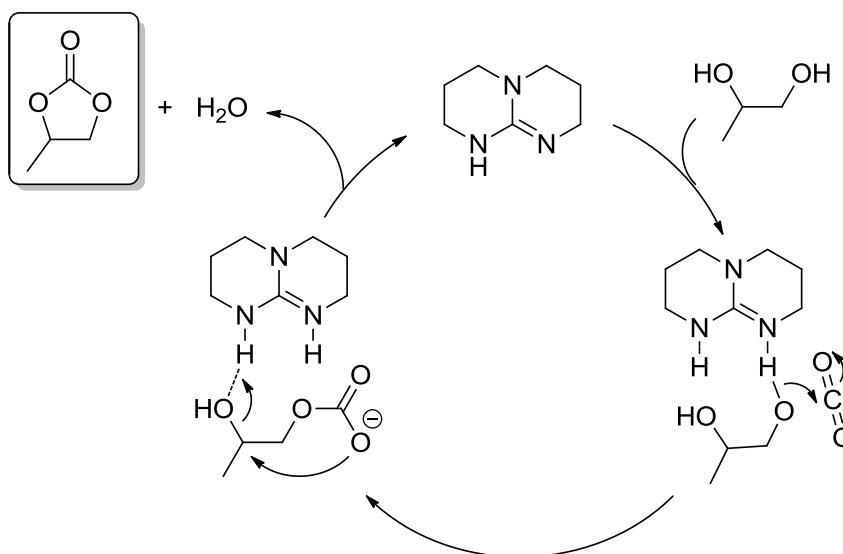
2.3. Rh-catalyzed Cyclic Carbonate Synthesis

Transition metal compound *e.g.* RhCl₃ has also been engaged with the aid of KI to promote the preparation of glycerol carbonate from CO₂ and glycerol [39] as shown in Scheme (8). Phosphine ligand such as PPh₃ or dppp [1,3-bis(diphenylphosphino) propane] is used to stabilize the rhodium complex and thus enhances the reaction. Moreover, the catalytic efficiency strongly depends on both the amount of KI and the reaction temperature.

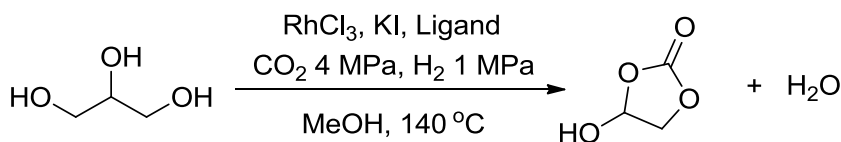
3. OTHER STRATEGIES FOR CYCLIC CARBONATE SYNTHESIS

In addition to direct synthesis from PG and CO₂, cyclic carbonate can also be prepared from the derivatives of 1,2-diols. Cyclic ketal, such as 1,4-dioxaspiro[4.5]decane which derives from cyclohexanone and glycol is able to react with CO₂ to provide EC in the presence of FeCl₃ without dehydration and nor thermodynamic limitation [40]. Transition metal complexes with functionalized fluorinated di-ketone ligand (CuL₂ or FeCIL) are also introduced as high active catalysts as demonstrated in Scheme 9. The ligand is believed to enhance the solubility of the metal catalyst. In addition, the solvent effect is significant. Toluene and CH₃CN work well, whereas CH₃OH drastically prevents EC formation, resulting in producing 1,1-dimethoxycyclohexane as the sole product.

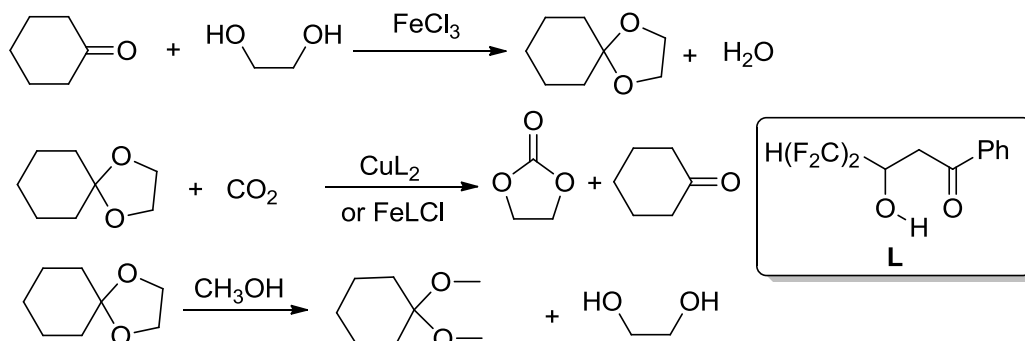
Urea is considered as an equivalent of CO₂ because it can be easily synthesized from CO₂ and NH₃ [41]. In this context, synthesis of cyclic carbonates from urea and 1,2-



Scheme 7. PG-activated route to TBD-catalyzed PC synthesis.



Scheme 8. Glycerol carbonate synthesis catalyzed by RhCl_3 .



Scheme 9. The synthesis of EC from cyclic ketal and CO_2 .

diols has many advantages, such as economic benefits, easy handling, low toxicity and so on. Most of all, this route exists no thermodynamic limitation and thus gives high yield of the target products under mild conditions [42]. Catalysts with appropriate acidic and basic properties such as ZnO can activate urea to form the isocyanate species [42], which then reacts with 1,2-diol leading to affording cyclic carbonate in high yield and selectivity as illuminated in Scheme 10.

On the other hand, transesterification of 1,2-diols with alkyl carbonates under mild conditions also has been widely investigated for the preparation of cyclic carbonates [43-45]. Basic catalysts are found to more active than acidic ones. For example, 100% yield and selectivity can be achieved when strong base such as NaOH , KOH or K_2CO_3 is used. Furthermore, the base-promoted mechanism is proposed as below. Glycerol reacts with a base to form glyceroxide anion **13**. The transesterification of **13** with DMC generates the intermediate **14** with the regeneration of the base. In the presence of the base, the intramolecular transesterification takes likely place to form glycerol carbonate as illustrated in Scheme 11.

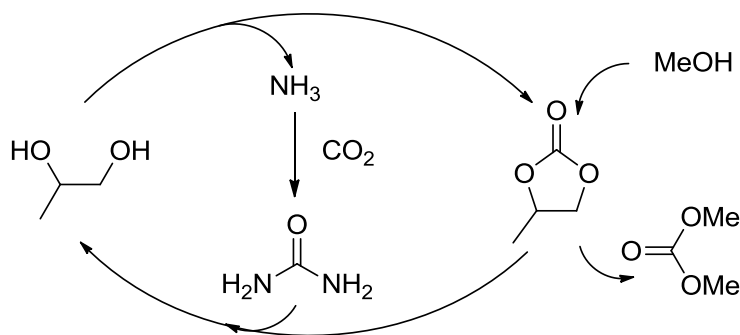
An alternative pathway is also developed to prepare glycerol carbonate from glycerol and CO_2 catalyzed by KI ,

in which propylene oxide is introduced as coupling agent (Scheme 12) [46]. The conversion of glycerol could be as high as 90% under optimal reaction conditions. Given that compounds with hydroxyl group can act as co-catalysts to promote the cycloaddition of CO_2 with epoxides through hydrogen bond formation, we can conjecture that glycerol and PG work not only as the reactants, but also as co-catalysts to promote the key step of the coupling reaction significantly, and make the reaction thermodynamically favorable [47-49].

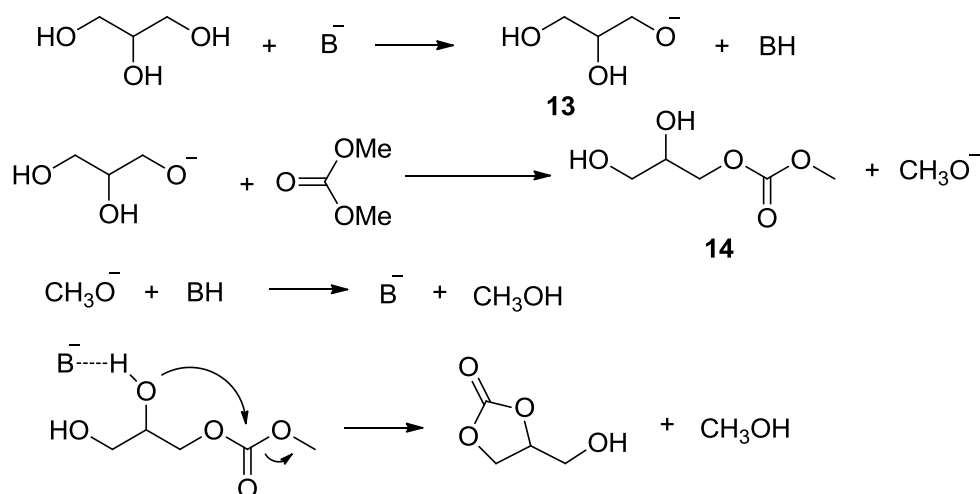
CONCLUSION

In this review article, the recent advances in the synthesis of cyclic carbonates from 1,2-diols and CO_2 , especially direct synthesis from 1,2-diols (EG, PG, glycerol) and CO_2 have been intensively summarized as shown in Scheme 13. Metallic oxides, metal carbonates, organic bases, and transition metal complexes are found to be efficient catalysts for this reaction. In addition, the catalytic cycles are discussed on a molecular level.

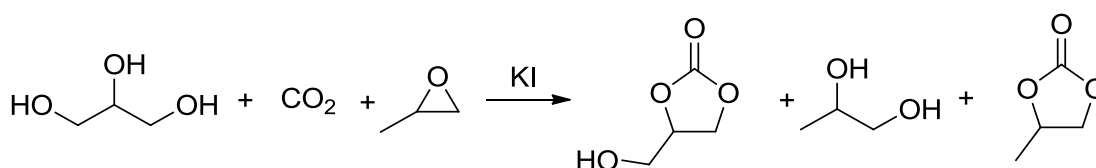
Despite the fact that only a handful of reported catalysts can get both high selectivity and yield of the carbonate simultaneously, effective synthesis of cyclic carbonates



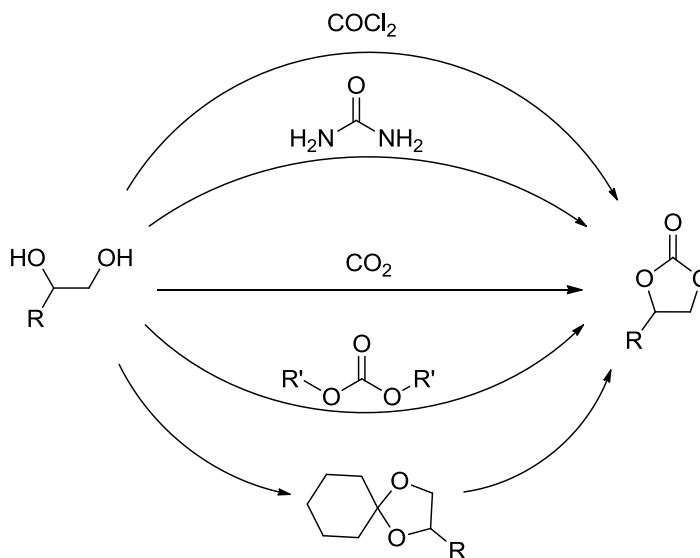
Scheme 10. Synthesis of cyclic carbonates via urea alcoholysis.



Scheme 11. The base-promoted transesterification of glycerol with DMC.



Scheme 12. The integration process of CO₂, glycerol and PO to produce cyclic carbonate.



Scheme 13. Approaches to cyclic carbonates from 1,2-diols and CO₂.

directly from 1,2-diols and CO₂ could be a useful methodology for academic research and potential application in industry. We believe this presentation would stimulate us to further develop more greener processes for the production of organic carbonates from CO₂.

CONFLICT OF INTEREST

Declared none.

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