

A Short Review of Recent Advances in Metal-Free Catalysts for the Chemical Fixation of CO₂ with Epoxides to Produce Cyclic Carbonates

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Abstract: The aim of “green chemistry” and “atom economy” is to utilize carbon dioxide and replace harmful reactants such as CO and phosgene for the production of cyclic carbonates. In this paper, metal-free catalysts including organic bases, ionic liquids and supported catalysts for the synthesis of cyclic carbonates by the cycloaddition of carbon dioxide to epoxides are reviewed. Recent advances in the design of the catalysts and the understanding of the reaction mechanism are summarized and discussed. The synergistic effects of organic bases and hydrogen bond donors, organic bases and nucleophilic anions, hydrogen bond donors and nucleophilic anions and active components and supports are highlighted. The ultimate goal is convert ion carbon dioxide into cyclic carbonates in a flow reactor directly from industrial flue gas at ambient temperature and atmospheric pressure. By using synergetic effects, a multi-functional approach can meet the design strategy of metal-free catalysts for carbon dioxide adsorption and activation as well as epoxide ring opening.

Keywords: carbon dioxide fixation, cycloaddition reaction, carbonylation with carbon dioxide.

1. INTRODUCTION

Carbon dioxide (CO₂) is one of the gases that contribute to the greenhouse effect [1], and an accumulation of CO₂ in the atmosphere has caused serious problems, which threatens environments and human health [2]. Thus, the capture and utilization of this gas have been attracting extensive attention in the whole world. In the last decade, much attention not only because of global warming but also because of the potential use of CO₂ as a safe, abundant, renewable and inexpensive C1 source for the formation of valuable chemicals [3].

Utilization of CO₂ as an ideal C1 building block becomes a hot and promising field in both academic and industrial respects. A large number of advantages promoted the wide and deep research on catalytic conversion of CO₂ into chemicals (C-O, C-N and C-C bond construction) and fuels [4, 6], however, CO₂ conversion still faces many challenges due to its thermodynamic stability and kinetic inertness. Consequently, most of the known studies used highly reactive substrates and/or severe reaction conditions to activate CO₂, limiting the application of such methods. In particular, the catalytic coupling of CO₂ with energy-rich substrates, such as epoxides and aziridines, to generate polycarbonates/polycarbamates and/or cyclic carbonates/carbamates has drawn significant attention over the past decades. To create C-C bonds with CO₂, the use of carbon nucleophiles is specifically limited to strong nucleophilic organolithiums and Grignard reagents, as well as phenolate [7-9]. Among various possible transformations, the atom-economic synthesis of cyclic carbonates from epoxides and CO₂ has been of great interest both industrially and academically in (fig 1) [10-12].

Cyclic carbonates are used in the synthesis of many industrially important compounds like dimethyl carbonate and polycarbonates and they find applications as solvents and intermediates for the synthesis of fine chemicals. Conventionally, these cyclic carbonates are synthesized using phosgene or CO, which are hazardous and environmentally unfriendly [13, 14], were avoided, and instead, CO₂ was incorporated as C1 resource into cyclic carbonate is formed [15].

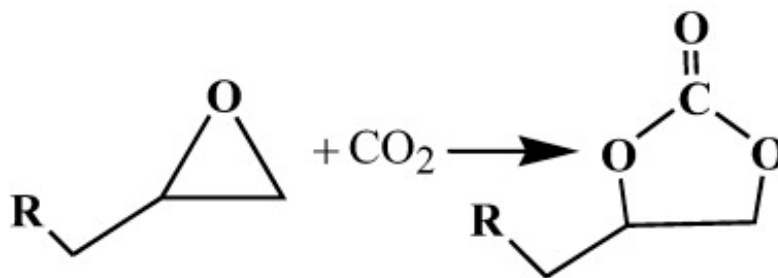


Figure1. Synthesis of cyclic carbonates from epoxides and CO₂ [15]

Cyclic carbonates are non-toxic, easily biodegradable, high polar and high boiling liquids, that are used as raw materials for industry in a wide range of applications: solvents of degreasing, diluents of epoxy resins and polyurethanes [16, 17], additives for fuels, chemical intermediates for the synthesis of polycarbonates and other polymeric substances [16, 18] and for dimethyl carbonate synthesis (DMC) by a trans-esterification process with methanol [19].

The main synthetic methods of access to cyclic carbonates are based on carbonylation or carboxylation processes. The former are achieved by reacting diols with toxic phosgene or with less toxic carbonyl derivatives, like dialkyl carbonates or urea. Although the phosgene method is simple to be realized and requires mild temperature conditions, it has the disadvantage of using a highly toxic and hazardous reagent. In addition, this suffers from two other drawbacks: the low selectivity in the reaction products and the cost of disposing of HCl, which is formed in stoichiometric amounts. The other two procedures, while being more eco-friendly routes, show the problems of requiring stoichiometric amounts of organic carbonates or urea, which have a cost, the need for high temperatures ($T > 130\text{ }^{\circ}\text{C}$) and for expensive catalysts based on metal oxides. Moreover, since the synthetic reactions are reversible, the conversion is never complete, and tedious separation steps are necessary. In the case of reactions with urea, the recycling of ammonia that is formed in stoichiometric amounts is mandatory. With regard to the carboxylation method, it is mostly accomplished by reacting CO₂ with olefins and oxygen, or directly CO₂ with epoxides or diols. Although these procedures are preferable to the phosgene route, as they have the advantage of using a greenhouse gas, they suffer from other problems, which still remain unsolved. In particular, procedures employing olefin and oxygen have the disadvantage of requiring drastic reaction temperatures and efficient control systems, being the olefin/oxygen mixtures potentially explosive. Protocols with epoxides are interesting, because they occur under milder conditions, but require expensive starting materials. Finally, procedures based on CO₂ and diols are to be preferred from the economical point of view, but usually occur at high temperatures and proceed with lower conversions [20]. To solve this problem, the numerous catalytic systems have been exploited such as metal-organic frameworks [21, 22], metal-salen complexes, phosphonium salts, quaternary ammonium salts, modified molecular sieves, metal-porphyrin, Lewis acids or bases, nanoparticles and various ionic liquid [23] etc. In particular, ionic liquid is an ideal catalyst for the cycloaddition of CO₂ with epoxides, because they have unique properties such as extremely low vapour pressure, thermal stability, wide liquid temperature range, etc. However, most of the catalytic systems are restricted due to the transition metals, co-catalyst requirement and expensive cost [24]. Moreover; the global supplies of the most used metals are decreasing alarmingly. Furthermore, the supplies of some metals are restricted to a small number of geographical areas, and the recycling rates for many metals are low. As a result, there are many elements that are considered “endangered”. For the sake of sustainability, it is desirable to develop alternative catalysts based on metal-free resources [25].

In this review, focus on the cycloaddition of CO₂ to epoxides using metal-free catalysts, including organic bases, ILs and supported catalysts. Recent advances in the design of metal-free catalysts as well as the related reaction mechanism are discussed. The synergistic effects are described in detail at the molecular level. The cooperative effects including those of hydrogen bond donors (HBDs) and organic bases, organic bases and nucleophilic anions, HBDs and nucleophilic anions as well as that of active components and supports are highlighted. The multi-functional approach and density functional theory (DFT) calculations are recommended for the design of efficient catalysts of this kind.



2. ORGANIC BASES AND IONIC LIQUID CATALYTIC SYSTEMS

It is generally accepted that the adsorption and activation of CO₂ is important for the cycloaddition reaction. As described in previous reports, nucleophilic organic bases such as amines, N-heterocyclic carbenes (NHCs), 1, 5, 7-triazabicyclo [4.4.0] dec-5-enium (TBD), 1, 8-Diazabicyclo [5.4.0] undec-7-ene (DBU), guanidines and pyridines are efficient for the adsorption and activation of CO₂ [26]. Ionic liquids such as (C(2,4,6)mimCl; DMimBr, TBABr,).

2.1. The cycloaddition reaction of propylene oxide and carbon dioxide catalyzed by TBDHBr.

It was chosen to investigate TBDHBr since they have shown good catalytic activity and allowed high yields to be obtained in the propylene carbonate synthesis 81%. The TBDHBr have two different possible configurations of minimum energy structures obtained at the RM1 level were further investigated using the density functional theory (DFT) method implemented in the Gaussian 09 package [27]. Configuration 1 (c1) shows that the Br⁻ anion interacts with the TBDH⁺ cation through two hydrogen bonds with both NH groups; the second configuration (c2) corresponds to an ion pair-like structure where the Br⁻ anion is above the cation TBDH⁺ (see Fig. 3). To see the influence of these two configurations on the catalytic mechanism, the PES that corresponds to path I has been fully investigated for both catalyst configurations. The potential energy surfaces are reported in Fig.4. The intermediates and the first transition state obtained for both configurations. It turns out that the most stable configuration is c1 by $\Delta G = 12 \text{ kcal mol}^{-1}$. The difference in energy between these two configurations can be attributed to the acidity of the N-H bond which allows for better stabilization of the anion in configuration 1

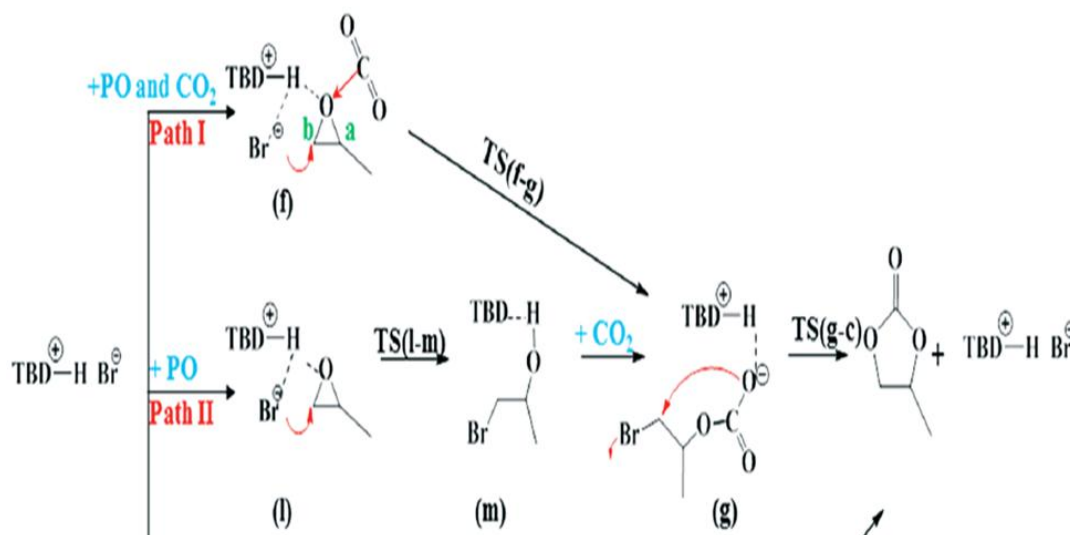


Figure2. Possible pathways for the cycloaddition between propylene oxide (PO) and carbon dioxide catalyzed by TBDHBr.

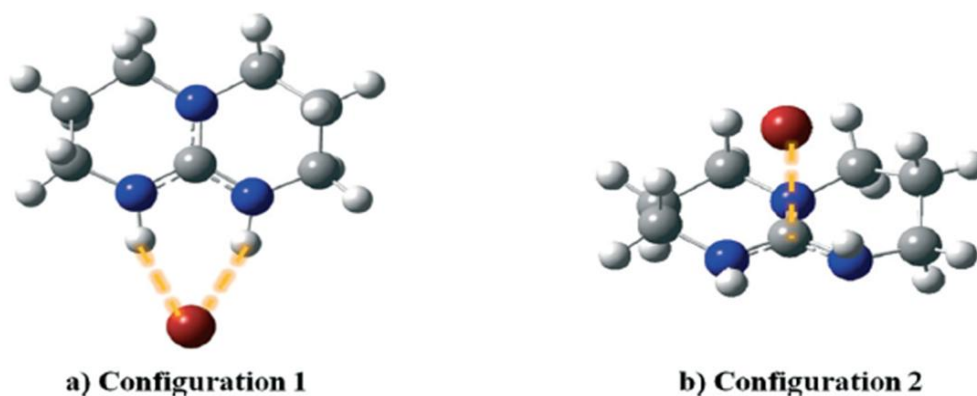


Figure 3. Optimized geometries of TBDHBr in two different configurations [27].

With regard to the charge distribution from the natural charge analysis on TBDH⁺, we found that the charges on the hydrogen atoms implied in the N–H bond are higher (0.406 e) than the one on the central carbon (0.389 e). This explains why Br[−] is preferentially stabilized by hydrogen bonds with the NH groups. Besides, for both configurations, the limiting step is related to the first transition state TS1 that is lower in the case of configuration 1 ($\Delta G_{TS1(f-g)} = 33.4 \text{ kcal mol}^{-1} < \Delta G_{TS1(i-j)} = 34.8 \text{ kcal mol}^{-1}$). So, we will only consider the pathway with TBDHBr in configuration 1. This is a two-step mechanism where the first transition state represents the rate-determining step ($\Delta G_{TS1(c1)} = 33.4 \text{ kcal mol}^{-1}$). As well as in the mechanism for TBDHBr, the epoxide is activated simultaneously by the nucleophilic attack of Br[−] on the non-substituted carbon of the epoxide and the electrophilic attack of carbon dioxide on the oxygen of the epoxide. Indeed, with TBDHBr, one of the oxygen atoms of CO₂ interacts preferentially with the positively charged central carbon atom of TBDH⁺. Moreover, in TS1(f–g), the oxygen of CO₂ interacts preferentially with the central TBDH⁺ carbon because it is the most positively charged atom after the hydrogen atoms of the N–H groups knowing that in this configuration, the hydrogen atoms of the N–H bonds already interact with Br[−] and are not accessible to stabilize the oxyanion. Then, in the TBDHBr mechanism, the intermediate species is a carbonate anion. It results from the formation of the C–Br bond between the bromide of the ionic liquid and the carbon of the opened epoxide in addition to the formation of the C–O bond between the carbon of carbon dioxide and the oxygen of the epoxide. This intermediate is stabilized by hydrogen bonds between the oxygen of the carbonate species and the hydrogen atom of one N–H bond. Finally, a second transition state, TS2 ($\Delta G_{TS2(g-c)} = 25.4 \text{ kcal mol}^{-1}$), must be overcome which represents the ring closure of the intermediate leading to the propylene carbonate. Interestingly, the ring opening of the epoxide (TS1) remains the rate determining step with a difference of 8 kcal mol^{−1} between TS1(f–g) and TS2(g–c).

2.2. Ionic Liquids

Ionic liquids have attracted much attention for their unique nature such as being environment-benign, highly stable, non-volatile and non-flammable. Ionic liquids can be employed as a solvent as well as a catalyst in cycloaddition reactions. Ionic liquids such as (C(2,4,6)mimCl; DMimBr, TBABr, TEA(Br-Cl)).

2.3. The Cycloaddition Reaction of Propylene Oxide and Carbon Dioxide Catalyzed by TBABr

It was chosen to investigate tetrabutyl-ammonium bromide (TBABr) since they have shown good catalytic activity and allowed high yields to be obtained in the propylene carbonate synthesis 48%. Mechanism After having fully optimized TBABr, propylene oxide (PO), propylene carbonate (PC) and CO₂ structures, the overall cycloaddition between PO and CO₂ has been modelled following pathway I. A tri-molecular van der Waals intermediate (a) is first formed between PO, CO₂ and TBABr. The position of CO₂ in this intermediate relative to PO remains the same with or without a catalyst [28]. Then, a first transition state, TS(a–b) ($\Delta G_{TS(a-b)} = 27.7 \text{ kcal mol}^{-1}$), must be overcome, corresponding to the ring opening of the epoxide. More precisely, TS (a–b) results from the nucleophilic attack of Br[−] on the non-substituted carbon of PO which contributes to the breaking of the C–O bond of PO and leads to the ring opening and formation of an oxy-anion. Simultaneously, due to the strong charge delocalisation on the oxygen atom, the observation is the nucleophilic attack of the oxy-anion towards CO₂ leading to its activation. After TS(a–b), an intermediate carbonate anion is formed (b) resulting not only from the C–Br bond formation between the oxy-anion and Br[−] but also from the formation of the

C–O bond between CO₂ and PO. This intermediate is stabilized by van der Waals interactions between the carbonate group and the alkyl chains of TBA⁺. Finally, a second step, TS(b–c) ($\Delta G_{TS(b-c)} = 17.2$ kcal mol⁻¹), connects this intermediate to the final propylene carbonate product. Indeed, TS(b–c) consists of the intramolecular ring closure of the intermediate (b) and the breaking of the C–Br bond which provides the cyclic carbonate and the regenerated ammonium salt.

Potential energy surface to clearly visualize the energies involved in this mechanism, the potential energy surface (PES) along the reaction coordinate has been drawn in Fig.5. The origin is fixed as the sum of the Gibbs free energy (G) of the isolated reactants: G(PO) + G(CO₂) + G(TBABr) at 298 K. Fig.5 shows the reaction profile for the nucleophilic attack on the substituted carbon of the epoxide ring as well as the nucleophilic attack on the non-substituted carbon. As mentioned above, this is a two-step mechanism where the first transition state corresponds to the rate-determining step in both cases. Indeed, in the two considered cases, this TS1 (TS (a–b) and TS(d–e)) is higher in energy by 9.8 kcal mol⁻¹ in pathway (i) and by 10.5 kcal mol⁻¹ in pathway (ii) in comparison with TS2 (TS(b–c) and TS(e–c)). This result reveals the necessity of having a catalyst with a highly nucleophilic anion for the reaction as the energy of the first transition state is mainly related to the ring opening of the epoxide by the nucleophilic attack of the anion of the ionic liquid. Comparing pathways (i) and (ii), it is worth noting that the nucleophilic attack is directed to the non-substituted carbon (pathway ii) with a difference of 1.5 kcal mol⁻¹ between both TS(a–b) and TS(d–e). The preferentiality of the nucleophilic attack on the non-substituted carbon also checked in the case of another catalyst (TBDHBr). Therefore, it has only considered the nucleophilic attack on the non-substituted carbon of propylene oxide [29].

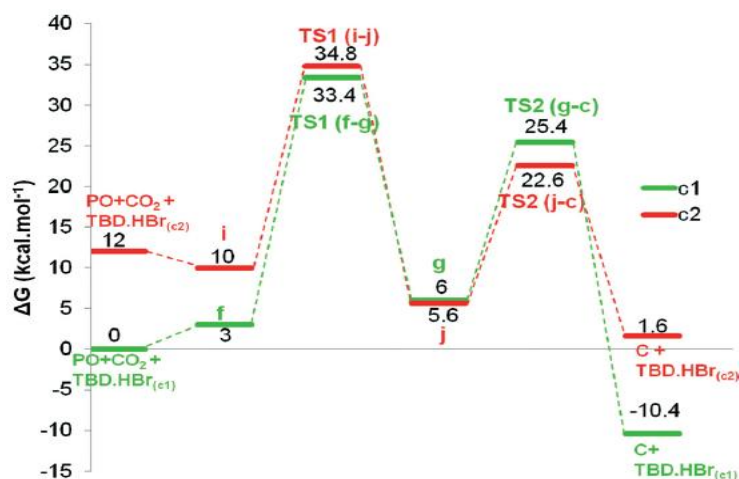


Figure4. Pathway I for the reaction between PO and CO₂ catalyzed by TBDHBr: c₁-configuration 1; c₂—configuration 2.

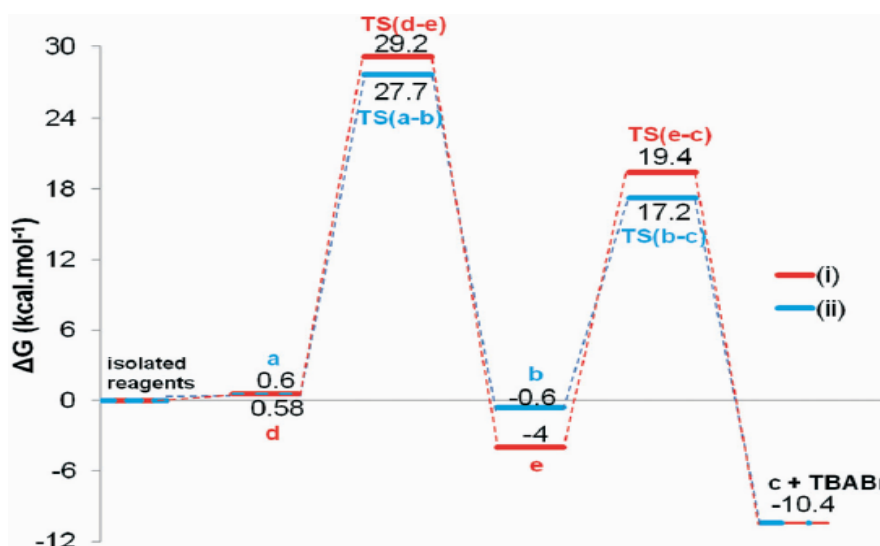


Figure5. Pathway I for the reaction between PO and CO₂ catalysed by TBABr: - i-nucleophilic attack on the substituted carbon of the epoxide ring; ii-nucleophilic attack on the non-substituted carbon of the epoxide ring.

3. CONCLUSION

Recent advances in the design of metal-free catalysts including organic bases, ILs, supported catalysts as well as progress in the cycloaddition mechanism were discussed. The synergistic effects were described in detail at the molecular level. The cooperative effects of HBDs and organic bases, organic bases and nucleophilic anions, HBDs and nucleophilic anions as well as that of the active component and support for the enhancement of catalytic activity were emphasized. The review affords insights into the design and development of efficient metal-free catalytic systems. The ultimate challenge is to design efficient metal-free catalytic systems for flow reactors where the cycloaddition reaction is conducted at ambient temperature and atmospheric pressure using CO₂ of low concentration such as “waste” CO₂. For CO₂ adsorption as well as the activation of CO₂ and epoxides, the use of the multi- synergetic strategy is advisable for the development of a suitable catalyst system organic base like TBDHBr and ionic liquids like TBABr for the cycloaddition reaction. The multi-functional approach was highlighted. In addition, DFT calculations are recommended for the advanced design of catalysts and better understanding of the catalytic mechanism.

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