

On the mechanism of CO₂ electro-cycloaddition to propylene oxides



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ABSTRACT

We herein present a systematic study on the mechanism of CO₂ electro-cycloaddition to propylene oxide, using both experimental and theoretical procedures. The study considers the analysis of mild and sustainable conditions to obtain cyclic carbonates from CO₂ recycling. Within the electrochemical approach, the application of an overpotential in the reaction enhances the reaction yield significantly with respect to the thermal pathway. The quantum-mechanical approach provides relevant information about the reaction mechanism. Specifically, the use of the Lewis acid catalyst Mg²⁺ in the presence of the [C₄C₁Im][Br] ionic liquid provides the best condition for the electro-synthesis. The theoretical predictions were confirmed by a new set of experiments.

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1. Introduction

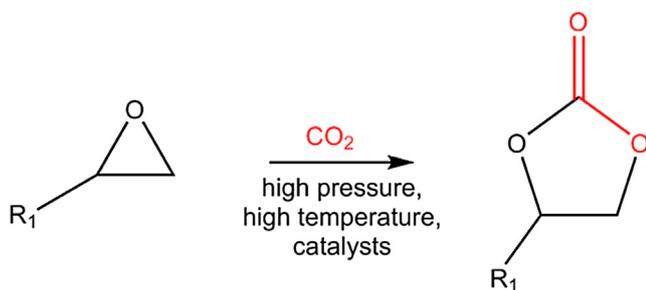
The anthropogenic concentration of CO₂ in the troposphere has increased alarmingly in recent decades. It is well-known that CO₂ emissions are the main responsible of the global warming [1–3]. Therefore, reducing emissions is a priority worldwide. So far, various strategies have been proposed to mitigate the increase of CO₂ concentration in the atmosphere. A useful and elegant approach involves the conversion of CO₂ into new products with added value, in a process called CO₂ capture [4–12]. In this line, several studies devoted to CO₂ fixation has been described in the past years. However, a common factor present in these processes is the use of high CO₂ pressures and high temperatures to obtain the desired product. For instance, Kruper and Dellar at the end of the last century, achieved the cyclic carbonates synthesis from the cycloaddition of carbon dioxide to epoxides, (see Scheme 1) using metalloporphyrins as catalyst. They reported conversion efficiencies close to 100% under extreme conditions: high pressure (780psi), at 100 °C and after 60 h of reaction [13]. Rather recently, Muralidharan and coworkers studied the catalytic synthesis of cyclic carbonates using metallic complexes of iminomethyl pyrrol at atmospheric pressure. However the high temperature used and the low yields achieved after 10 h makes this protocol unpractical to be used at industrial scale [14]. On the other hand, one of the

most innovative fixing processes involves the use of Ionic Liquids (IL) as (green) reaction media. For instance, Yoshida and co-workers described the reaction of CO₂ with propargylic amines to form 2-oxazolidinones by using a series of IL as solvent [15–17].

Another interesting and useful fixing process in these reaction media implies the synthesis of cyclic carbonates from epoxides. For instance, North and Kleij have published a series of articles regarding this field by using different Aluminum catalysts [18,19]. Both articles suggest the use of cheap and nontoxic metal derivatives as catalysts. In the same line, other authors suggest the use of different catalysts for improving the reaction scope [2,4,6,7,11–13,15,20–24]. In order to improve the classical thermal method to prepare cyclic carbonates, the electro-synthesis of these compounds in ionic liquids have been proposed [25]. This method has some significant advantages over the thermal one for it avoids the use of conventional organic solvents. In order to increase the yields obtained in the electro-synthesis of cyclic carbonates, different strategies have been applied, many of them involve the use of co-catalysts that activate the epoxide ring, thereby stabilizing the alkoxide generated. In this context, the use of halides and sacrificial anodes has proven to be particularly useful, by increasing the amount of product formed [24,26,27]. The inclusion of IL in the reaction system makes this reaction greener, mainly because the solvent can be recovered, and allowing the reaction to occur at milder conditions [21,25,28]. However, a fundamental requirement is the application of –2.4 V vs Ag/AgCl overpotential, so that the energy cost of this reaction is probably

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Scheme 1. Kruper and Dellar thermal synthesis of cyclic carbonates from reference 3.

one of the main disadvantages of this protocol for their application at industrial scale. Even though the electrochemical approach appears as a powerful alternative for fixation of atmospheric CO₂, where several mechanistic aspects remains unclear.

In this work, a mechanistic approach to the electrochemically promoted cycloaddition of carbon dioxide to epoxides is presented. The effect of reduced CO₂ towards the anion radical CO₂^{•-} is a key piece of information to set up a rational and complete reaction mechanism (*vide infra*). Additionally, a series of experiments have been carried out in order to check if the quantum chemistry predictions coherently explain the experimental observations. In this sense, this work provides useful insight oriented to develop and design new benign CO₂ fixation processes.

2. Results and discussion

2.1. Electrochemical results

In the electrochemical reaction between propylene oxide and CO₂, yields obtained after controlled potential electrolysis were 72.8%, 41.1% and 26.1% for [C₄C₁Im][Br], [C₄C₁Im][BF₄] and [C₄C₁Im][NTf₂] as solvent, respectively. In a similar fashion, the reaction between CO₂ with epichlorohydrin and styrene oxide were carried out in [C₄C₁Im][Br], [C₄C₁Im][BF₄] and [C₄C₁Im][NTf₂] as solvents. Yields obtained were 3.0%, 0.7% and 0.58% in the reaction with epichlorohydrin in all three solvents, respectively. On the other hand in the reaction with styrene oxide in [C₄C₁Im][Br], [C₄C₁Im][BF₄] and [C₄C₁Im][NTf₂] yields were 14.4%, 9.1% and 8.1%, respectively. Considering the yields obtained we can conclude that in fact the presence of bulky groups decreases the yield, which in case of styrene oxide is six times lower than propylene oxide. In a similar fashion, the presence of an electroattractive group in the epoxide produces a dramatic decrease in the conversion yield. It is clear that the reaction is favored when using [C₄C₁Im][Br] as reaction medium, where the order in reactivity is in direct concordance with the pK_a of the conjugate acid of the anion: pK_a(HBr) = -8, pK_a(HBF₄) = -0.4, pK_a(HNTf₂) = 1.7. From this analysis it can be inferred that viscosity of the ionic liquid and hydrophobic character of the anion are not significant factors in the yield of the reaction as might be expected from a diffusion controlled electrochemical process. Since [C₄C₁Im][Br] is the most active solvent toward the synthesis of the respective cyclic carbonate, Lewis basicity of the anion must be considered as one of the main factors to understand the role of this species in the reaction mechanism. On the other hand the potential applied in the electrolysis ensures the formation of the CO₂^{•-} radical anion necessary to carry out the coupling with the epoxide. Indeed, CO₂^{•-} radical anion formation has been demonstrated previously by other authors [29,30]. In those works the anion was produced after a single one electron transfer at -2.1 V vs NHE electrode in average; depending on the solvent and the electrodic surface. In

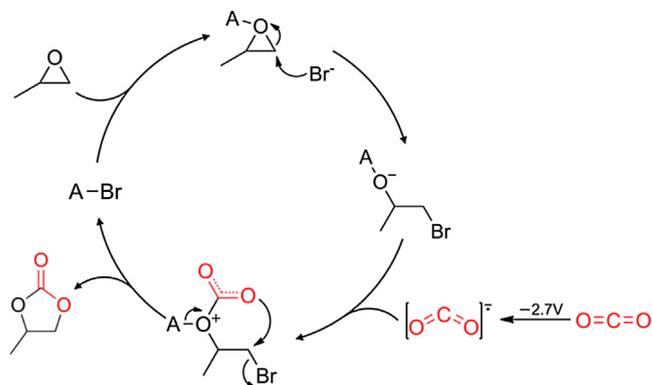
ionic liquid media formation of cyclic carbonates has been reported in metallic electrodes at similar electrode potential, namely, -2.4 V vs Ag/AgCl. It has been recognized that the IL medium provides the right environment to stabilize the radical anion; in some cases preventing dimerization or polymerization processes through intermolecular interactions. The role of the cation of the ionic liquid is also a determinant contributor by avoiding the formation of oxalate and other by products [31].

In order to establish the role of the applied overpotential, electrolysis experiments have been carried out at open circuit conditions *i.e.* without the application of potential, under the mild conditions described above. In this situation the reaction does not take place and, as a result, only precursors are detected. Hence, in order to produce the cyclic carbonate electrochemical overpotential must be applied. The role of the activated carbon dioxide anion radical is crucial since at -2.4 V vs Ag/AgCl the generation of CO₂^{•-} is guaranteed [25,32]. The role of this species will be considered in the next sections. In the same way, the role of the sacrificed electrode remains unclear [33]. During the experiments carried out, a plate of Mg was used as sacrificial electrode detecting Mg²⁺ in solution after the carbonate synthesis. The role of Mg²⁺ as co-catalyst (Lewis Acid) will be discussed later.

Reaction mechanisms for the preparation of cyclic carbonates have previously been reported for systems that use pressurized carbon dioxide [20]. This model includes a first opening of the epoxide ring, a subsequent stabilization of the intermediate formed, and then the cycloaddition of the carbon dioxide as depicted in Scheme 2. However, since carbon dioxide at -2.4 V vs Ag/AgCl is no longer a linear and neutral molecule, the reaction mechanism is not trivial, and its role will be discussed below.

2.2. Theoretical results

Considering the electrolysis outcome, where [C₄C₁Im][Br] appears as the best solvent with a yield of 72.8%, we decided to perform a theoretical analysis using this IL. In addition, it is well known that the performance of the electrolysis may be improved if a Lewis acid is present (Mg²⁺ in this case) [33]. The use of Zn anode (and other metals) has been already tested and studied by other authors in many of these works is possible to observe that Zn²⁺ species in solution does not stabilize the open epoxide ring [33]. In our case, due to the electrochemical potential applied to the system (-2.4 V), and considering that the reduction potential of both cations are -2.38 V and -0.76 V for Mg²⁺ and Zn²⁺ respectively; it is very possible that if we use a Zn anode, the cations formed may be reduced again in the cathode. In case of Mg, due to its high potential, reduction at -2.4 V is more difficult. Therefore, in order to obtain relevant information about the role of



Scheme 2. Proposed mechanism for the catalytic cycle in the reaction of CO₂ with propylene oxide. The specie "A" is a general Lewis acid.

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