



# **New Trends in the Conversion of CO<sub>2</sub> to Cyclic Carbonates**

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Received: 1 April 2020; Accepted: 26 April 2020; Published: 27 April 2020



**Abstract:** This work concerns recent advances (mainly in the last five years) in the challenging conversion of carbon dioxide (CO<sub>2</sub>) into fine chemicals, in particular to cyclic carbonates, as a meaningful measure to reduce CO<sub>2</sub> emissions in the atmosphere and subsequent global warming effects. Thus, efficient catalysts and catalytic processes developed to convert CO<sub>2</sub> into different chemicals towards a more sustainable chemical industry are addressed. Cyclic carbonates can be produced by different routes that directly, or indirectly, use carbon dioxide. Thus, recent findings on CO<sub>2</sub> cycloaddition to epoxides as well as on its reaction with diols are reviewed. In addition, indirect sources of carbon dioxide, such as urea, considered a sustainable process with high atom economy, are also discussed. Reaction mechanisms for the transformations involved are also presented.

Keywords: carbon dioxide; cyclic carbonate; diol; epoxide; catalysis; CO<sub>2</sub> conversion

## 1. Introduction

Modern life is sustained by an unremitting stream of energy delivered to final users as fuels, electricity and heat. Currently, over 80% of the world's primary energy supply is provided by fossil fuels carbon sources (oil, coal or natural gas). Since the industrial revolution, i.e., for the last two centuries, fossil fuels, generated from biomass over millions of years, have been extensively used in anthropic activities, thereby increasing carbon dioxide emission into the atmosphere. Over the last few decades it has become clear that carbon dioxide released in this way is affecting the climate stability of the biosphere (see Figure 1) with countless consequences. Scientists predict social, environmental, economic and health issues if the actual trend continues: melting glaciers, droughts, early snowmelt, extreme weather changing, wildfires, water shortages, rising sea level, new pests, infectious diseases and air pollution, just to mention a few [1–4].

In December 2015, the United Nations conference on climate change (the 21st Conference of the Parties, COP21) brought public awareness to the steps required to slow down global warming and set a framework to mitigate climate change by agreeing on 17 sustainable development goals. Moreover, the Intergovernmental Panel on Climate Change (IPCC) set as a goal to keep the warming under 2 °C above preindustrial levels and pursuing efforts to limit the temperature increase to 1.5 °C above preindustrial levels [3].

Thus, it is urgent to adopt behaviors to reduce anthropogenic emissions of carbon dioxide. Among all the measures, there are four considered more significant: (i) the reduction of energy consumption by increasing its efficiency; (ii) the replacement of fossil fuels with renewable energy sources; (iii)  $CO_2$  capture and storage (CCS) and (iv)  $CO_2$  capture and usage (CCU).



**Figure 1.** Evolution of Earth's average temperature in comparison with the atmospheric carbon dioxide over the last decades. Reproduced with permission from [4], copyright 2020, NOAA Climate.gov.

While CCS is currently the most efficient way to reduce  $CO_2$  emissions in the atmosphere, the recycling of carbon dioxide, that is,  $CO_2$  conversion into valuable chemicals would be the most promising one as it decreases this greenhouse gas emissions making it a part of the solution as carbon feedstock [1,5]. In fact, as a readily available, cost-efficient, non-toxic, non-flammable and sustainable carbon feedstock,  $CO_2$  is an attractive raw material as a C1-building block. However,  $CO_2$  is also a challenging molecule to activate as it is thermodynamically stable (carbon is in its highest oxidation state) and kinetically inert (requires the input of a large amount of energy) in many known transformations.

One approach to surpass the carbon dioxide chemical inertia would be the use of energy-rich substrates such as epoxides or aziridines that would defeat the high energetic activation barrier to originate heterocycles. Strong nucleophiles (e.g., Grignard reagents, organoboranes, organolithium or organozinc compounds) could also be used to form new C–C bonds with carbon dioxide. However, often such procedures require high pressures and harsh reaction conditions, thus limiting their practical applications in the chemical industry.

To overcome  $CO_2$ 's kinetic stability, catalysts and catalytic processes have been developed to quickly achieve the reaction equilibrium allowing the reaction to take place under mild conditions. Thus, a significant number of successful researches on the coordination chemistry of  $CO_2$  with the ultimate aim of discovering new catalysts for  $CO_2$  conversion has been reported [6] (see Scheme 1). In this respect, homogeneous catalysis is important and its potential for  $CO_2$  conversion was already discussed in several reviews [7–10]. Added-value chemicals including organic carbonates [11] urethanes [12], carbamates [10], lactones [10], pyrenes [10], formic acid and its derivatives [13] are well-known to be synthesized by homogeneous catalytic processes. However, only a few energy-efficient processes employing  $CO_2$  have been commercialized.

Two main approaches to convert carbon dioxide into fine chemicals can be considered according to their energetics. One is the reductive  $CO_2$  conversion that requires a large amount of energy and quite powerful reducing agents, such as hydrogen, and it is used to produce chemicals like methanol or formic acid [8,14]. The other one is non-reductive (the +4-oxidation state of carbon is maintained), either moderately endothermic or exothermic, and widely used to provide products like carbonates, polycarbonates, urea, polyurethanes, carboxylates, pyrenes, lactones or carbamates [8,10,15,16].



**Scheme 1.** Outline of chemical conversion (organic) processes of carbon dioxide. Adapted with permission from [6], copyright 2017, Elsevier.

The following sections will address the non-reductive conversion of carbon dioxide to cyclic carbonates (Figure 2) including the synthesis of cyclic carbonates from diols and  $CO_2$ , which is considerably more challenging than their well-established formation from the reaction of epoxides and  $CO_2$ .



**Figure 2.** General structure of a cyclic carbonate (**a**) and examples of commonly produced cyclic carbonates (**b**).

### 2. Carbon Dioxide to Carbonates

Cyclic carbonates, in particular, five-membered ones, are used as excellent (high boiling point) polar aprotic solvents [17,18], industrial lubricants, electrolytes for lithium ion batteries [19], synthetic building blocks for polymeric materials [20,21] and monomers to produce polycarbonates [6,8] as well as other fine chemicals. Their features such as high boiling and flashpoints, low toxicities, odor levels and evaporation rates, biodegradability and solubility in a large range of solvents make them a target of interest.

Cyclic carbonates can be produced by different routes that directly, or indirectly, use carbon dioxide (Scheme 2). As early as 1883, the reaction of the highly toxic carbonyl dichloride (commonly known as phosgene) and ethane-1,2-diol (usually designated as ethylene glycol) to produce ethylene carbonate was reported by Nemirowsky et al. [9] (Scheme 2a). Other C1 building blocks such as dimethyl carbonate [22,23], urea [24–28], CO [29–31] and CO<sub>2</sub> [32–48] have also been converted with diols to yield cyclic carbonates.



Scheme 2. Routes to produce a cyclic carbonate, excluding inorganics. (a) Phosgene, (b) dimethyl carbonate, (c) urea, (d) CO, and (e)  $CO_2$  have been converted with diols to yield cyclic carbonates. Also, (f) halohydrins, (g) propargyl alcohols, (h) alkenes and (i) epoxides have been used as starting materials. Adapted with permission from [9], copyright 2017, Springer Nature.

The use of non-toxic dimethyl- or diethyl-carbonate (Scheme 2b) requires the presence of bicarbonate methyl trioctyl phosphonium salts as catalysts to promote the transesterification of the di-alkyl carbonate with the 1,n-diol ( $2 \le n \le 6$ ) towards the formation of cyclic and linear products [22,23]. In particular, 1,2-propanediol and ethylene glycol afford selectively propylene- and ethylene-carbonate with yields up to 95% and 90%, respectively (Table 1). In contrast, the reaction of dimethyl carbonate with higher diols, such as 1,3-butanediol, produces linear  $C_8$ – $C_{10}$  di-carbonates as the almost exclusive products. This is a remarkable discovery, since these di-carbonate derivatives are not otherwise accessible in good yields by conventional base catalyzed methods. Such significant differences of product distribution seem to be ascribed to the structure (branching and relative position of OH groups) of diols and to the role of cooperative (nucleophilic and electrophilic) catalysis [22].

Entry	Catalyst	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	Glycol Conversion (%)	Urea Conversion (%)	Selectivity (%)
1	CaO	9.5	43.7	79.9	82.2
2	$La_2O_3$	21	48.3	87.4	82.4
3	MgO	7.4	56.0	94.1	89.8
4	ZnO	6.7	62.6	97.8	95.2
5	$ZrO_2$	33.4	20.6	70.8	43.9
6	$Al_2O_3$	136.5	19.0	71.2	40.3

**Table 1.** Catalytic performance of metal oxides in the synthesis of ethylene carbonate, as a function of their surface area [27].

Reaction conditions: temperature 423 K, pressure 11 kPa and time 180 min. Note: the selectivity to the carbonate was based on the urea conversion.

Urea can be considered as a potential feed for indirect carbon dioxide utilization (Scheme 2c). For example, in the presence of a suitable Lewis acid catalyst (e.g., potassium silicate, K<sub>2</sub>SiO<sub>3</sub>) different organic carbonates such as glycerol carbonate, ethylene carbonate and propylene carbonate can be synthesized from polyol (glycerol, ethylene glycol and propylene glycol, respectively) feedstocks.

These reactions mechanism involves the formation of carbamates and their decomposition into the respective carbonates [24]. Simple metal salts (e.g., FeBr<sub>2</sub>) can also be successfully used [26] as catalysts for producing cyclic carbonates. Compared with the traditional routes to obtain cyclic carbonates, the synthetic pathway using urea and diols (or polyols) presents many advantages such as cheap and easily available raw material without toxicity and danger of explosion; mild reaction conditions and higher carbonates yield. Moreover, it can be considered a sustainable process with high atom economy as the only stoichiometric byproduct formed is ammonia [26].

Transition-metal (e.g., palladium) catalyzed oxidative carbonylation, where the direct carbonylation of diols with CO under catalytic oxidative conditions is performed, is another alternative method to produce cyclic carbonates (Scheme 2d). The main issue with this method is the lack of a general, practical and efficient approach for different diol substrates [25,29,30].

In addition, halohydrins [36], propargyl alcohols [38,39] and even alkenes [40] can be used as starting materials to obtain cyclic carbonates from reaction with carbon dioxide.

1,2-Halohydrins (Scheme 2f) appear to be a convenient class of starting materials for producing cyclic carbonates. They can be easily prepared by treatment of alkenes with halogens in the presence of water. Moreover, they also serve as starting material for epoxides, well known substrates for the cycloaddition of  $CO_2$  to yield cyclic carbonates. However, only a few methods involving 1,2-halohydrins have been developed and most of them require high temperature and/or high pressure. Hirose et al. [36] investigated the conversion of  $CO_2$  to cyclic carbonates using 1,2-halohydrins and developed a simple and effective mild reaction procedure at atmospheric pressure to prepare five-membered cyclic carbonates in the presence of  $K_2CO_3$  in the commercially available non-anhydrous and non-deoxygenated dimethylformamide (DMF).

Reaction of carbon dioxide with propargylic alcohols (Scheme 2g) can efficiently lead to  $\alpha$ -alkylidene cyclic carbonates through carboxylative cyclization, a promising and green route to fix CO<sub>2</sub> [38,39].  $\alpha$ -Alkylidene cyclic carbonates are important heterocyclic compounds having a wide range of applications in organic synthesis as building blocks in the formation of  $\alpha$ -hydroxy ketones and 5-methyleneoxazo-lidin-2-one derivatives. However, most of the reported catalyst systems suffer from some drawbacks, such as, requiring high reaction temperature and/or CO<sub>2</sub> pressure [38], using noble metal or complicated catalysts. A promising use of a zinc salt to catalyze reactions of CO<sub>2</sub> and propargylic alcohols to obtain  $\alpha$ -alkylidene cyclic carbonates was reported recently. Hu et al. [38] found that the ZnI<sub>2</sub>/NEt<sub>3</sub> catalyst system is very effective for reactions performed at room temperature under solvent-free conditions, and the yields of the target products are very high.

The use of alkenes for the CO<sub>2</sub> transformation in cyclic carbonates (Scheme 2h) is another alternative. Wu et al. [40] developed a mechanism-guided design of a multistep flow system that enabled an efficient general process for the synthesis of cyclic carbonates from alkenes and CO<sub>2</sub>. According to the authors, the flow system proved to be an ideal platform for multicomponent reactions because it was straightforward to introduce reagents at specific stages without their interacting with each other or with reaction intermediates prone to destruction by them. The system reported exhibited superior reactivity, increased yield and broader substrate scope relative to conventional batch conditions and suppressed the formation of undesired byproducts, such as epoxides and 1,2-dibromoalkanes.

However, among all the chemical routes presented in Scheme 2, the currently most attractive one, especially with respect to sustainability, is the atom-economic addition of  $CO_2$  to epoxides (Scheme 2i). Successful catalytic systems are usually homogeneous Lewis acid metal-based coordination compounds [15,42,44,46] combined with a strong nucleophile. Where the nucleophile can, by itself, catalyze the reaction [47], the presence of metal complex usually facilitates the  $CO_2$  insertion by lowering the energetic activation barrier of the ring opening. The general synthetic mechanism is initiated by the coordination of the oxygen atom of the epoxide to the Lewis acid, forming a new metal–O bond. Then, the epoxy ring undergoes nucleophilic attack with the formation of a metal-alkoxide (by epoxy ring opening). The carbon centre of  $CO_2$  of the metal-alkoxide is subject to an attack leading to a metal coordinated carbonate. The leaving group is eliminated, and the five-membered ring is

formed [46]. If, some time ago, high catalytic activities have required the use of harsh operation conditions, in particular high temperatures, which decrease the desired process sustainability, in recent years, many catalytic systems were found to be able to activate carbon dioxide with epoxides at room temperature and/or under low  $CO_2$  pressure [47,48]. Nevertheless, the search for new catalytic systems highly active under mild conditions [15,46] is a constant.

Recently, cyclic carbonates were produced [49] using wool powder, i.e., fine particles produced from natural wool fibbers, that acted as a catalyst for the cycloaddition coupling of carbon dioxide to mono-substituted terminal epoxides (e.g., propylene oxide) to produce cyclic carbonates (e.g., propylene carbonate) in solvent-free conditions. SEM, XPS and FTIR analyses of the wool powder indicated the presence of amide, hydroxyl, carboxyl groups, sulfonic acid and amine groups on their surface, which can act as hydrogen bond donors and accelerate the cycloaddition reaction by promoting the ring-opening of the epoxide (through coordinating of the hydrogen bonding donor in the wool powder to the oxygen atom of the epoxide) and forming an hydrogen bond. Moreover, the surface amine groups can absorb carbon dioxide to produce carbamates (confirmed by XPS), thus activating CO<sub>2</sub>. Halide (e.g., bromide, chloride or iodide) salts were used as cocatalysts and a synergetic effect was found between potassium iodide and the wool fibbers. In fact, the coordination of hydrogen bonding donor in wool powder with the O atom of epoxide (via hydrogen bonding) leads to the polarization of the C-O bonds of epoxide and the iodine anion attacks the less sterically hindered  $\beta$  carbon atom of the epoxide, leading to ring-opening of epoxide. Then, the activated carbon dioxide inserts, and an alkyl carbonate anion are formed. The cyclic carbonate is formed through intramolecular cyclic elimination and the catalytic system is simultaneously regenerated. The mechanism proposed by the authors [49] is depicted in Scheme 3. The catalytic system can be repeatedly used for five cycles without activity loss. Moreover, it exhibited good tolerance to various functional groups (e.g., alkyl, aryl, alkenyl, alkoxy, ether or halogen) with potential applicability in industry.



**Scheme 3.** Proposed reaction mechanism for the cycloaddition of carbon dioxide to propylene epoxide catalyzed by wool powder (WP) and potassium iodide. Reproduced with permission from [49], copyright 2018, Elsevier.

Currently, the industrial production of cyclic carbonates involves either the transesterification of diols with phosgene in an energy-intensive process or the cycloaddition of  $CO_2$  to epoxides [46,50]. Despite the latter route exhibiting 100% atom economy and industrial scalability, the synthesis of epoxides [48] combined with their high volatility and reactivity are problematic. Thus, recently, more stable, biodegradable 1,2-diols have been proposed as promising alternative starting materials for the synthesis of cyclic carbonates. If they could be directly synthesized from  $CO_2$  and diols, the carbonate formation process will become more valuable as production costs will be reduced while being a green chemical route. The advances in this respect are addressed in the following section.

#### 3. Carbonates from Diols

The reaction of a diol with carbon dioxide is neither thermodynamically nor kinetically favored due to the formation of water as byproduct [51]. Attempts to overcome this problem include the implementation of a suitable catalytic system and a dehydrating agent. In principle, the catalytic reaction for the production of cyclic carbonates from diols and carbon dioxide could use similar catalysts to those employed for the formation of linear carbonates.

A large number of catalytic systems have been developed for the production of cyclic carbonates including alkali metal salts, ammonium salts, ionic liquids, metal oxides (Table 1), transition metal and main group complexes [8,9,46]. However, most of these catalysts currently suffer from drawbacks such as low reactivity or selectivity, the need for a cosolvent or of a large excess of chemical dehydrating agents as well as the requirement for high pressure and/or temperature. Moreover, some of the chemical routes lack industrial and/or economic viability due to the risk associated to the use of poisonous compounds or to the low target product yield. Thus, the exploration of highly efficient catalytic systems for the cyclic carbonates synthesis operating at low temperature and low carbon dioxide pressure still remains challenging. In this respect, the use of diols and  $CO_2$  to form cyclic carbonates became a topic of great interest.

The first diols used as substrates and combined with carbon dioxide to generate 5-membered cyclic carbonates were ethylene glycol (EG), propylene glycol (PG) and glycerol. The last one attracted a new interest since it is a byproduct of the production of biodiesel and therefore is available in larger amounts. These reactions, independently if done with alcohols or diols are plagued with a serious limitation of the coproduction of water. Therefore, the effectiveness of any catalyst needs to take in account if its activity is dependent of added water traps such as acetonitrile (MeCN).

Inorganic catalysts usually have high thermal stability and mechanical strength, meaning easier regeneration and longer catalytic life than organic ones. Metal oxides such as  $CeO_2$ ,  $ZrO_2$  and  $CeO_2$  supported in  $ZrO_2$  solid solutions were initially investigated by Tomishige et al. [52] as catalysts for the carboxylation of ethylene glycol and propylene glycol. In addition,  $ZrO_2$  and  $CeO_2$  [53] based catalysts have been used in the synthesis of dialkyl carbonates. Honda et al. [33] achieved direct synthesis of propylene carbonate from carbon dioxide and 1,2-propanediol in excellent yield (>99%) using a carboxylation/hydration cascade catalyst of  $CeO_2$  with 2-cyanopyridine, even at a low  $CO_2$  pressure of 0.8 MPa. This catalytic system was applied to synthesize several cyclic carbonates, including 6-membered ring carbonates that are typically difficult to obtain in high yields (62% to >99%). Very recently, Tomishige et al. [45] reported the results of the synthesis of a cyclic carbonate from  $CO_2$ , diols and 2-cyanopyridine. The use of the hydration reaction of 2-cyanopyridine to 2-picolinamide, which is also catalyzed by  $CeO_2$ , is the key factor for improving the cyclic carbonate yields. Several vicinal diols were reacted with carbon dioxide to generate the corresponding five-membered ring carbonates in high yield. Several reactivity issues, regarding the secondary-secondary vicinal OH groups were overcoming, resulting in the production of five-membered ring carbonates in high yields.

The synthesis of six-membered ring carbonates in high yield is much more difficult than that of the formation of five-member ring carbonates [45] as six-membered ring carbonates have higher reactivity and lower stability than the five-membered ring carbonates. 6-, 7- and 8-membered ring cyclic carbonates are of particular interest as monomers for ring-opening polymerization towards

more sustainable polymers. The first report of the synthesis of 7- and 8-membered cyclic carbonates directly from  $CO_2$  is due to McGuire et al. in 2018 [54] through a one-pot synthesis using a diol,  $CO_2$  (1 atm), tosyl chloride and mild bases (e.g., triethylamine or 2,2,6,6-tetramethylpiperidine) at ambient temperature. The main advantage of this one pot method is the avoidance of strong moisture sensitive bases that can lead to a decrease in the cyclic carbonate yield. The protocol has been successfully applied to the synthesis of a wide scope of cyclic carbonates and the yields obtained were comparable, or exceeded, those obtained by phosgene methods. Density Functional Theory (DFT) calculations using 2,2-dimethyl-1,3-propanediol as model substrate (Figure 3) shed some light on the reaction mechanism for the synthesis of 5- to 8-membered cyclic carbonates from diols and  $CO_2$  [54,55]. According to the calculations,  $CO_2$  insertion happens first, and the formation of the cyclic carbonate proceeds via tosylation of the carbonate followed by addition/elimination (Figure 3). Therefore, the stereochemistry of the diol is retained in the cyclic carbonate product.



**Figure 3.** DFT computed free enthalpy diagram for the direct coupling of CO<sub>2</sub> with 2,2-dimethyl-1,3-propanediol using 2 equiv. of NEt<sub>3</sub> and 1 equiv. of TsCl (pathway of less energy). Reproduced with permission from [54], copyright 2018, Elsevier.

*N*-heterocyclic carbenes (NHCs) have gained interest as organocatalysts for reactions using carbon dioxide as substrate [32,49] due to their ability (with their lone pair of electrons) to act as nucleophiles activating  $CO_2$  through the formation of imidazolium carboxylates (designated as the NHC– $CO_2$  adduct). NHCs can be generated by deprotonation with a suitable base or by a direct single electron cathodic reduction of imidazolium cations.

Cyclic carbonates were achieved by Bobbink et al. [32,49] from the reaction of diols and carbon dioxide, using environmentally friendly metal-free *N*-heterocyclic (e.g., imidazolium or thiazolium) carbene catalysts, performed at atmospheric pressure in the presence of an alkyl halide (e.g., dibromomethane,  $CH_2Br_2$ ) and cesium carbonate ( $Cs_2CO_3$ ). The base and the alkyl halide were found essential for the reaction to occur. Two possible reaction mechanisms were proposed by the authors [32]: the main one for the *N*-heterocyclic carbene-catalyzed reaction (Scheme 4) and other, secondary, non-catalytic, (Scheme 5) as the authors found that 25% of the cyclic carbonate was obtained in the absence of carbon dioxide (but where the addition of  $CO_2$  increased the carbonate yield up to 81%). In Scheme 4, step 1 concerns the activation of carbon dioxide by the carbene generating the carbene– $CO_2$  adduct. Then, in step 2, the alkoxide (I) is formed and the parallel attack of the carbene– $CO_2$  adduct on dibromomethane occurs. Next, in step 3, the nucleophilic attack of the alkoxide

on the intermediate (II) leads to the formation of intermediate (III) and elimination of the leaving group, i.e., bromomethanol. Due to its instability, bromomethanol is expected [56] to be decomposed to formaldehyde ( $CH_2O$ ) and hydrogen bromide (HBr). In step 4, occurs the deprotonation of the secondary hydroxyl group of the diol and, thus, results in the formation of intermediate (IV). The final step addresses the intramolecular addition of the alcohol in intermediate (IV) affording the cyclic carbonate. Simultaneously the catalyst is regenerated.



**Scheme 4.** Proposed mechanism for the *N*-heterocyclic carbene-catalyzed coupling of diols with CO<sub>2</sub> to form cyclic carbonates. The substituents of the catalyst are omitted for clarity. Reproduced with permission from [32], copyright 2016, Royal Society of Chemistry.



**Scheme 5.** Proposed mechanism for the non-catalytic reaction of diols and CO<sub>2</sub> to form cyclic carbonates. Reproduced with permission from [32], copyright 2016, Royal Society of Chemistry.

The minor non-catalytic formation of cyclic carbonates depicted in Scheme 5 [32] is initiated by the attack of cesium carbonate to 1-bromobutane (step 1) leading to the formation of dibutyl carbonate (II). Then, in a similar way found for the catalytic mechanism of Scheme 4, step 2 proceeds with the reaction

of the alkoxide (I) with dibutyl carbonate (II) leading to the formation of (III) and to the elimination of butanol. In step 3 the secondary hydroxyl group in the species (III) undergoes deprotonation resulting in the formation of intermediate (IV). The cyclization occurs in step 4 with the subsequent elimination of the second leaving group and the formation of the desired cyclic carbonate.

Both of the above reaction (catalytic and non-catalytic) mechanisms appear to occur concurrently to produce the cyclic carbonate.

Wu et al. [57] investigated the synthesis of cyclic carbonates from  $CO_2$  and diols, through electrogenerated NHCs, in which room temperature ionic liquids (RTILs) play the dual role of green solvents and precursors of NHCs. The reaction of NHCs with  $CO_2$  to form the corresponding carboxylates have been reported by many authors, but the progress of the addition reaction was for the first time detected by Wu et al. [57], which was supported by electrochemical data. The authors firstly assessed the validity of electrogenerated carbenes by electrochemical reduction of the RTIL [BMIM][BF<sub>4</sub>] (BMIM = 1-butyl-3-methylimidazolium) in common organic solvents (e.g., acetonitrile or dimethyl formamide) and subsequently removed classical organic solvents for the 4-phenyl-1,3-dioxolan-2-one synthesis (as a model product) and replace them by the RTIL to be used as medium as well as NHC precursor. In addition, room temperature ionic liquids are good electrically conductors, therefore the use of a supporting electrolyte was not required. The authors extended the scope of the RTILs (e.g., to [BMIM][BF4] and [PeMIM][BF4]) used in the procedure aiming at to evaluate their efficiency as NHCs precursors and solvents. Both RTILs were found to be good precursors of NHCs, with [BMIM][BF<sub>4</sub>] leading to a better yield of 4-phenyl-1,3-dioxolan-2-one, which may be mainly due to its lower viscosity and higher conductivity than [PeMIM][BF<sub>4</sub>]. In fact, high RTIL viscosities strongly affect the rate of mass transport within a solution and a low-rate mass transport may result in a longer reaction time to get a satisfactory yield value. Besides the RTIL itself, other experimental parameters (e.g., current density) influence significantly the reactivity and the yield of the electrochemical process. The authors reported [57] that different cathodes led to different yields of desired cyclic carbonate. The yields are also affected by the temperature since high reaction temperatures decrease the viscosity of the RTIL and increase their conductivity [58]. Moreover, the temperature has also influence on the solubility of  $CO_2$ . Dimethylformamide (DMF) [59] is usually selected as a reaction solvent as it is able to activate carbon dioxide. As expected, other polar aprotic solvents, such as dimethyl sulfoxide (DMSO) or dimethylacetamide (DMA), could also be used. However, Bobbink et al. [49] reported that no reaction was detected in toluene when the synthesis of the model product 4-phenyl-1,3-dioxolan-2-one was tested. The progress of the addition reaction was studied by linear sweep voltammetry (LSV) of the reaction. Firstly, to get NHCs, electrolysis of [BMIM][BF<sub>4</sub>] in DMF under galvanostatic control was performed and then, the current was switched off and the electrolyte was scanned by LSV. The oxidation peak current was slightly reduced after 5 min stirring under the atmosphere of dinitrogen. On the other hand, 5 min of carbon dioxide bubbling, instead of dinitrogen, led to a sharp decrease of the oxidation peak current indicating that the CO<sub>2</sub> reaction with NHCs to form the NHC-CO<sub>2</sub> adduct resulted in a decrease of free electroactive NHCs. Therefore, the peak current of oxidation also decreased. Thus, the cyclic voltammetric data supports that NHCs generated by cathodic reduction react with carbon dioxide to form NHC-CO adducts, then each NHC-CO<sub>2</sub> transfers the carbon dioxide to the diol to produce the corresponding cyclic carbonate in the presence of methyl iodide and potassium carbonate (Scheme 6).

Concerning the synthesis of glycerol carbonate, which presents a variety of applications (e.g., as solvent, in batteries, polymerization and other reaction intermediates), a procedure using carbon dioxide, glycerol and 2-cyanopyridine (as the dehydrating agent), catalyzed by  $CeO_2$  was reported [60] to provide a high (78.9%) yield of the target product. Quite important reaction parameters in these systems were the redox and acid-base properties of the catalyst as well as its composition and morphology. The presence of a sufficient number [61] of weak acid and base sites and a sufficiently high surface area was required for optimal catalyst performance. Moreover, the authors found that  $CeO_2$  nanorods with the most abundant basic sites and oxygen vacancies led to the highest yield of

glycerol carbonate, while the sponge-like  $CeO_2$  with the medium basic sites and least defect sites provided the lowest yield. A significant role is also played by the dehydrating agents in order to shift the equilibrium to the desired products since the carbonylation of glycerol with carbon dioxide is controlled and limited by thermodynamics.



**Scheme 6.** Proposed reaction mechanism for the synthesis of cyclic carbonates via electrogenerated NHCs. Reproduced with permission from [57], copyright 2012, ESG.

General limitations from coproduced water on the formation of cyclic carbonates from diols [62] have promoted a large amount of published studies to examine the effect of chemical or physical drying agents on the extent of the reaction. Although all tested methods were successful in increasing the yield of the carbonate product, additional steps, such as the separation of the reacted drying agent from the reaction solution, the increase in the number of byproducts, the regeneration of the drying agent or simply the control of the reactivity of the drying agent for protection of the catalyst, had to be introduced in the catalytic process. Besides adding, at least, an extra layer of complexity to the reaction, the real important issues, however, are the extra cost and effort associated with their implementation and their potential to poisoning the catalyst.

## 4. Conclusions

The reactions of conversion of carbon dioxide into fine chemicals, in particular to cyclic carbonates, has gained considerable attention over the last years aiming to reduce  $CO_2$  emissions in the atmosphere and subsequent global warming effects.

In this review we summarized recent progress, mainly in cyclic carbonate synthesis starting from carbon dioxide and diols, as a promising sustainable alternative to the current industrial ones. Besides different types of catalysts (e.g., homogeneous, heterogeneous, metal-based, coordination compounds or organocatalysts) also several solvents (e.g., ionic liquids) and methods (e.g., electrochemically producing the catalyst) have been studied aiming to promote greener procedures. In several cases the experimental work was nicely complemented by theoretical calculations. The gained knowledge and insights into the interaction between catalytic species and substrates helped to rationalize the experimental results and might allow the design of new catalysts and processes.

The use of alternative starting materials including certain diols for the one-pot synthesis of cyclic carbonates could become an interesting alternative to epoxides, especially if they are derived from sustainable sources [63].

Author Contributions: Writing original draft, E.J.C.L., A.P.C.R. and L.M.D.R.S.M.; review and editing, L.M.D.R.S.M. All authors have read and agree to the published version of the manuscript.

**Funding:** This research and APC were funded by Fundação para a Ciência e Tecnologia (FCT), project UIDB/00100/2020 of Centro de Química Estrutural.

Conflicts of Interest: The authors declare no conflict of interest.

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