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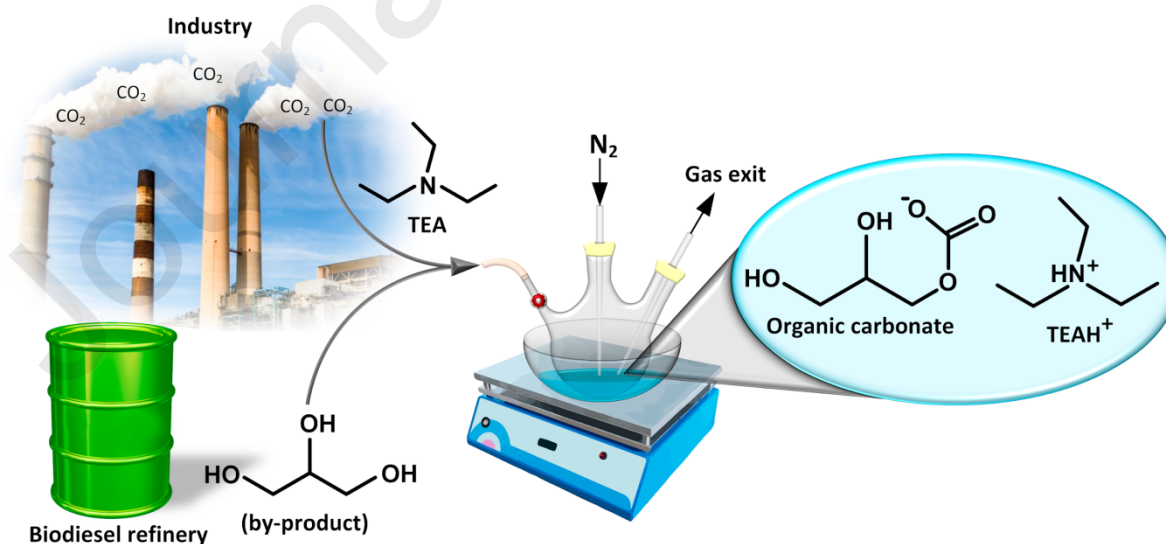
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Graphical Abstract:



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Abstract: Although CO₂ capture by alkanolamine aqueous solutions is a well-established technology, it demands high energy penalties and water consumption. Therefore, the development of new methods for CO₂ removal is still a challenge. Herein, we employed the Density Functional Theory (DFT) to explore the potential of different mixtures composed of glycerol and nitrogen-containing bases to capture CO₂. By combining glycerol, CO₂ and the bases, it was possible to show that aliphatic amines are able to form intermolecular hydrogen bonds with the primary hydroxyl groups of glycerol, increasing their nucleophilicity and assisting the reaction with CO₂ to form glycerol carbonate as the most stable product. To confirm that glycerol carbonate would be experimentally obtained from the given mixture, we selected triethylamine (TEA) to assist glycerol (Gly) in its reaction with CO₂. The resulting product was characterized by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), 1D and 2D Nuclear Magnetic Resonance spectroscopy (¹H and ¹³C NMR) and Thermogravimetric Analysis (TGA). The ATR-FTIR results showed that TEA is protonated after bubbling CO₂ in the glycerol/TEA mixture, suggesting that the reaction with CO₂ occurs after deprotonation of glycerol, forming organic carbonates, as also indicated in the NMR spectra. The combined theoretical and experimental results indicate that TEA is able to activate glycerol in its reaction with CO₂ to form organic carbonates, being an alternative procedure for CO₂ capture.

Keywords: CO₂ capture, glycerol, triethylamine, organic carbonates, glycerol activation, DFT calculation.

1. Introduction

The increasing emission of carbon dioxide (CO₂) by anthropogenic sources, such as thermoelectric power plants, deforestation, industry, and transport sectors has been considered as one of the main causes for the accelerated global warming [1,2]. The consequences could be disastrous, severely affecting ecosystems, human health, and oceans, leading to a possible irreversible scenario [3,4]. Therefore, many efforts have been devoted to the development of CO₂ capture and storage (CCS) technologies, aiming at the effective reduction of CO₂ emission from several sources to the atmosphere [5].

A possible way for CO₂ emission reduction is its selective capture from the gas mixture. In principle, this can be achieved by different procedures, *e.g.* membrane permeation [6–8], adsorption on porous solids [9–11], MOFs [12–14], COFs [15], amine-functionalized silica [16,17], and graphene [18], or absorption by basic liquid solutions [19–22]. The latter process works as a kind of chemical filtration and is the most mature technology in the context of industrial post-combustion CO₂ capture [23]. Aqueous basic solutions, particularly those of alkanolamines, stand out among the most commonly employed medium for CO₂ absorption [24,25]. The alkanolamines are bifunctional molecules containing both amine and hydroxyl groups. Upon reaction with CO₂, both carbamates and carbonates might be formed, although the formation of carbamates has been more frequently reported [26], *e.g.* upon bubbling CO₂ into a 30 wt.% monoethanolamine (MEA) aqueous solution at room temperature, carbamate is the main product [27]. The formation of carbonates may occur using tertiary or sterically hindered

alkanolamines [28,29], in which the direct nucleophilic attack of the amino functional group on CO₂ or deprotonation of the intermediate zwitterion is hampered [30].

Although the CO₂ capture in alkanolamine aqueous solutions is a well-established process, several drawbacks still need to be overcome, such as heavy energy penalties because amine regeneration demands high-energy consumption [9,31], equipment corrosion and formation of thermally stable salts [32–34]. In addition, this technology is water-intensive, which can be a problem in arid regions. Therefore, improvement of the reaction conditions is still a requirement to increase the overall efficiency of the capture and regeneration processes [35].

To overcome some of the operational problems mentioned above, one alternative is to drive the reaction to the formation of carbonates, instead of carbamates. Because of the higher capacity of nitrogen to delocalize its lone electron pair compared to the oxygen atom, the C-N bond in carbamates is stronger than the C-O bond in carbonates [36]. Therefore, a lower energy requirement would be expected in the regeneration process of the carbonate derived compounds. In this context, the design of new absorbents that would drive the reaction to the preferential formation of carbonates instead of carbamates is an interesting strategy to obtain more efficient systems for the CO₂ capture and regeneration processes.

The alcohol function by itself is not basic enough to react with CO₂. However, when combined with other chemical functions that would activate it by increasing its nucleophilicity, the reaction with CO₂ may become spontaneous. This could be achieved by mixing the alcohol with bases leading to a system able to form organic carbonates. One example of such systems is the CO₂-binding organic liquids (CO₂-BOLs) [37,38]. The

CO₂-BOLs are usually composed of a solution of an alcohol and an amidine or guanidine base, which produces amidinium or guanidinium organic carbonates, respectively, after reacting with CO₂ [39,40]. Common bases used in CO₂-BOLs are 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) [41,42], which are among the strongest bases employed in organic processes. Concerning the alcoholic moiety, primary alcohols [43], alkanolamines [44], saccharides [45], alcohol-functionalized ionic liquids [46], and glycerol [20,41,42] have been employed. Among the alcohols, glycerol is an attractive choice due to its low cost as a by-product of biodiesel production, corresponding to 10-20% of the total volume of biodiesel produced. In addition, glycerol is biodegradable, eco-friendly, thermally stable and nontoxic solvent [47]. Therefore, finding additional utilization for glycerol is still a challenging task. Although the use of CO₂-BOLs represents advancement in the CO₂ capture context, the use of DBU and TBD strong bases makes the process expensive to scale-up.

The present study was firstly motivated by Density Functional Theory (DFT) investigations, which showed that in a mixture of glycerol and primary, secondary or tertiary common organic amines, such as MeNH₂, Me₂NH, Me₃N, or Et₃N, CO₂ preferentially reacts with glycerol rather than with the amine to form carbonate. These organic amines activate glycerol by forming an intermolecular hydrogen bond with it, resulting in increased nucleophilicity of the hydroxyl group of glycerol. To confirm the theoretical findings, we carried out a set of experiments by bubbling CO₂ into a mixture of TEA and glycerol. Although TEA shows some disadvantages, such as not being biodegradable [48], we selected it for the experiments as proof of concept because it is commercially available in its anhydrous form – a condition required to avoid the formation

of inorganic carbonate/bicarbonate due to hydrolysis by water – and also because tertiary amines do not allow a direct competitive reaction with CO_2 to form carbamates. The products obtained in the reactions were characterized by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), 1D and 2D Nuclear Magnetic Resonance spectroscopy (^1H and ^{13}C NMR) and Thermogravimetric Analysis (TGA).

2. Experimental

2.1 Computational studies

We employed the CAM-B3LYP density functional to evaluate the energy for the reaction of CO_2 with glycerol in the presence of a representative set of organic bases: guanidine (iminomethanediimine), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), diazabicyclo[5.4.0]undec-7-ene (DBU), ammonia (NH_3), methylamine (MeNH_2), dimethylamine (Me_2NH), trimethylamine (Me_3N), triethylamine (TEA), ethylenediamine (EDA) and 1,2-dimethylethylenediamine (DMEDA). We investigated the formation of three different products: i) carbamates, by a direct reaction of the base with CO_2 ; ii) carbonates, by the reaction of glycerol with CO_2 ; iii) and bicarbonates, after a proton transfer from the conjugated acid to the carbonate. All quantum chemical calculations were performed with the Density Functional Theory (DFT) model using the Gaussian 09 software, revision D.01, and default convergence criteria [49]. Full geometry optimizations were carried out using the hybrid exchange-correlation CAM-B3LYP (Coulomb-attenuating method Becke, 3-parameter, Lee-Yang-Par) functional [50] with the Pople 6-311++G(2d,2p) basis set [51]. This combination of functional and basis set yielded

satisfactory results for the reaction of ethylenediamine with CO₂ [52]. For all the stationary points, the second-order Hessian matrices were calculated at the same computational level, confirming them as minimum-energy structures on the potential energy surface. The normal mode calculations allowed us to compute the thermodynamic parameters at 298.15 K and 1 atm, using the standard statistical thermodynamic equations for an ideal gas [53]. Implicit solvation was included by the self-consistent reaction field approach (SCRF) using the integral equation formalism for the polarizable continuum model (IEFPCM), simulating water ($\epsilon = 78.3553$) as solvent [54,55].

2.2 Materials

The following chemicals and gases were used without purification: glycerol (Gly) ($\geq 99.8\%$, Vetec), triethylamine (TEA) ($\geq 99.5\%$, Aldrich), compressed nitrogen gas (99.9%, White Martins) and carbon dioxide (99.9%, Phywe).

2.3 CO₂ absorption experiments

The CO₂ absorption experiments were carried out using the system represented in Fig. S1a. Prior to the CO₂ absorption experiment, N₂ flow was passed through the mixture of TEA and glycerol in a 3:1 molar ratio under magnetic stirring for 10 min. This molar ratio was used in an attempt to activate the three hydroxyl groups of glycerol. The CO₂ flow was turned on (20 mL min⁻¹) and the reaction remained under stirring at 30 (± 1) °C for 30, 60 and 120 min. Aliquots were collected and analyzed before bubbling CO₂ (0 min) as well as at 30, 60 and 120 min of reaction times.

2.4 Characterizations

The product obtained from the reaction of CO₂ with glycerol in the presence of TEA (**TEA-Gly-CO₂**) was characterized by Nuclear Magnetic Resonance spectroscopy (NMR). ¹H and ¹³C NMR spectra were collected using a Varian NMR spectrometer at 500 and 125 MHz, respectively. The sample was prepared using dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) purchased from Cambridge Isotope Laboratories dried using molecular sieves (3 Å). Chemical shifts were referenced against residual proton resonances in DMSO-*d*₆ (2.50 ppm, ¹H; 39.5 ppm, ¹³C). Abbreviations: chemical shift (δ, ppm); multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet) and br (broad).

The product was also characterized by Fourier Transform Infrared (FTIR) spectroscopy using Agilent Varian 660-IR spectrometer equipped with an Attenuated Total Reflectance (ATR) module. Thermogravimetric Analysis (TGA) was used to determine the decomposition of the product **TEA-Gly-CO₂**. The curves were obtained in a Shimadzu TGA-60 instrument using aluminum crucibles in the range of 25-350 °C, at a heating rate of 10 °C min⁻¹, and under N₂ flow (50 cm³ min⁻¹).

3. Results and discussion

3.1 Computational results

We computed a set of structures with the ternary combination of glycerol, CO₂, and the organic base (Scheme 1). The formation of carbamate was simulated by the direct reaction between CO₂ and the base, to form an intermediate zwitterion interacting with

glycerol (species **2** in Scheme 1). The formation of carbonate was simulated by the reaction of one of the hydroxyl groups of glycerol with CO₂ and the base acting as an ancillary. Although the hydroxyl group itself is not basic enough to react with CO₂, the base may activate it after formation of an intermolecular hydrogen bond between the base and the glycerol (species **1**, Scheme 1). The existence of the intermolecular hydrogen bond was confirmed both by its interaction enthalpy ($\Delta H^{298} = -6.19 \text{ kcal mol}^{-1}$) and by the donor-acceptor distance (1.775 Å). This hydrogen bond activates glycerol to perform a nucleophilic attack on the acid carbon of CO₂, which occurs accompanied by a concerted proton transfer from the glycerol to the base (species **3**, Scheme 1). Depending on the base strength, the proton can be donated back to the carbonate, forming organic bicarbonate (species **4**, Scheme 1). It is expected that strong bases would preferentially react with the CO₂, while weak bases would not be able to activate glycerol enough to promote the reaction with CO₂. Therefore, the strength of the base should be modulated to achieve the desired features: the preferential activation of glycerol in a reaction with low activation energy and favorable thermodynamic conditions, rather than the base itself reacting with CO₂. This was the rationale behind our computational simulations. Surprisingly, we found that the most common alkylamine bases are able to activate the glycerol, as shown in the following sections.

As glycerol presents primary and secondary hydroxyl groups, the regioselectivity was investigated by computing the relative stabilities of the conjugated bases of glycerol, the glyceroxide anion, to identify the most favorable hydroxyl functional group for the reaction with CO₂. The maximum number of intramolecular hydrogen bonds was kept in all the structures (see the Supplementary Information containing the molecular structures and the cartesian coordinates). The results show that the deprotonation of the primary hydroxyl

group is preferential over the secondary one by $\Delta H^{298} = 1.17 \text{ kcal mol}^{-1}$ ($0.54 \text{ kcal mol}^{-1}$ in terms of Gibbs free energy). In both cases, the formation of either the primary or the secondary glyceroxide anion, two intramolecular hydrogen bonds stabilize the negative charge located on the deprotonated hydroxyl group. All the following calculations were carried out considering that CO_2 would preferentially react with one of the terminal hydroxyl group of glycerol. Scheme 1 shows the possible products that may be formed in the reaction between CO_2 and glycerol activated by the base. In this scheme, **1** represents a pre-reactive complex formed by glycerol and the base (B) connected by a hydrogen bond; **2** represents the zwitterion formed in the nucleophilic attack of the base on the acid carbon atom of CO_2 interacting with glycerol; **3** represents the glycerol carbonate, formed after reaction of glycerol with CO_2 , interacting with a protonated base; and **4** represents the bicarbonate derived from **3**, interacting with the base. Table 1 shows the results for a set of strong, weak, and median bases. We report the relative enthalpy and the Gibbs free energy values (in kcal mol^{-1}) taking the pre-reactive complex **1** and CO_2 as reference.

(Insert Scheme 1)

(Insert Table 1)

Table 1 shows that the combination of carbonate/protonated base (species **2**, Scheme 1) is the most stable arrangement among the investigated intermediates, excepting for the guanidine base (entry **1**), which is strong enough to directly react with CO_2 forming a stable zwitterion. The results show that even for TBD and DBU, which are also able to

produce carbamates by reacting with CO₂ [41,42], the activation of glycerol by proton abstraction concerted with the nucleophilic attack of the resulting glyceroxide anion onto CO₂, is the preferred pathway. Because of the high basicity of compounds in entries **1-3**, we observed a remarkable exothermic and exergonic profile for both reactions, formation of either carbamate or carbonate may occur. This suggests a high-energy demand for the CO₂ desorption step, which is one of the main drawbacks of using amine aqueous solutions for CO₂ capture, which must be avoided [6,9,31].

Interestingly however, while the formation of carbamates is not favored, the reaction *via* activated glycerol forming carbonate/bicarbonate may occur using bases weaker (entries **4-10**) than TBD and DBU. The low exothermicity for the reaction forming a carbonate intermediate, although still with negative change in the Gibbs free energy, points towards an easily reversible process, a highly relevant requirement for CO₂ release after capture. Bicarbonate formation after a proton transfer from the protonated base to the carbonate (species **4**, Scheme 1) was also investigated. However, excepting for ammonia ($\Delta H^{298} = -2.1$ kcal mol⁻¹ and $\Delta G^{298} = 3.5$ kcal mol⁻¹), the bases are strong enough to capture the proton back, even starting the geometry optimization with a structure favoring the bicarbonate species, indicating that the bicarbonate derivatives are not stable for the other bases.

To verify whether the reaction would also be possible from the kinetic point of view, we computed the activation energy for the conversion of **1** into **3**. The activation energy was obtained as the difference between the Gibbs free energy of the transition structures (for converting **1** into **3**, Scheme 1) and the corresponding pre-reactive complexes (species **1**, Scheme 1). For the bases in entries **4-10**, the activation Gibbs free energy for the direct reaction is below 5.5 kcal mol⁻¹, an indication that the reactions may indeed be fast. In

particular, the results indicate that the reaction should occur with the tertiary amines Me_3N and Et_3N .

To test the hypothesis that a low-cost tertiary aliphatic amine base is able to activate glycerol for further reaction with CO_2 , we selected the triethylamine (Et_3N , TEA) to experimentally investigate its behavior in the reaction between glycerol and CO_2 . From a practical perspective, TEA shows interesting properties because it is liquid with low vapor pressure (51.75 mmHg at 20 °C), water soluble (112 g L^{-1} at 20 °C), and it has a boiling point (bp. 89.3 °C) that would allow work up at room temperature [56,57].

3.2 Experimental studies: characterization of TEA-Gly- CO_2 reaction product

The reaction between CO_2 and glycerol (Gly) in the presence of Et_3N (TEA) was carried out in a system as represented in Fig. S1a. The product – named as **TEA-Gly- CO_2** – was prepared by bubbling CO_2 (20 mL min^{-1}) in a mixture of TEA and Gly with a 3:1 molar ratio at 30 (± 1) °C under magnetic stirring for 30, 60 and 120 min. At the end of each reaction time, the magnetic stirring and CO_2 flow were stopped, and two phases were observed, the lower phase containing the desired product and the upper phase containing the remaining base (Fig. S1b). We collected the product at different reaction times (30, 60 and 120 min) as well as before bubbling CO_2 (control experiment, 0 min), and analyzed them by ATR-FTIR, ^1H and ^{13}C NMR and TGA.

Fig. 1 shows the ATR-FTIR spectra of the starting reagents (TEA and Gly) and the TEA-Gly mixture (3:1) before and after bubbling CO_2 for 30, 60 and 120 min. The spectra of the **TEA-Gly- CO_2** product show a band at 3288 cm^{-1} assigned to the stretching

vibrations of O-H groups from glycerol. The protonation of TEA was associated with the appearance of a new band at 1635 cm^{-1} , due to the R_3NH^+ group. The band at 1287 cm^{-1} was assigned to the asymmetric stretching vibration mode of C-O-C from the carbonate formation. The bands at 1459 and 1395 cm^{-1} were associated with the asymmetric and symmetric stretching vibrations of COO^- from carbonate [58,59]. A weak band at 1728 cm^{-1} in the spectra of the **TEA-Gly- CO_2** product for all reaction times might be assigned to the C=O stretching mode due to bicarbonate species [58–60]. However, the theoretical calculations indicated that the bicarbonates are not stable in the presence of the bases. One alternative is to assign this band to the carbonate group (species **3**, Scheme 1) participating in intramolecular hydrogen bonds with the remaining hydroxyl groups of glycerol [61].

The spectra obtained in the reaction times 30, 60 and 120 min are all identical. The bands at 1728 and 1287 cm^{-1} , associated with C=O and C-O-C stretching vibrations, respectively, are absent in the mixture of TEA and Gly (3:1) (0 min). Also, the bands at 1459 and 1395 cm^{-1} due to the COO^- group were not observed in the mixture of TEA and Gly (3:1), indicating that there is not any formation of carbonate before bubbling CO_2 in the mixture, as expected.

(Insert Fig. 1)

To ensure that the bands assigned to the carbonate in the spectra of Fig. 1 were due to the reaction between CO_2 and the mixture of TEA and Gly (3:1), we measured the ATR-FTIR spectrum of the mixture TEA and Gly (3:1) after 120 min (**TEA-Gly-120min**),

without bubbling CO₂, under stirring and N₂ atmosphere, Fig. 2a. No band due C-O-C stretching vibrations of carbonate was detected. In addition, the absence of the band at 1635 cm⁻¹ due to the R₃NH⁺ group in the **TEA-Gly-120min** spectrum suggests that the base protonation occurs only in the presence of CO₂, indicating that TEA (pK_b = 3.25) might not be strong enough to deprotonate glycerol. Instead, the free electron pair from TEA is participating in an intermolecular hydrogen bond with glycerol and unavailable for the nucleophilic attack on the CO₂ molecule [19]. We also investigated the possibility for the reaction between glycerol and CO₂ in the absence of TEA, Fig. 2b. This was carried out by bubbling CO₂ through glycerol for 30, 60, 90 and 120 min. ATR-FTIR spectra of the samples were similar to the pure glycerol spectrum, indicating that there is no reaction between CO₂ and glycerol in the absence of TEA.

(Insert Fig. 2a-b)

¹H NMR spectra of the TEA and Gly mixture (3:1) before and after bubbling CO₂ for 120 min are shown in Fig. S2-S4. The signal assignments are in Table S1. ¹H NMR spectrum of the TEA and Gly mixture (3:1) (Fig. S2) before bubbling CO₂ shows a quartet at 2.45 ppm assigned to H4 and a triplet at 0.94 ppm due to H5 from TEA [62,63]. Two double doublets at 3.30–3.41 ppm are assigned to H1 and H3 of glycerol, and a multiplet at 3.45–3.48 ppm is due to H2 of glycerol. The O-H groups appear as a broad singlet at 4.21 ppm [64].

The ^1H NMR spectrum of the product **TEA-Gly- CO_2 -120min** (Fig. S3) shows three sets of multiplets in the range of 3.29–3.50 ppm, assigned to H1', H2' and H3' of glycerol. New multiplets in the range of 1.30–1.39 and 0.84–0.91 ppm are assigned to H4' and H5', respectively, of TEA after protonation, showing an upfield shift of these signals after bubbling CO_2 in the TEA-Gly mixture [65]. A broad multiplet at 4.14–4.16 ppm, Fig. S4, suggests an overlapping of the signals due to O-H of glycerol and N-H of protonated TEA [43]. The appearance of a multiplet at 7.66–7.70 ppm (Fig. S4) could be attributed to either the hydrogen of the bicarbonate group or to the O-H group of glycerol involved in an intramolecular hydrogen bond with carbonate. As the theoretical calculations indicate that only ammonia can form bicarbonate species, this signal is most probably due to the OH groups of glycerol involved in intramolecular hydrogen bonds.

The ^{13}C NMR spectra of the TEA-Gly mixture (3:1) before and after bubbling CO_2 for 120 min are shown in Fig. 3. The signal assignments are described in Table 2. For non-hydrogenated carbon atoms, the ^1H NMR in 2D ^1H - ^{13}C – Heteronuclear Multiple Bond Correlation (HMBC) spectra are shown in Fig. 4.

Signals at 45.7 and 11.5 ppm in the ^{13}C NMR spectrum of the TEA-Gly mixture (3:1) were assigned to C4 and C5, respectively, of TEA [62,63]. C1 and C3 of glycerol were related to the signal with the highest intensity at 63.0 ppm. The signal at 72.3 ppm was attributed to C2 of glycerol [44].

The ^{13}C NMR results (Fig. 3) indicate that part of glycerol did not react with CO_2 , resulting in a mixture of the product and the initial reagents. Carbon signals in the HMBC spectra were assigned based on the literature data for a similar system, Fig. 4 [54,57]. The ^{13}C NMR spectrum of **TEA-Gly- CO_2 -120min** (Fig. 3) shows signals at 38.1 and 10.5 ppm,

assigned to C4' and C5' of protonated TEA. These signals were assigned considering the correlations between H4' and H5', shown in Fig. 4b. The signal at 67.4 ppm was attributed to C1'/3' of glycerol after reaction with CO₂. This result, in addition to the signal at 166.7 ppm, due to the carbonyl of the carbonate, suggests the formation of monocarbonate [66]. Carbonate and bicarbonate species cannot be distinguished in this spectrum because of the fast proton transfer between them, in addition to the low intensity of the signal of the quaternary carbon. The concentration of the carbonate product after dilution in DMSO-*d*₆ may also influence the signal intensity [67,68]. Signals in the range of 131.6–128.4 ppm were associated with the carbon of CO₂ dissolved in the medium [66].

(Insert Fig. 3)

(Insert Table 2)

Fig. 4a shows the partial HMBC 2D NMR spectrum of **TEA-Gly-CO₂-120min**. The spectrum shows the carbon signal at 166.7 ppm attributed to carbonate species exhibits a long-range correlation with H1'/3' of glycerol at 3.29–3.40 ppm. A second correlation is related to the hydrogen signal of glycerol O-H at 4.14–4.16 ppm. This result suggests that the product formed is a C-1'/3' monocarbonate interacting via hydrogen bonds with the remaining hydroxyl groups of glycerol [61].

The partial HMBC 2D NMR spectrum of **TEA-Gly-CO₂-120min** (Fig. 4b) shows a correlation between H4' and H5' of protonated TEA at 1.30–1.39 and 0.84–0.88 ppm,

respectively, with C4' and C5' (38.1 and 10.5 ppm respectively), confirming that protonation of the base after bubbling CO₂ in the TEA-Gly mixture (3:1) resulted in an upfield shift of these carbon signals. The signals at 22.1–29.7 ppm, which appeared after protonation of TEA, could not be assigned.

(Insert Fig. 4a-b)

Fig. S5 shows the TGA curves of glycerol, TEA and the TEA-Gly mixture (3:1) before and after bubbling CO₂ for 60 and 120 min. In the TGA/DTA curves of **TEA-Gly-CO₂-60min** (Fig. 5a) and **TEA-Gly-CO₂-120min** (Fig. 5b) there are two main weight losses accompanied by two exothermic events. One weight loss is for the decomposition of glycerol, occurring in the range of 150–250 °C. The second one, in the range of 80–150 °C for **TEA-Gly-CO₂-60min** (23.0 %) and **TEA-Gly-CO₂-120min** (23.3%), is for CO₂ desorption. These comparable weight losses indicate that increasing the reaction time did not significantly improve CO₂ absorption in the TEA-Gly mixture. They correspond to 6.6 mol of CO₂ per kg of solvent (**TEA-Gly-CO₂-60min**) and 6.9 mol of CO₂ per kg of solvent (**TEA-Gly-CO₂-120min**), respectively. This suggests *ca.* 3:1 stoichiometric ratio between CO₂ and glycerol. However, the HMBC 2D NMR spectrum of **TEA-Gly-CO₂-120min** indicates that only monocarbonate species is formed. Most likely the excess of CO₂ in the TGA experiment comes from CO₂ dissolved in the TEA-Gly mixture, as dissolved CO₂ was also identified in the ¹³C NMR spectrum. For comparison purpose, a 30 % (w/w) monoethanolamine water solution has an absorption capacity of 3.0 mol CO₂ per kg of solution [69]. A ternary system composed by choline chloride, Gly and 1,1,3,3-

tetramethylguanidine (TMG) shows an absorption capacity of 2.4 mol of CO₂ per kg of solvent [70].

(Insert Fig. 5a-b)

4. Conclusions

Computation of a ternary combination of CO₂, glycerol and organic bases indicates that it is possible to select bases of intermediate strength which, instead of directly reacting with the CO₂ to form carbamates, they would preferentially activate glycerol, favoring formation of an organic carbonate. Particularly, we could identify that tertiary amines, such as trimethylamine and triethylamine (TEA) are strong enough to activate glycerol for reaction with CO₂, while they are not strong enough to directly react with CO₂. These bases can form an intermolecular hydrogen bond with the primary hydroxyl groups of glycerol, increasing the glycerol nucleophilicity and favoring the CO₂ capture. In addition, our results suggest that these weaker bases (as compared with guanidine, TBD, and DBU) are associated with less exothermic and exergonic reactions, pointing towards an easier reversible process (CO₂ desorption).

The CO₂ absorption experiments in a mixture of TEA and glycerol showed the formation of an organic carbonate, confirming the theoretical prediction. The amount of absorbed CO₂ is 6.6 ((TEA-Gly-CO₂-60min) and 6.9 ((TEA-Gly-CO₂-120min) mol of CO₂ per kg of solvent. Experimental optimization, for example changing the base and

reducing the medium viscosity, may lead to the development of a promising system for CO₂ capture.

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Scheme 1

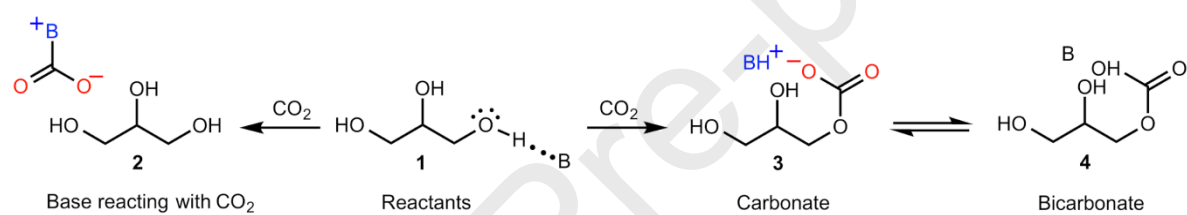


Figure 1

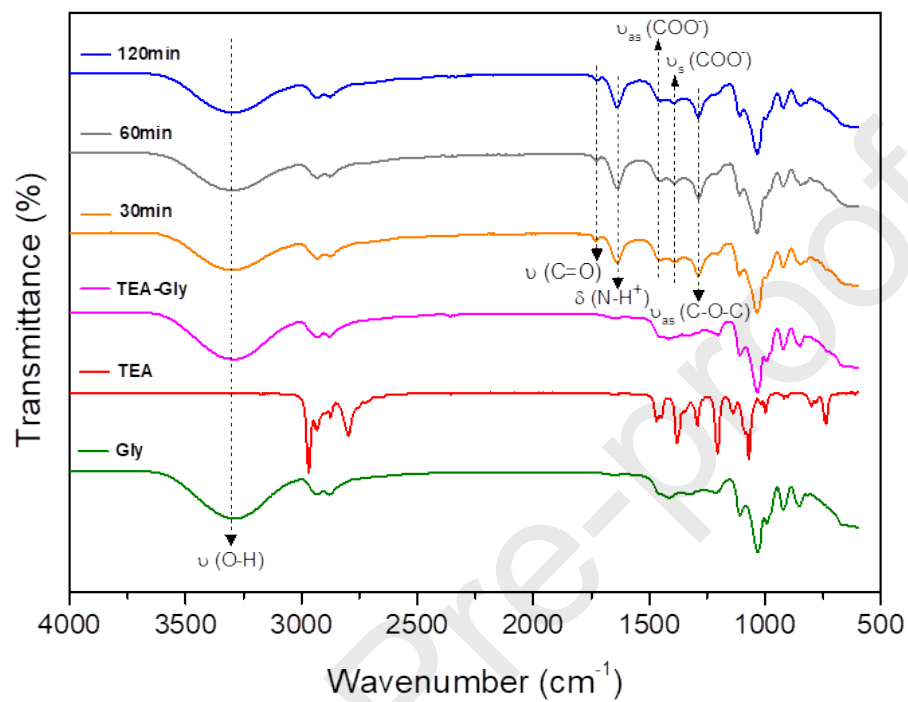


Figure 2

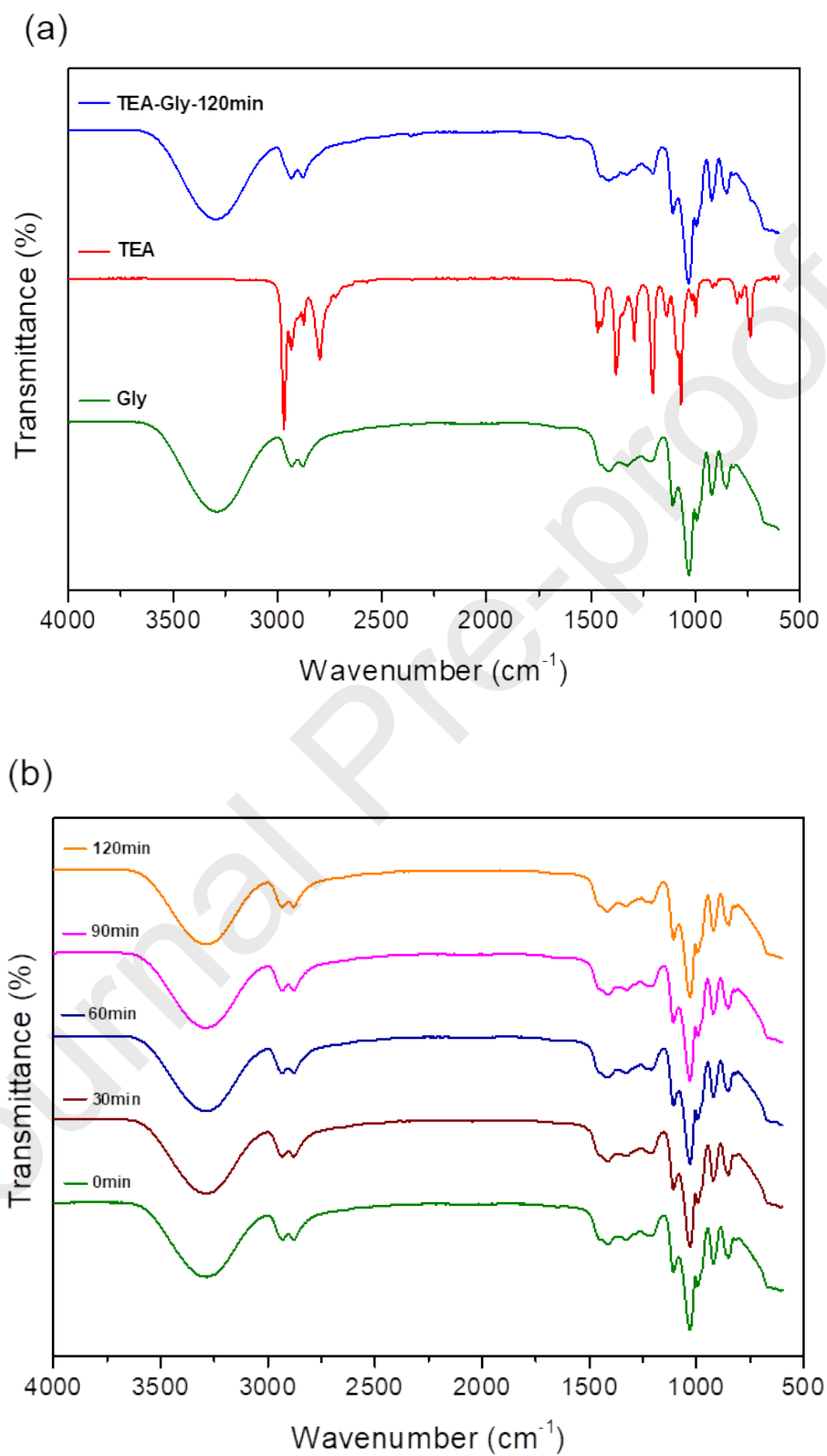


Figure 4

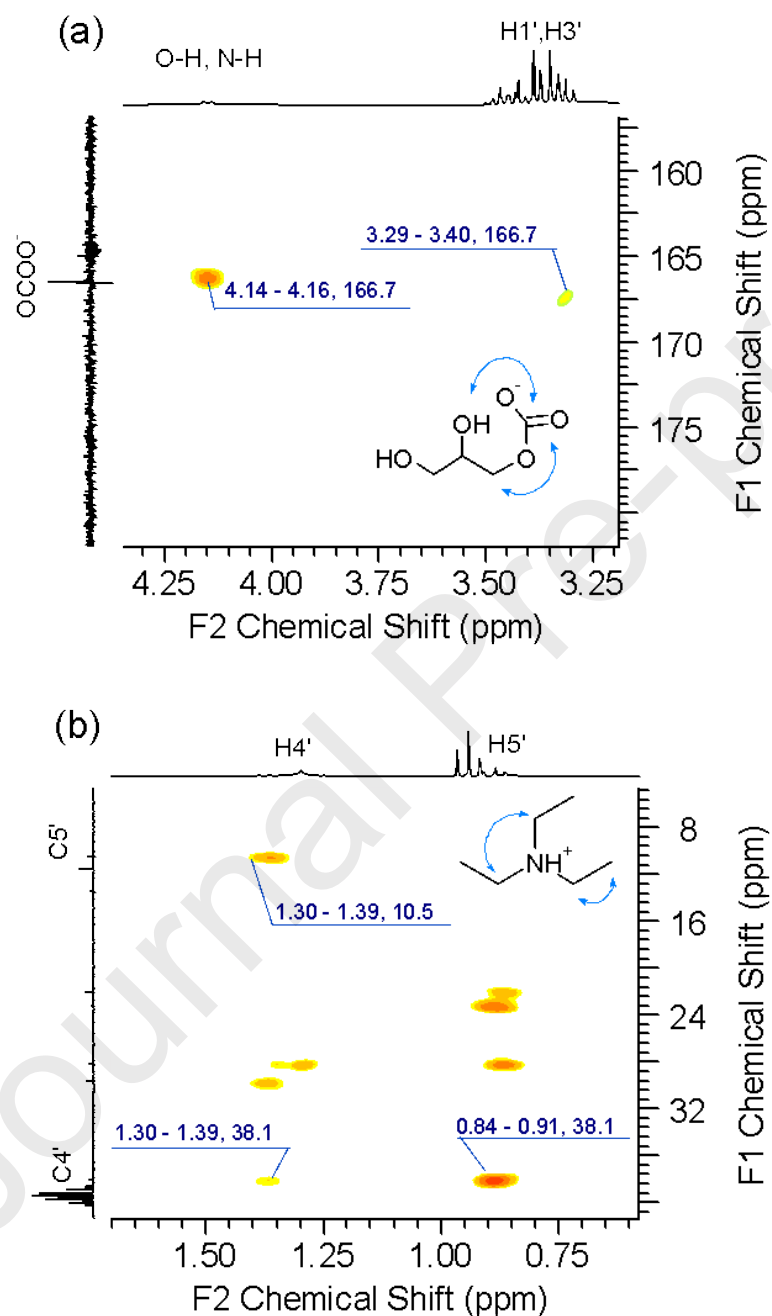
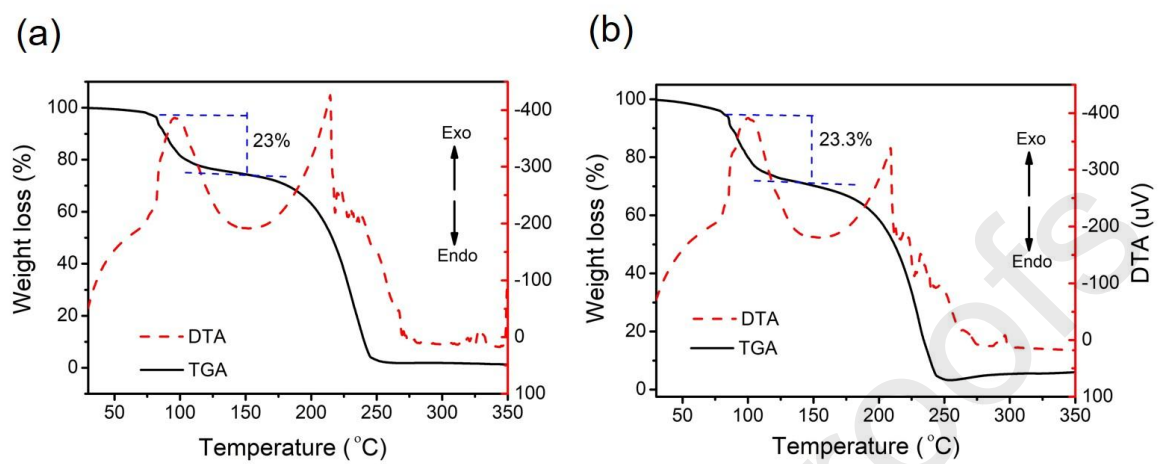


Figure 5



List of Scheme, Table and Figure Captions

Scheme 1. CO₂ capture by the system glycerol-base and the possible products **2**, **3** and **4**.

Table 1. Relative energies (in kcal mol⁻¹) of the products **2**, **3** and **4** relatives to the reactants **1** calculated with CAM-B3LYP/6-311++G(2d,2p).

Table 2. Main chemical shifts (ppm) and assignments observed in ¹³C NMR spectra showed in Fig. 3 (25 °C, 125 MHz, DMSO-*d*₆).

Figure 1. ATR-FTIR spectra of triethylamine (TEA), glycerol (Gly), TEA-Gly mixture (3:1) and the **TEA-Gly-CO₂** product formed after bubbling CO₂ for 30, 60 and 120 min.

Figure 2. (a) ATR-FTIR spectra of the TEA, Gly and TEA-Gly mixture after 120 min under stirring and N₂ atmosphere. (b) ATR-FTIR spectra of glycerol (0 min) and glycerol after bubbling CO₂ for 30, 60, 90 and 120 min.

Figure 3. ¹³C NMR spectra of TEA-Gly mixture (3:1) before (TEA-Gly) and after bubbling CO₂ for 120 min (**TEA-Gly-CO₂-120min**) (25 °C, 125 MHz, DMSO-*d*₆).

Figure 4. (a) Partial HMBC 2D NMR spectrum of **TEA-Gly-CO₂-120min** showing the carbon correlations of carbonate species. (b) Partial HMBC 2D NMR spectrum of **TEA-Gly-CO₂-120min** showing the C-H of protonated TEA correlations.

Figure 5. (a) TGA/DTA analyses of **TEA-Gly-CO₂-60min** product (b) TGA/DTA analyses of **TEA-Gly-CO₂-120min** product.

Table 1

Entry	Base	2		3	
		ΔH^{298}	ΔG^{298}	ΔH^{298}	ΔG^{298}
1	Guanidine	-12.8	-7.5	-12.2	-7.8
2	TBD	-12.0	-8.2	-16.3	-11.2
3	DBU	-6.4	-0.5	-13.0	-8.9
4	NH ₃	4.8	11.1	-1.6	4.1
5	MeNH ₂	0.9	6.4	-4.4	0.8
6	Me ₂ NH	-1.0	4.8	-5.8	-1.2
7	Me ₃ N	3.4	6.9	-6.2	-1.5
8	Et ₃ N (TEA)	5.7	8.0	-10.0	-6.1
9	EDA	3.0	5.8	-5.0	-0.9
10	DMEDA	6.0	8.0	-6.8	-2.9

Table 2

TEA-Gly		TEA-Gly-CO ₂ -120min	
#C	ppm	#C	ppm
1,3 Gly	63.0	1',3' Gly	67.4
2 Gly	72.3	2' Gly	72.3
4 TEA	45.7	4' TEA	38.1
5 TEA	11.5	5' TEA	10.5
-	-	CO ₂	128.4–131.6
-	-	OCOO ⁻	166.7

Highlights

- DFT calculations predict formation of carbonates from glycerol reacting with CO₂.
- Tertiary alkylamines may activate glycerol for reaction with CO₂.
- Intermolecular hydrogen bond increases glycerol nucleophilicity.
- FTIR and ¹³C NMR and ¹H-¹³C HMBC spectra suggest formation of organic carbonate.