

On the mechanism of CO₂ electro-cycloaddition to propylene oxides



Sebastián Gallardo-Fuentes^a, Renato Contreras^a, Mauricio Isaacs^b, Jessica Honores^b,
Diego Quezada^b, Esteban Landaeta^b, Rodrigo Ormazábal-Toledo^{c,*}

^a Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653-SCL, Santiago, Chile

^b Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Avda. Vicuña Mackenna 4860, Macul, Santiago, Chile

^c Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653-SCL, Santiago, Chile

ARTICLE INFO

Article history:

Received 12 January 2016

Received in revised form 9 June 2016

Accepted 27 June 2016

Available online 16 July 2016

Keywords:

CO₂ recovery

Electro-cycloaddition

Density functional calculations

Reaction mechanism

Ionic liquids

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.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

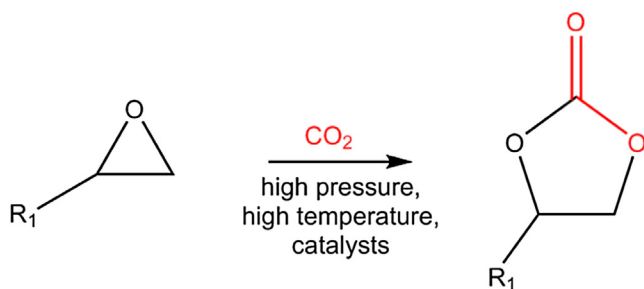
The anthropogenic concentration of CO₂ in the troposphere has increased alarmingly in recent decades. It is well-known that CO₂ emissions are the main responsible of the global warming [1–3]. Therefore, reducing emissions is a priority worldwide. So far, various strategies have been proposed to mitigate 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

* Corresponding author.

E-mail address: rormazabal@u.uchile.cl (R. Ormazábal-Toledo).



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

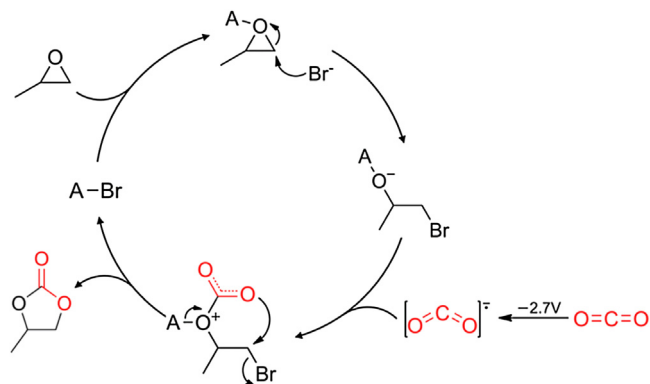
ionic liquid media formation of cyclic carbonates has been reported in metallic electrodes at similar electrode potential, namely, -2.4 V vs Ag/AgCl. It has been recognized that the IL medium provides the right environment to stabilize the radical anion; in some cases preventing dimerization or polymerization 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.

CO₂, IL, Mg²⁺ and the overpotential on the mechanism of the title reaction, full explorations of relevant possible potential energy surfaces were performed.

First of all, a fundamental question to answer is about the effect that the extra electron produces on the electrochemical process and on the reaction mechanism. Based on the electrochemical data, the reaction is strongly favored when overpotential is applied. It has been previously reported that this extra electron is the responsible of the enhanced reactivity of CO₂ [33–35]. The enhanced reactivity may be related to the distortion of the commonly linear structure of neutral CO₂ towards a bent structure of the associated radical anion that result in a strong activation at the electrophilic center of CO₂. In order to prove this hypothesis, we scanned the potential energy surface of CO₂ against the bond O=C=O angle in both cases, in its neutral form and as CO₂^{•−}, its radical anion form (see Fig. 1). This scan was performed at both the M06-2x/6-31+G(d,p) and CBS-QB3 levels of theory [36,37]. The choice of two different levels of theory was made in order to evaluate the theoretical models against their computational stability. The computational approach includes one method commonly used to evaluate the kinetics of chemical reactions [36] and a more robust one defined in the limit of a complete basis set method [37].

As it may be seen from Fig. 1, for the neutral CO₂ in a bent configuration (curve with squares in Fig. 1) the energy increases exponentially when the scan of the O—C—O angle is varied within the (110°–180°) range. Note that for both levels of theory the response is essentially the same, thereby showing that the energy response is method and basis set independent. When CO₂ bears an extra electron (curves with circles in Fig. 1) both methods qualitatively predict that the linear form is highly unstable with respect to CO₂ in its basal form at ∠O—C—O = 180°. However as the O—C—O angle is decreased, a minimum at c.a. 137° appears, thereby confirming that CO₂^{•−} is not a linear species, as previously proposed [38].

Even though CO₂^{•−} is more stable in its bent configuration, the question now is focused on its reactivity as nucleophile or

electrophile. This question is more interesting to answer if we focus on its local rather than its global reactivity. For this purpose, two different methods to quantify local chemical reactivity were employed. First of all, we focused on the local reactivity as described by the electrophilic and nucleophilic Fukui functions. Starting from their local values at every point \vec{r} in space of the molecular region, we can define a semi-local Fukui function basin by using a simple integration method reported elsewhere [39,40]. This semi-local Fukui functions basins allows finding those zones within the molecular fragment that are more susceptible to release electronic charge (nucleophilic zones) or to accept electronic charge (electrophilic zones).

The second approach which is complementary to the Fukui functions formalism is the Electronic Localization Function (ELF) analysis [41]. This approach allows finding those molecular regions where is more probable to find a pair of electrons. The result of the regional reactivity analysis using both approaches is depicted in Fig. 2.

Fig. 2 reveals key pieces of information related to site activation promoted by a geometry distortion from linear to bent configurations of CO₂ in their corresponding ground states (linear for neutral CO₂, left side, and bent for the corresponding radical anion, right side in Fig. 2). Let us first consider the analysis based on the Fukui function basins formalism (Fig. 2, upper line). It may be seen that linear CO₂ displays a trivial regional reactivity picture: for the linear configuration, the reactivity is located at the extreme of CO₂. However, for the bent radical anion ground state (right hand side in Fig. 2), a strong activation appears at the electrophilic carbon atom. In other words, the capture of an extra electron by CO₂ together with a transition from linear to bent configurations results in the creation of a hole at the carbon site in the anion radical. In round words, the ground state of bent CO₂^{•−} becomes electrophilically activated for a nucleophilic attack.

In the same way the ELF analysis reveals similar responses: for the linear ground state of neutral CO₂, we observe four basins: two corresponding to core basins located at the extreme of CO₂ and two others that correspond to valence domains. However, for bent

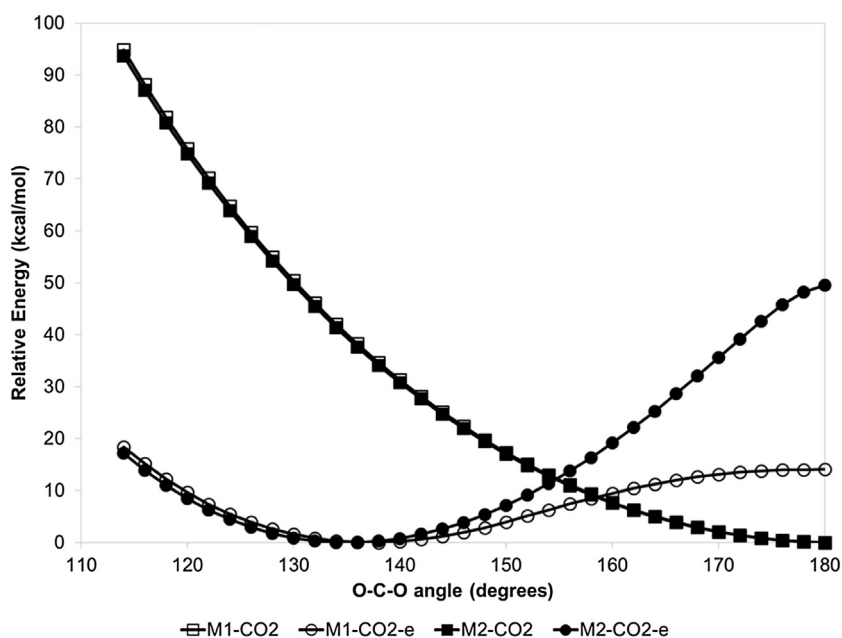


Fig. 1. Scan of the O—C—O angle for CO₂ (squared curves) and CO₂^{•−} (circled curves). Levels of theory are M06-2x/6-31+G(d,p) (M1 method) and CBS-QB3 (M2 method).

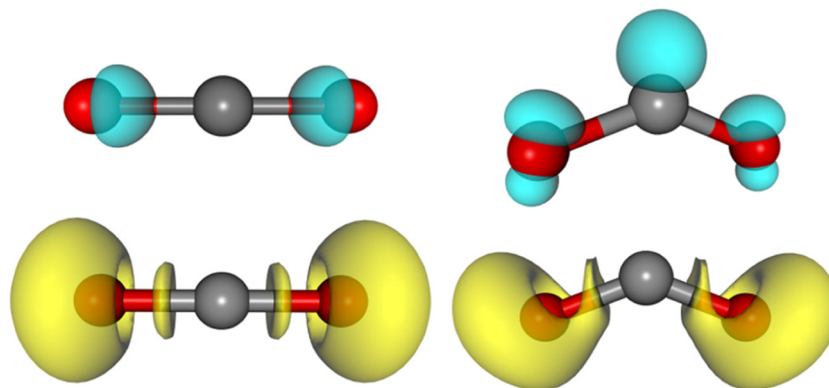


Fig. 2. Electrophilic Fukui Function (upper) and Electron Localization Function (lower) basins for the possible configurations of CO₂ (left) and CO₂^{•-} (right).

ground state of CO₂, there is again the formation of an electrophilic hole that facilitates the approach of a nucleophile, thereby enhancing the efficiency of the reaction towards epoxides.

2.3. Potential energy surface analysis: the mechanism

For the reaction between substituted epoxide and CO₂ the proposed catalytic mechanism may be summarized as shown in Scheme 2. This mechanism is based on the thermal catalytic cycle proposed by Dupont and coworkers [20]. In this work, we present an alternative route that incorporates an electro-synthetic procedure that uses the ionic liquid [C₄C₁Im][Br] whose anion (Br⁻) acts as the ring opening agent in a first step. In a subsequent step, bent radical anion CO₂^{•-} is nucleophilically attacked by the already open epoxide. Finally, the product is obtained by the ring closure step. The regeneration of the catalyst is achieved by the interaction of the departing Br⁻ ion and the Lewis Acid Mg²⁺ [42]. There remain however, to elucidate whether or not the cation of the ionic liquid can act as the Lewis acid catalyst in competition with Mg²⁺. Other mechanisms have been suggested in literature considering a decomposition of ionic liquid as co-catalysts [19]. The main difference with the mechanism proposed by Dupont is that the mechanism proposed by North considers the use of tetrabutylammonium bromide instead of an imidazolium based salt (as in the present report). In this sense, the decomposition process in the electrochemical conditions may be safely discarded considering that after the end of the catalytic cycle, ¹H NMR spectra shows that the ionic liquid solution remains unaffected. Nevertheless, both authors pointed out on the key role that halides fulfill on the reaction mechanism. In this way, the use of Br⁻ as nucleophile for the reaction in the simulation may be the best choice.

In order to prove our working hypothesis, we prepared three possible scenarios to simulate the ring opening step assisted by Br⁻ anion, as depicted in Fig. 3. The first model (TS1-C₄C₁Im) considers

the interaction between the epoxide in the presence of the [C₄C₁Im]⁺ cation, Br⁻ and CO₂. This route entails an energy barrier to open the epoxide of 27.5 kcal/mol. The second case (TS1-Mg) considers the interaction between the epoxide in the presence of Mg²⁺, Br⁻ and CO₂. This route is characterized by an energy barrier to open the epoxide of 6.8 kcal/mol. Finally, we considered the direct interaction between the bent radical anion CO₂^{•-}, and the epoxide, assisted by the Br⁻ anion of the IL (TS1-CO₂).

Note that the kinetically favored pathway is that described by TS1-Mg that clearly suggests an anion effect of the IL as ring opening agent and the Lewis acid Mg²⁺ as the catalyst (see Fig. 4). The analysis of the complete energy profile shows that the probability of having electron capture by the epoxide can safely be discarded because, according to Fig. 5, the intermediate Int2-e is favored when CO₂ is acting in its reduced bent configuration.

The last point to be discussed is about the origin of the catalytic effect of Mg²⁺. By comparing the profiles catalyzed by Mg²⁺, [C₄C₁Im]⁺ and CO₂ (See Fig. 3), there exists a difference of about 10 kcal/mol in the activation energy, in favor of the TS1-Mg structure. This response may be analyzed using Pearson's HSAB principle: Mg²⁺ is a hard acid and the oxygen anion in the open epoxide ring is a hard base. On the other hand, the cation [C₄C₁Im]⁺ may safely be considered as a soft acid because its size (i.e. a more polarizable molecule). Bent CO₂^{•-} on the other hand is a high polarizable species, and therefore soft [43].

It is important to point out at this stage, how the overpotential applied impacts the complete mechanism. In order to understand the role of the overpotential in the ring opening stage, we simulated this process with and without the addition of an extra electron (see Fig. 5).

The reaction barrier for these steps are 6.8 and 8.9 kcal/mol for TS1-Mg (ring opening without an extra electron) and TS1-Mg-e (ring opening with an extra electron), respectively. It is important to point out that in both cases CO₂ molecule is quasi-linear. The

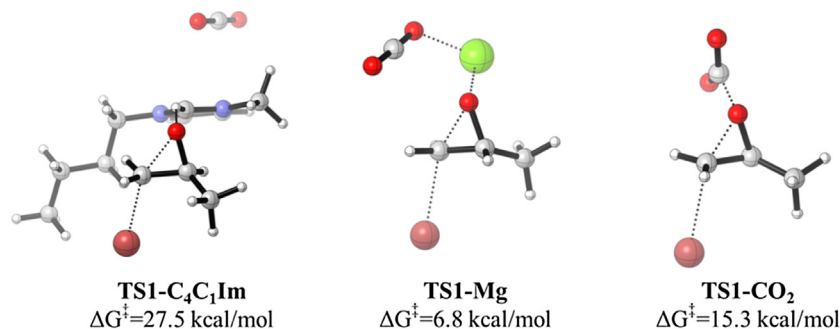


Fig. 3. Ring opening transition state catalyzed by (a) [C₄C₁Im]⁺ cation, (b) Mg²⁺ and (c) uncatalyzed.

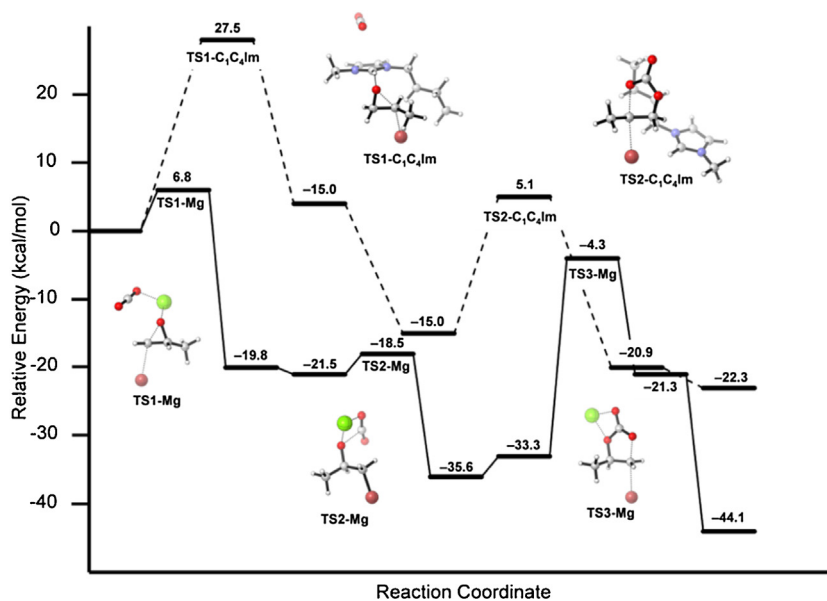


Fig. 4. Free Energy Profiles for the cycloaddition between CO₂ and propylene oxide catalyzed by Mg²⁺ (solid line) and [C₄C₁Im]⁺ cation (dashed line).

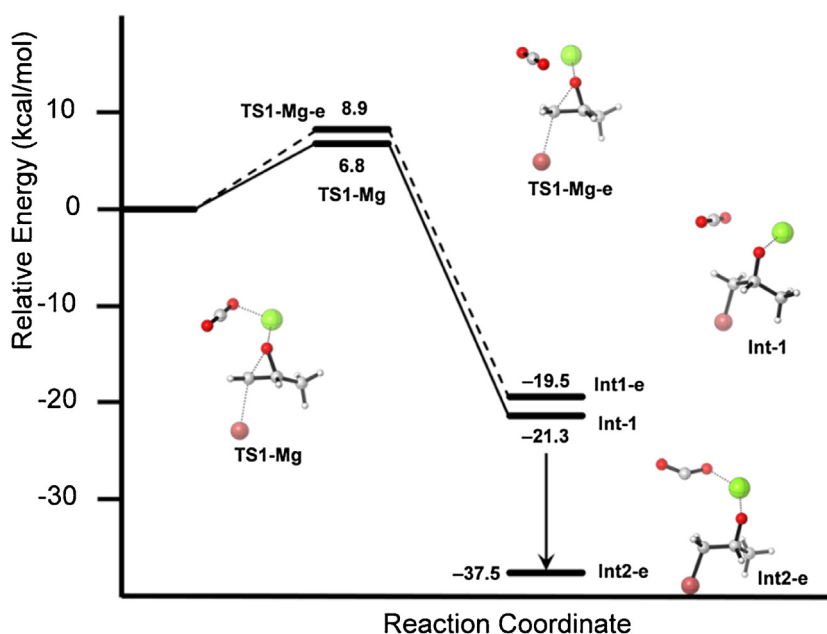


Fig. 5. Free energy profile for the reaction between CO₂ and propylene oxide catalyzed by Mg²⁺ with an extra electron (CO₂^{•-} solid line) and without an extra electron (neutral linear CO₂ dashed line).

intermediates Int-1 and Int1-e are also similar in energy, being CO₂ linear too. However, the relevant difference appears when CO₂^{•-} is in its bent configuration, because in this case the energy of Int2-e is almost 17 kcal/mol lower (see Fig. 5). This result reinforces the role of the overpotential (an extra electron in the calculation) in the reaction allowing the formation of an electrophilically activated CO₂^{•-} species. In this case, the role of the overpotential is to bend the CO₂ molecule, thereby stabilizing the system and consequently promoting the nucleophilic attack of oxygen to carbon and ring closure steps. Note that, in Int2-e CO₂^{•-} is bent in 132°, close to the experimental value of 137° when CO₂^{•-} is isolated [38]. Additionally, the ring closing step is rate determining when the system is coordinated by Mg²⁺ and it is favored by 5 kcal/mol in the simulation, in the presence of applied overpotential.

Using the useful information provided by the theoretical procedure, a set of new experiments were designed and performed in the same conditions. They were as follows:

(i) First of all, we performed the electrolysis of propylene oxide without the application of overpotential. After 12 h of electrolysis no product was detected by GC-MS, UV-vis or FT-IR spectroscopy. This result is relevant for it implies that at ambient temperature and atmospheric pressure the reaction is not taking place in the absence of the overpotential. In other words, this experiment reveals the importance that the application of overpotential has in the mechanism allowing the carbonate formation in mild conditions.

(ii) On the other hand, electrolysis of propylene oxide was performed at -2.4 V vs Ag/AgCl but using a Pt wire as counter

electrode instead of Mg belt. Using the experimental procedure described previously, no product was obtained after 12 h of reaction. This result confirms the catalytic role of Mg (as Mg²⁺) possibly assisting the ring opening of oxirane, in agreement with the theoretical predictions. In this sense, the role of ionic liquid cation may be further clarified. Additionally, MgBr₂ was added to the cell, as a source of Mg²⁺. The results show that under these conditions the cyclic carbonate conversion yield was 50.1%, thereby confirming the catalytic effect of Mg²⁺. In this sense, Ionic Liquids represent an optimal solvent for the synthesis of cyclic carbonates under mild conditions, but the addition of a hard Lewis Acid improves the reaction yield since it promotes the oxirane ring opening. In the original work by Dupont, the role of cation remains unclear since both [C₄C₁Im]⁺ and [C₄C₁C₁Im]⁺ (the cation 1-butyl-2,3-dimethylimidazolium) gave similar yields. Several explanations were suggested to the activation of CO₂ or epoxide by imidazolium rings, but our proposal suggests that in any situation a hard Lewis acid must be added to the solution of oxirane/ionic liquid/CO₂.

According to experimental results presented the information obtained from a theory assisted model describes well the mechanism of electro-cycloaddition. The comparative studies performed, reveals that the catalyst Mg²⁺ is key specie within the reaction mechanism.

2.4. Conclusions

In summary, the reaction between CO₂ and several epoxides have been studied using both electrochemical and theoretical procedures. Within the electrochemical approach the use of overpotential in the reaction yields a more efficient reaction and a sustainable way to obtain cyclic carbonates from CO₂ under mild conditions. 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 of the synthesis. The theoretical predictions were confirmed by a new set of experiments.

3. Experimental

3.1. Materials

All the solvents and propylene oxide were obtained from Sigma Aldrich and were used without any further purification. Carbon dioxide (extra pure 99.99%) was purchased from INDURA. [C₄C₁Im][Br], [C₄C₁Im][BF₄] and [C₄C₁Im][NTf₂] were purchased directly from Sigma Aldrich. Seller certified that in case of BF₄, traces of halides are below 25 mg/kg. All solvents were dried during 8 h at 90 °C under vacuum prior to use.

3.2. Cyclic carbonate preparation

The preparation of cyclic carbonates was carried out by controlled potential electrolysis using a BASi Power Module 3 into an undivided glass cell. Using a three electrode arrangement; a copper foil (3 cm²) Sigma Aldrich as working electrode, an Ag/AgCl electrode as a pseudo reference electrode [44] (0.34 V vs Fc/Fc⁺) and a Pt wire of 14 cm² or Mg belt of 14 cm² as counter electrodes or sacrificial anodes. Ionic liquids [C₄C₁Im][Br], [C₄C₁Im][BF₄] and [C₄C₁Im][NTf₂] (15 mL), and the respective epoxide (10 mmol) were mixed into the electrochemical cell and the resulting solution was saturated with CO₂ before the reaction begins. During the electrolysis, −2.4 V vs Ag/AgCl was applied and carbon dioxide bubbling remained constant during 12 h at room temperature and atmospheric pressure. CO₂ was passed through a Drierite column before entering in the electrochemical cell.

Products extraction from the reaction cell was carried out using 3 portions of 50 mL of diethylether. Extracts were analyzed and quantified using a Shimadzu Multispec 1501 UV–vis spectrometer. A typical procedure consisted in preparation of a calibration curve with a standard propylene carbonate; relating its absorption maxima (206 nm) with the carbonate concentration. Range of concentration to prepare the calibration curve was between 10–100 mM. Samples were obtained from the extracted product and an UV–vis spectrum was carried out, its concentration was calculated using the previously prepared calibration curve. Yield was calculated considering the amount of propylene oxide added to the system and the final amount of product determined.

¹H NMR signals registered to the product obtained and the electrolyzed ionic liquid and are listed below.

[C₄C₁Im][Br] after electrolysis: ¹H NMR (400 MHz, CDCl₃, 298 K), δ(ppm): 0.56–0.64 (t, 3H, −CH₃), 0.94–1.13 (m, 2H, −CH₂−), 1.49–1.64 (m, 2H, −CH₂−), 3.79 (s, 1H, N-CH₃), 3.98–4.06 (t, 2H, N-CH₂−) 7.34–7.44 (d, 2H, N-CH-CH-N), 9.76 (s, 1H, N-CH-N).

Propylene carbonate: ¹H NMR (400 MHz, CDCl₃, 298 K), δ(ppm): 1.34–1.37 (d, 3H, CH₃), 3.88–3.96 (t, 1H, CH₂), 4.42–4.50 (t, 1H, CH₂), 4.68–4.85 (m, 1H, CH).

3.3. Computational procedures

All calculations were carried out using the M06-2x/6-31 + G(d, p) level of theory, unless otherwise is stated. Transition states were characterized by the presence of an anomalous vibration; additionally an IRC calculation was performed to confirm that reactants, intermediates and/or products are smoothly connected passing by the transition state geometry. All calculations were carried out with Gaussian 09 [45].

Acknowledgements.

This work was supported by FONDECYT1160061, 3140525 and 1141199; Project RC 130006, CILIS, granted by Fondo de Innovación para la Competitividad, del Ministerio de Economía, Fomento y Turismo, Chile; and CONICYT grants 21120876, 21120676, 21130709 and 21130214.

References

- [1] A.J. Weaver, C. Hillaire-Marcel, Global warming and the next ice age, *Science* 304 (2004) 400–402.
- [2] J.G. Canadell, C. Le Quééré, M.R. Raupach, C.B. Field, E.T. Buitenhuis, P. Ciais, T.J. Conway, N.P. Gillett, R.A. Houghton, G. Marland, Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks, *Proc. Natl. Acad. Sci. U. S. A.* 104 (2007) 18866–18870.
- [3] L.-S. Lau, C.-K. Choong, Y.-K. Eng, Carbon dioxide emission, institutional quality, and economic growth: empirical evidence in Malaysia, *Renew. Energy* 68 (2014) 276–281.
- [4] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Co(III) porphyrin/DMAP: An efficient catalyst system for the synthesis of cyclic carbonates from CO₂ and epoxides, *Tetrahedron Lett.* 45 (2004) 2023–2026.
- [5] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis, CO₂ capture by a task-specific ionic liquid, *J. Am. Chem. Soc.* 124 (2002) 926–927.
- [6] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe, O.M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture, *Science* 319 (2008) 939–943.
- [7] X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO₂ capture, *Energy Fuel* 16 (2002) 1463–1469.
- [8] M. Pera-Titus, Porous inorganic membranes for CO₂ capture: present and prospects, *Chem. Rev.* 114 (2014) 1413–1492.
- [9] T.D. Pham, Q. Liu, R.F. Lobo, Carbon dioxide and nitrogen adsorption on cation-exchanged SSZ-13 zeolites, *Langmuir* 29 (2013) 832–839.
- [10] M. Hasib-ur-Rahman, F. Larachi, CO₂ capture in alkanolamine-RTIL blends via carbamate crystallization: route to efficient regeneration, *Environ. Sci. Technol.* 46 (2012) 11443–11450.
- [11] B. Gurkan, B.F. Goodrich, E.M. Mindrup, L.E. Ficke, M. Massel, S. Seo, T.P. Senftle, H. Wu, M.F. Glaser, J.K. Shah, E.J. Maginn, J.F. Brennecke, W.F. Schneider,

- Molecular design of high capacity, low viscosity, chemically tunable ionic liquids for CO₂ capture, *J. Phys. Chem. Lett.* 1 (2010) 3494–3499.
- [12] V. Manovic, E.J. Anthony, Competition of sulphation and carbonation reactions during looping cycles for CO₂ capture by CaO-based sorbents, *J. Phys. Chem. A* 114 (2010) 3997–4002.
- [13] W.J. Kruper, D.V. Dellar, Catalytic formation of cyclic carbonates from epoxides and CO₂ with chromium metalloporphyrins, *J. Org. Chem.* 60 (1995) 725–727.
- [14] H. Vignesh Babu, Cu(II) complexes of 2,5-bis[N-(2,6-diisopropylphenyl)iminomethyl]pyrrole: synthesis, structures and their high catalytic activity for efficient cyclic carbonate synthesis, *Dalton Trans.* 42 (2013) 1238–1248.
- [15] M. Yoshida, T. Mizuguchi, K. Shishido, Synthesis of oxazolidinones by efficient fixation of atmospheric CO₂ with propargylic amines by using a silver/1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) dual-catalyst system, *Chem. Eur. J.* 18 (2012) 15578–15581.
- [16] J. Hu, J. Ma, Q. Zhu, Z. Zhang, C. Wu, B. Han, Transformation of atmospheric CO₂ catalyzed by protic ionic liquids: efficient synthesis of 2-oxazolidinones, *Angew. Chem. Int. Ed.* 54 (2015) 5399–5403.
- [17] M.-Y. Wang, Q.-W. Song, R. Ma, J.-N. Xie, L.-N. He, Efficient conversion of carbon dioxide at atmospheric pressure to 2-oxazolidinones promoted by bifunctional Cu(II)-substituted polyoxometalate-based ionic liquids, *Green Chem.* 18 (2016) 282–287.
- [18] W. Clegg, R.W. Harrington, M. North, R. Pasquale, Cyclic carbonate synthesis catalysed by bimetallic aluminium-salen complexes, *Chem. Eur. J.* 16 (2010) 6828–6843.
- [19] M. North, R. Pasquale, Mechanism of cyclic carbonate synthesis from epoxides and CO₂, *Angew. Chem. Int. Ed.* 48 (2009) 2946–2948.
- [20] A.-L. Girard, N. Simon, M. Zanatta, S. Marmitt, P. Goncalves, J. Dupont, Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide, *Green Chem.* 16 (2014) 2815–2825.
- [21] Q. He, J.W. O'Brien, K.A. Kitselman, L.E. Tompkins, G.C.T. Curtis, F. Kerton, M.: Synthesis of cyclic carbonates from CO₂ and epoxides using ionic liquids and related catalysts including choline chloride-metal halide mixtures, *Catal. Sci. Technol.* 4 (2014) 1513–1528.
- [22] R.L. Paddock, S.T. Nguyen, Chemical CO₂ Fixation: Cr(III) salen complexes as highly efficient catalysts for the coupling of CO₂ and epoxides, *J. Am. Chem. Soc.* 123 (2001) 11498–11499.
- [23] C.J. Whiteoak, N. Kielland, V. Laserna, E.C. Escudero-Adán, E. Martin, A. Kleij, W.: a powerful aluminum catalyst for the synthesis of highly functional organic carbonates, *J. Am. Chem. Soc.* 135 (2013) 1228–1231.
- [24] H. Yasuda, L.N. He, T. Sakakura, C. Hu, Efficient synthesis of cyclic carbonate from carbon dioxide catalyzed by polyoxometalate: the remarkable effects of metal substitution, *J. Catal.* 233 (2005) 119–122.
- [25] H. Yang, Y. Gu, Y. Deng, F. Shi, Electrochemical activation of carbon dioxide in ionic liquid: synthesis of cyclic carbonates at mild reaction conditions, *Chem. Commun.* (2002) 274–275.
- [26] Y. Xiao, B.L. Chen, H.P. Yang, H. Wang, J.X. Lu, Electrosynthesis of enantiomerically pure cyclic carbonates from CO₂ and chiral epoxides, *Electrochem. Commun.* 43 (2014) 71–74.
- [27] X.B. Lu, D.J. Darensbourg, Cobalt catalysts for the coupling of CO₂ and epoxides to provide polycarbonates and cyclic carbonates, *Chem. Soc. Rev.* 41 (2012) 1462–1484.
- [28] J. Sun, S.I. Fujita, M. Arai, Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids, *J. Organomet. Chem.* 690 (2005) 3490–3497.
- [29] A. Gennaro, A.A. Isse, M.G. Severin, E. Vianello, I. Bhugun, J. Savéant, M.: Mechanism of the electrochemical reduction of carbon dioxide at inert electrodes in media of low proton availability, *J. Chem. Soc. Faraday Trans.* 92 (1996) 3963–3968.
- [30] E. Lamy, L. Nadjo, J.M. Saveant, Standard potential and kinetic parameters of the electrochemical reduction of carbon dioxide in dimethylformamide, *J. Electroanal. Chem.* 78 (1977) 403–407.
- [31] L. Sun, G.K. Ramesha, P.V. Kamat, J.F. Brennecke, Switching the reaction course of electrochemical CO₂ reduction with ionic liquids, *Langmuir* 30 (2014) 6302–6308.
- [32] M. Feroci, M. Orsini, L. Rossi, G. Sotgiu, A. Inesi, Electrochemically promoted C–N bond formation from amines and CO₂ in ionic liquid BMIm-BF₄: Synthesis of carbamates, *J. Org. Chem.* 72 (2007) 200–203.
- [33] B.R. Buckley, A.P. Patel, K.G.U. Wijayantha, Electrosynthesis of cyclic carbonates from epoxides and atmospheric pressure carbon dioxide, *Chem. Commun.* 47 (2011) 11888–11890.
- [34] M. Feroci, I. Chiarotto, M. Orsini, G. Sotgiu, A. Inesi, Carbon dioxide as carbon. Source: activation via electrogenerated O₂- in ionic liquids, *Electrochim. Acta* 56 (2011) 5823–5827.
- [35] X. Gao, G. Yuan, H. Chen, H. Jiang, Y. Li, C. Qi, Efficient conversion of CO₂ with olefins into cyclic carbonates via a synergistic action of I₂ and base electrochemically generated in situ, *Electrochem. Commun.* 34 (2013) 242–245.
- [36] Y. Zhao, D. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* 120 (2008) 215–241.
- [37] G.P.F. Wood, L. Radom, G.A. Petersson, E.C. Barnes, M.J. Frisch, J.A. Montgomery, A restricted-open-shell complete-basis-set model chemistry, *J. Chem. Phys.* 125 (2006) 094106.
- [38] K.O. Hartman, I.C. Hisatsune, Infrared spectrum of carbon dioxide anion radical, *J. Chem. Phys.* 44 (1966) 1913–1918.
- [39] R.R. Contreras, P. Fuentealba, M. Galván, P. Pérez, A direct evaluation of regional Fukui functions in molecules, *Chem. Phys. Lett.* 304 (1999) 405–413.
- [40] P. Fuentealba, P. Pérez, R. Contreras, On the condensed Fukui function, *J. Chem. Phys.* 113 (2000) 2544–2551.
- [41] B. Silvi, A. Savin, Classification of chemical bonds based on topological analysis of electron localization functions, *Nature* 371 (1994) 683–686.
- [42] H. Sun, D. Zhang, Density functional theory study on the cycloaddition of carbon dioxide with propylene oxide catalyzed by alkylmethylimidazolium chlorine ionic liquids, *J. Phys. Chem. A* 111 (2007) 8036–8043.
- [43] R.G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963) 3533–3539.
- [44] G.A. East, M.A. Del Valle, Easy-to-Make Ag/AgCl reference electrode, *J. Chem. Educ.* 77 (2000) 97.
- [45] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Gaussian, Inc., Wallingford, CT, USA, 2009.