

# A Unified Approach to CO<sub>2</sub>–Amine Reaction Mechanisms

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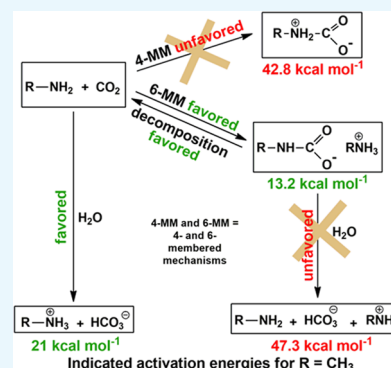


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**ABSTRACT:** A unified CO<sub>2</sub>–amine reaction mechanism applicable to absorption in aqueous or nonaqueous solutions and to adsorption on immobilized amines in the presence of both dry and humid conditions is proposed. Key findings supported by theoretical calculations and experimental evidence are as follows: (1) The formation of the 1,3-zwitterion,  $\text{RH}_2\text{N}^+-\text{COO}^-$ , is highly unlikely because not only the associated four-membered mechanism has a high energy barrier, but also it is not consistent with the orbital symmetry requirements for chemical reactions. (2) The nucleophilic attack of CO<sub>2</sub> by amines requires the catalytic assistance of a Brønsted base through a six-membered mechanism to achieve proton transfer/exchange. An important consequence of this concerted mechanism is that the N and H atoms added to the C=O double bond do not originate from a single amine group. Using ethylenediamine for illustration, detailed description of the reaction pathway is reported using the reactive internal reaction coordinate as a new tool to visualize the reaction path. (3) In the presence of protic amines, the formation of ammonium bicarbonate/carbonate does not take place through the widely accepted hydration of carbamate/carbamic acid. Instead, water behaves as a nucleophile that attacks CO<sub>2</sub> with catalytic assistance by amine groups, and carbamate/carbamic acid decomposes back to amine and CO<sub>2</sub>. (4) Generalization of the catalytic assistance concept to any Brønsted base established through theoretical calculations was supported by infrared measurements. A unified six-membered mechanism was proposed to describe all possible interactions of CO<sub>2</sub> with amines and water, each playing the role of a nucleophile and/or Brønsted base, depending on the actual conditions.



## INTRODUCTION

The increasingly rapid development of amine-based adsorbents for the removal of CO<sub>2</sub> from large point sources or via direct air capture to mitigate the greenhouse gas effect is currently close to commercial-scale implementation. Although many practical issues are yet to be fully addressed such as oxidative degradation and other deactivation processes,<sup>1</sup> there has been significant progress in fundamental understanding of CO<sub>2</sub>–amine interactions under a variety of adsorption conditions.<sup>2,3</sup> A similar effort is being deployed for the development of viable amine absorption technologies for CO<sub>2</sub> capture.<sup>4</sup>

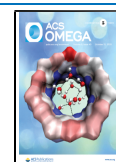
The main species actually detected upon the interaction of CO<sub>2</sub> with supported amines or amine solutions are strikingly similar. In a series of reports, Kortunov et al.<sup>5–8</sup> applied in situ <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) to systematically investigate the chemistry of CO<sub>2</sub> absorption under a wide range of conditions, including different temperatures and pressures. They studied a variety of amines and promoters, in both aqueous and nonaqueous solvents. Depending on the prevailing conditions, the following species were detected in different proportions: ammonium carbamate, carbamic acid, and carbonate/bicarbonate. Only ionic species occurred in aqueous solutions, whereas carbamic acid was detected in particular in polar nonaqueous solvents.<sup>8</sup> Likewise, CO<sub>2</sub> adsorption over supported amines generates carbamic acid and alkylammonium carbamate and/or bicarbonate, depending

on the amine loading and the adsorption conditions.<sup>9</sup> Such species were characterized mostly by Fourier transform infrared (FTIR)<sup>10–16</sup> and <sup>13</sup>C solid-state NMR,<sup>17–20</sup> and to a lesser extent, <sup>15</sup>N NMR<sup>21,22</sup> and X-ray diffraction.<sup>23</sup> They are typically stabilized through hydrogen bonding with other species, including amines, water, and hydroxyl groups.<sup>18–20,23–25</sup> In addition to proton transfer (vide infra), hydrogen bonding plays a critical role in CO<sub>2</sub> binding, providing additional stability to both products and reaction intermediates, thus lowering the energy barriers.<sup>26</sup> Furthermore, the nature of the chemical species formed and the amine efficiency, that is, the CO<sub>2</sub>/N ratio, were found to depend on the surface density of amine groups.<sup>16,19,24,27</sup> Although the formation of alkylammonium carbamate is often dominating under dry conditions, Cendak et al.<sup>19</sup> found that at low surface density, supported amines give rise mainly to carbamic acid, whereas at high density, the formation of alkylammonium carbamate prevails. Carbamic acid was also demonstrated to occur in the absence of moisture, on primary amine-bearing metal–organic

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**Table 1.** Activation Energy  $E_a$  and Free Gibbs Energy  $\Delta_r G^*$  in kcal mol<sup>-1</sup> for the Reaction Involving CO<sub>2</sub> and Several Amines under Dry and Wet Conditions in the Gas State and in the Presence of CCl<sub>4</sub> and H<sub>2</sub>O Solvents

		CH <sub>3</sub> NH <sub>2</sub>	H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	CH <sub>3</sub> NH <sub>2</sub> /CH <sub>3</sub> NH <sub>2</sub> <sup>a</sup>	CH <sub>3</sub> NH <sub>2</sub> /H <sub>2</sub> O <sup>a</sup>	CA <sup>b</sup> + H <sub>2</sub> O	H <sub>2</sub> O/CH <sub>3</sub> NH <sub>2</sub> <sup>a</sup>
$E_a$	gas	42.8	26.5	13.2	16.5	47.3	21.0
$\Delta_r G^*$	gas	44.8	32.6	25.9	27.7	55.4	18.5
	CCl <sub>4</sub>	41.8	23.4	16.7	24.7	54.9	20.5
	H <sub>2</sub> O	31.3	5.2	2.4	15.1	53.1	9.4

<sup>a</sup>The first compound is the nucleophile (Lewis base), and the second compound is the assisting species (Brønsted base). <sup>b</sup>CA designates carbamic acid formed by the addition of methylamine and CO<sub>2</sub>.

frameworks,<sup>21</sup> or other hydrophobic media.<sup>23</sup> In contrast, under humid conditions, carbamate and bicarbonate were found to be the dominating species.<sup>21,24</sup>

With regard to the reaction mechanism, based on the nature of the products and their evolution, Kortunov et al.<sup>5</sup> surmised that the first step is a nucleophilic attack of CO<sub>2</sub> carbon by amine (Lewis base), leading to zwitterion RH<sub>2</sub>N<sup>+</sup>–COO<sup>–</sup>, which will be referred to as 1,3-zwitterion, where 1 and 3 indicate the positive and negative centers, respectively. Depending on the actual conditions, the 1,3-zwitterion may undergo an intermolecular proton transfer with another amine (Brønsted base) to form ammonium carbamate<sup>5</sup> or an intramolecular hydrogen transfer to afford carbamic acid.<sup>8</sup> As for water, it may also behave as a nucleophile, reacting with CO<sub>2</sub> to afford carbonic acid, which in turn reacts with amine to generate carbonate/bicarbonate.<sup>5,6</sup> It may also hydrate the carbamate anion to form carbonate/bicarbonate, releasing one amine molecule for further reaction with CO<sub>2</sub>.<sup>5,7</sup> As in amine solutions, the formation of 1,3-zwitterions during CO<sub>2</sub> adsorption over supported amines was often mentioned but never observed.<sup>13,15,28</sup>

Parallel to the experimental work, theoretical studies were conducted to unravel the nature of adsorbed species and elucidate the CO<sub>2</sub> capture mechanism by supported amines in the presence and absence of moisture.<sup>10,13,14,25,28–31</sup> Didas et al.<sup>10</sup> and others<sup>14,28,30,31</sup> demonstrated that the energy barrier for the formation of carbamic acid using two amine molecules per CO<sub>2</sub> (ca. 16 kcal mol<sup>-1</sup>) was much lower than that for the one-to-one reaction (ca. 40–50 kcal mol<sup>-1</sup>). Presumably, one amine acting as a nucleophile (Lewis base) attacks the CO<sub>2</sub> carbon, whereas the other (Brønsted base) facilitates the proton transfer/exchange. There is evidence that surface hydroxyl groups<sup>25,29</sup> and water molecules<sup>25,32</sup> are also capable of assisting the proton transfer process.

Nonetheless, despite the apparently simple species involved and decades of effort, the mechanisms of CO<sub>2</sub> interaction with amines, whether immobilized or in solution, are still a matter of debate. For example, 1,3-zwitterions introduced since the 1960s<sup>33,34</sup> have been mentioned repeatedly in the literature but never detected, and their involvement in CO<sub>2</sub>–amine interactions has been controversial. Numerous kinetic and computational arguments were put forward both in favor<sup>34,35</sup> and against<sup>28,36,37</sup> the formation of 1,3-zwitterions in aqueous amines. Alternatively, other investigations pointed out that the nucleophilic attack of CO<sub>2</sub> carbon by the amine is *assisted* or *catalyzed* by another species such as amine, water, or OH groups, playing the role of a Brønsted base to achieve the proton transfer/exchange required for the formation of ion pairs, such as ammonium carbamate,<sup>5,10,25,28,29</sup> obviating the intermediacy of 1,3-zwitterions. This intermolecular mechanism is strongly supported by kinetic<sup>36,37</sup> and theoretical<sup>28,29,38</sup> data.

The main questions to be addressed in the current work are as follows: How likely does carbamic acid or ammonium carbamate form through the intermediacy of a 1,3-zwitterion? Does the formation of ammonium bicarbonate/carbonate involve the reaction of water with CO<sub>2</sub> or the hydrolysis of carbamate species? Is there a unified mechanism for the interaction of CO<sub>2</sub> with amines and water, whether in solution or at the solid–gas interface? Accordingly, the objectives of the current work are threefold: (i) provide theoretical and experimental evidence that the mechanisms of CO<sub>2</sub> reaction with protic amines under different conditions, including adsorption under dry or humid conditions, and absorption in aqueous or organic solvents take place through a six-membered mechanism, without the intermediacy of the widely reported 1,3-zwitterion; (ii) demonstrate based on theoretical and experimental data that the formation of bicarbonate/carbonate occurs via an amine-assisted nucleophilic attack of CO<sub>2</sub> by water, instead of the highly popular carbamate hydrolysis; and (iii) establish a unified mechanism for all interactions of CO<sub>2</sub> with amines and water, each playing the role of a nucleophile and/or Brønsted base, depending on the actual conditions.

Our calculations dealt primarily with CO<sub>2</sub>–amine–water interactions in the gas state to uncover the intrinsic reactivity of these species. Solvent effects were also discussed using water and CCl<sub>4</sub> as representative polar and nonpolar solvents. The most salient theoretical findings were further supported by specifically designed FTIR and NMR experiments.

## ■ EXPERIMENTAL SECTION

**Modeling Methods.** Density functional theory (DFT) calculations were carried out using the Gaussian 09 software package<sup>39</sup> associated with B3LYP,<sup>40</sup> M06-2X,<sup>41</sup> and PW6B95<sup>42</sup> functionals. All the obtained data are listed in Table 1 and Table S1. As seen, all three methods gave consistent results with no systematic departure from each other. As shown in Table S1, a full optimization at the MP2 level and single point calculations at the CCSD(T)//B3LYP/6-311++G(d,p) level in the gas phase for amine–CO<sub>2</sub> reaction fitted better with the B3LYP results. Hence, the discussion will be based primarily on data of the latter functional. Optimization of geometrical structures of the reactants, transition states, and products was performed using the 6-311++G(d,p) basis set.<sup>43</sup> This included polarization and diffuse functions, which are required for investigating dipolar species. All stationary points of the potential energy surface (PES) corresponded to the local minima, all with real vibrational frequencies, or to transition states characterized by only one imaginary frequency. Energy, force, and internal coordinate profiles were obtained from the intrinsic reaction coordinate (IRC) analysis.<sup>44–46</sup> To include solvent effects, if any, additional full optimization calculations were carried out using water and CCl<sub>4</sub> as representative polar and nonpolar solvents, respectively. The polarizable continuum

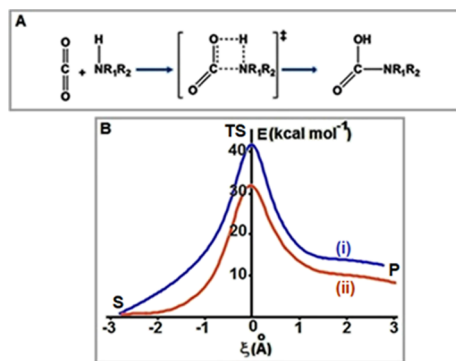
model<sup>47</sup> was used with the three abovementioned functionals B3LYP, M06-2X, and pw6b95. To discuss solvent effects, we used the free Gibbs activation energy, which stems from statistical thermodynamics, rather than the activation energy, which is more appropriate to discuss molecular properties.

**Preparation of Adsorbents.** Propylamine-grafted silica was prepared as described elsewhere.<sup>48</sup> A predried Q-10 CARIAC silica (Fuji Silysia, Japan) support of 1 g was dispersed in 40 mL of toluene in a 100 mL two-neck round bottom flask immersed in an oil bath. After 30 min of stirring at room temperature, 0.3 mL of distilled water was added while stirring continued for 30 min. The temperature of the mixture was then raised to 100 °C. After 30 min, 2 mL of (3-aminopropyl)trimethoxysilane was added, and the mixture was kept under reflux for 2 h. The flask was cooled down to room temperature, and the material was filtered, washed with toluene and ethanol, and dried under vacuum at 60 °C for 5 h. The amine content was determined by decomposition using a thermogravimetric analyzer. The material was first heated in N<sub>2</sub> up to 800 °C at 10 °C/min and then in air at 800 °C for 10 min. The amine content based on the weight loss beyond 200 °C was 4.4 mmol/g.

**FTIR Spectroscopy.** In situ FTIR experiments were specifically designed to demonstrate that CO<sub>2</sub> adsorption on immobilized amines under humid condition takes place through a six-membered mechanism assisted by water (here D<sub>2</sub>O). Measurements were carried out on a Nicolet 6700 spectrometer equipped with a mercury cadmium telluride (MCT) detector, using ambient air as the background (Figure S1). Self-supported translucent wafers of about 5 mg and 1 cm diameter were placed inside a stainless-steel IR cell equipped with CaF<sub>2</sub> windows. The sample was thermally pretreated in N<sub>2</sub> at 120 °C for 2 h to remove any adsorbed species. Then, the cell was allowed to cool down to room temperature, and a spectrum was recorded through 128 scans under nitrogen. The material was exposed for 15 min to N<sub>2</sub> saturated in D<sub>2</sub>O at 20 °C, then regenerated at 120 °C, and a spectrum was recorded. A similar experiment was carried out replacing N<sub>2</sub> by 15% CO<sub>2</sub>/N<sub>2</sub>.

## RESULTS AND DISCUSSION

**Reaction Mechanism for Carbamate/Carbamic Acid Formation. Four-Membered Mechanism.** Figure 1A shows



**Figure 1.** Direct formation of carbamic acid: (A) four-membered mechanism and (B) energy profile for the reaction shown in (A): (i) in the gas state and (ii) in the presence of water as solvent. S indicates the substrate (amine), TS is the transition state (1,3-zwitterion), and P is the product (carbamate/carbamic acid).

the reaction mechanism of a primary or secondary amine with CO<sub>2</sub>, confirming that this is a single-step reaction, with the 1,3-zwitterion being a transition state TS. Calculations in the gas state showed that carbamic acid, the ultimate product of the reaction, is obtained by a concerted elementary reaction through a single transition state with synchronous formation of C–N and O–H bonds. The energy barrier (Gibbs activation energy resp.)  $E_a$  ( $\Delta_r G^*$  resp.) for the four-membered mechanism outlined in Figure 1A was found to be 42.8 (44.8 resp.) and 40.0 (41.0 resp.) kcal mol<sup>−1</sup>, for primary and secondary amines (Table S2), respectively. Several authors reported high activation energy barriers of the order of 40–50 kcal mol<sup>−1</sup> for a 1:1 reaction between CO<sub>2</sub> and amines,<sup>10,14,28,30,31</sup> indicating that this mechanism is unlikely to occur.

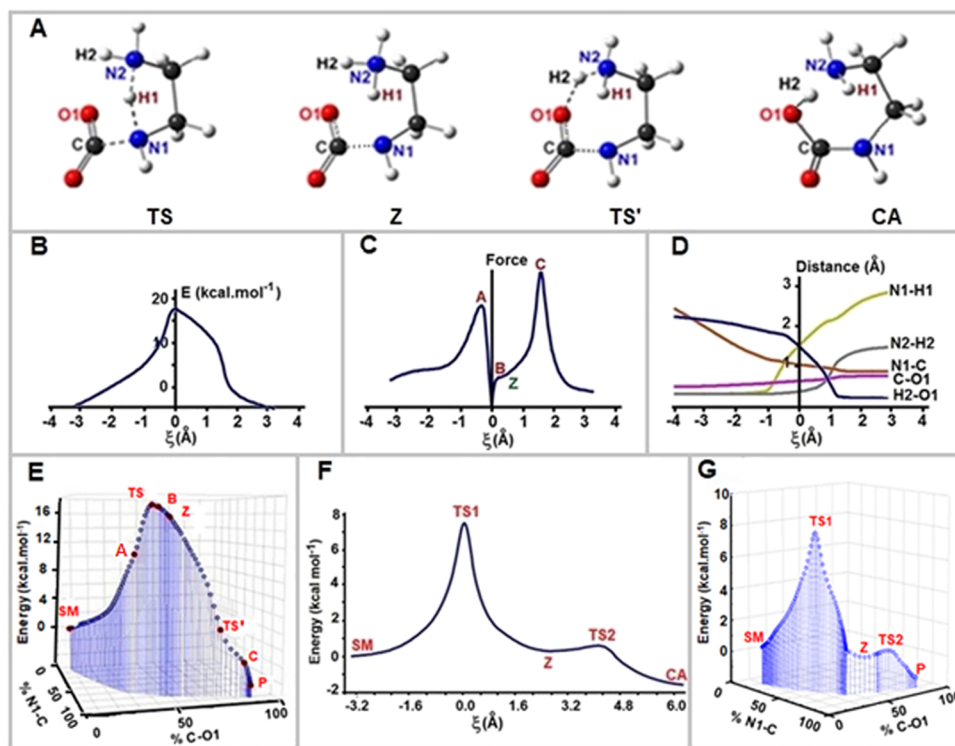
We also investigated the effect of CCl<sub>4</sub> and H<sub>2</sub>O solvents on the reaction of CO<sub>2</sub> and methylamine. In both cases, the activation energy was lower than that in the gas state (Table 1), the lowest being in the presence of water (Figure 1B). As shown in Table 1, the activation free energy for the four-membered mechanism of the CO<sub>2</sub>–methylamine reaction involving 1,3-zwitterions remained high in the presence of not only CCl<sub>4</sub> (41.8 versus 44.8 kcal mol<sup>−1</sup> in the gas state) but also even in water (31.3 kcal mol<sup>−1</sup>).

**Catalytic assistance** by a Brønsted base involving a six-membered mechanism may significantly lower the energy barrier.<sup>10,28,31</sup> Interestingly, this mechanism indicates that the hydrogen atom that binds to the oxygen atom does not originate from the same amine group whose nitrogen attaches to CO<sub>2</sub>. This is demonstrated below in three representative instances, based on theoretical and experimental arguments.

**Self-Assistance in CO<sub>2</sub> Adsorption over Diamines.** The reaction of CO<sub>2</sub> with ethylenediamine in the gas state shows that the catalytic assistance of a Brønsted base is a *requirement* rather than a convenient procedure to generate a low-energy transition state. Figure 2A depicts the optimized structures of the transition state TS, the 1,6-zwitterion Z, the quasi-transition state TS', and carbamic acid CA, corresponding to the CO<sub>2</sub> reaction with H<sub>2</sub>N–(CH<sub>2</sub>)<sub>2</sub>–NH<sub>2</sub>. Figure 2B shows the energy profile in the gas state of the carbamic acid formation obtained by the IRC option of Gaussian 09. The calculated activation energy barrier was 26.5 kcal mol<sup>−1</sup> (Table 1), and the two ends in this curve corresponded to the reactants and the expected carbamic acid product. The transition state TS is the outcome of the N1 atom approaching the CO<sub>2</sub> carbon atom C, and the hydrogen H1 leaving. Interestingly, this hydrogen does not approach the nearby O1 oxygen of CO<sub>2</sub> but it moves toward the other nitrogen atom N2, leading to the formation of an ammonium group. Notice that the transition state forms a six-membered ring as shown in Figure 2A and corresponds to an imaginary frequency of i926 cm<sup>−1</sup>. In TS, the H1 to N1 and N2 distances were 1.46 Å and 1.17 Å, respectively, while the H2–O1 distance was 2.09 Å. Moreover, a N1–C distance of 1.53 Å was close to the final bond length in carbamic acid, estimated to be 1.48 Å. Notice that similar calculations using diamines with up to 5 carbon chain spacers gave similar activation energies and mechanisms.

After completion, this process leads to a 1,6-zwitterion Z (Figure 2A). Unless the zwitterion is stabilized by polar species such as the solvent or surface OH groups, one hydrogen atom of the ammonium group, H2, is detached and binds asynchronously to the negatively charged oxygen (Figure 2A), giving rise to carbamic acid CA (Figure 2A). In the





**Figure 2.** CO<sub>2</sub> reaction with ethylenediamine: (A) calculated structures; (B) energy profile of carbamic acid formation in the gas state, (C) the corresponding force profile, and (D) variation of selected internuclear distances versus reaction coordinate in the gas state. (E) RIRC versus N1–C and C–O1 internuclear distances in the gas state expressed in terms of % change from reagents to final product carbamic acid; (F) energy profile of carbamic acid formation in water; and (G) RIRC versus % N1–C and % C–O1 in water. In figure (E–G), SM indicates the reactants associated with the supermolecule, P is the product (carbamic acid), Z is the 1,6-zwitterion, TS, TS1, and TS2 are transition states, A and B are the limits of the TS zone of influence, TS' is the quasi-transition state, and C is the start of the product finalization zone.

corresponding quasi-transition state TS' (Figure 2A), H2 was located at 1.16 and 1.39 Å from O1 and N2, respectively. It is clear that the six-membered mechanism stems directly from the CO<sub>2</sub> interaction with the two amine groups, without any external artifact. Therefore, the nitrogen and hydrogen atoms that add up to the carbonyl of CO<sub>2</sub> originate from two different amine groups. Using propylenediamine, Heldebrant et al.<sup>49</sup> provided spectroscopic evidence for the occurrence of 1,7-zwitterionic carbamate, consistent with the proposed self-assistance mechanism.

To elucidate the reaction mechanism, it is customary to consider the energy profile (Figure 2B), the force profile obtained as an RMS gradient norm (Figure 2C), and the variations of selected internal coordinates (Figure 2D) as a function of the intrinsic reaction coordinate. Considering the variations of pertinent internuclear bond distances such as N1–H1, N2–H2, and C–O1, the reaction progress can be described as depicted in Figure 2C. At the onset of the reaction, the energy starts to increase at coordinate ca. –1.59 Å, whereas the transition state TS zone of influence lies between the two maxima A and B located at coordinates –0.37 and 0.11 Å of the force profile. The species Z (Figure 2C) associated with the asymptotic behavior of the energy profile section corresponding to the transition state TS is located at coordinate 0.58 Å and has a 1,6-zwitterion structure (Figure 2A) as further confirmed by natural bond orbital (NBO) calculations.<sup>50</sup>

This localization was enabled by the newly introduced tool for investigating PESs referred to as reactive internal reaction coordinates (RIRCs).<sup>46</sup> A N1–C distance of 1.50 Å in the 1,6-

zwitterion represents the typical length of a single bond. The C–O1 distance increased from its original length of 1.22 Å in CO<sub>2</sub> to 1.26 Å in the 1,6-zwitterion. The third maximum, C, located at coordinate 1.59 Å (Figure 2C) corresponds to the transition state TS' (Figure 2A) controlling the transfer of proton H2 from N2 to O1, leading to carbamic acid (Figure 2A). Analysis of Figure 2D, which represents the evolution of the internuclear distances of active bonds, that is, those that break or form, shows clearly that the formation of carbamic acid involves two asynchronous processes. The 1,6-zwitterion formation stage ends with the N1–H1 bond being almost broken (equal to 1.8 Å) and N1–C bond being almost established (equal to 1.49 Å), just after the occurrence of the transition state TS. Furthermore, the N2–H2 bond begins to break up at coordinate 1.59 Å, while H2 approaches O1 to establish the O1–H bond.

Our work shows that the 1,6-zwitterion forms first as a long-lived active transitory species acting as an intermediate species in the formation of carbamic acid via an asynchronous process. It is usually named the hidden reaction intermediate (HRI). Being a transient species, the 1,6-zwitterion does not correspond to a local minimum, that is, to a metastable state, but its presence is associated with a flat region of the potential surface. Therefore, it is difficult to gain further insights into such species with the conventional quantum chemistry tools such as the energy profile or contour plot. To address this shortcoming, we developed an alternative methodology enabling the visualization of the reaction path versus two internal coordinates referred to as RIRCs.<sup>46</sup> Such coordinates often represent the distances associated with bonds that form

or break. The RIRC is a 3D representation of the reaction path (Figure 2E) independently from the PES. It provides a visual representation of the energy as a function of the internal coordinates, not the reaction coordinate. This representation is highly informative because internal coordinates are easier to apprehend than reaction coordinates. Coordinates  $x$  and  $y$  in the RIRC shown in Figure 2E correspond to the percent formation of the C–N1 bond and the percent cleavage of the  $\pi$  C=O1 bond, respectively. The 1,6 zwitterion is precisely located as it corresponds to an inflexion point in the reaction path (Figure 2E). This finding was made possible because the RIRC is a 3D representation as opposed to the 2D IRC.

As in the case of monoamine, the nonpolar aprotic solvent  $\text{CCl}_4$  did not affect the proposed mechanism for diamines. Its role was limited to decreasing the energy barrier (Table 1). However, in the presence of water as a solvent, the energy profile (Figure 2F) no longer reflects an asynchronous concerted mechanism with a single transition state but becomes a characteristic of a two-step reaction with two transition states TS1 and TS2, each corresponding to the transfer of a single hydrogen atom. Hence, the 1,6-zwitterion becomes an actual reaction intermediate that evolves instantaneously into carbamic acid because the second transition state is associated with an extremely low energy barrier.

The structure of 1,6-zwitterions together with the NBO analysis show that the C–N1 bond was completely established (Tables S3 and S4), the N2 nitrogen had three N–H bonds, consistent with an ammonium group, and O1 was negatively charged because it had three lone pairs, although partially conjugated with the C=O2  $\pi$  electrons. Consistently, the bond indices for C–N1, C–O1, and C–O2 as indicated by the corresponding Wiberg indices were 1.1, 1.3, and 1.5, respectively.

Figure 2G clearly shows the energy evolution as the percent formation of the C–N1 bond and the percent cleavage of the  $\pi$  C=O1 bond, respectively. The two reaction steps are well separated. It is seen that at the 1,6-zwitterion stage, the C–N bond was ca. 80% established, whereas the C–O1 bond was only 20% shorter than its final length in carbamic acid.

**Amine– $\text{CO}_2$  Reaction Assisted by Another Amine.** The foregoing discussion of the six-membered mechanism of  $\text{CO}_2$  interaction with a diamine was extended to single primary or secondary amines. Figure S2A shows the optimized structure of TS, ammonium carbamate, and the TS' that transforms directly into carbamic acid, using methylamine for illustration. This is the same mechanism as for the diamine, shown in Figure 2A. The calculated activation barrier of 13.2 kcal mol<sup>−1</sup> (Table 1) is consistent with literature data.<sup>10,51</sup> Notice that the activation free energies for  $\text{CO}_2$  reaction with ethylenediamine and methylamine assisted by another amine were similar (32.6 versus 25.9 kcal mol<sup>−1</sup>), whereas the corresponding activation energies were significantly different (26.5 versus 13.2 kcal mol<sup>−1</sup>). Because the activation energy may be regarded as the enthalpy contribution, it is concluded that the entropic contribution is about 50% for methylamine versus 19% for ethylenediamine, indicating that the discussion of reaction mechanisms should not rely solely on activation energies.

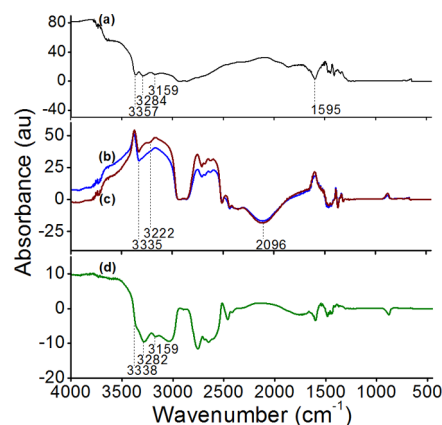
In all amine-containing media, the actual species detected by spectroscopic techniques such as NMR and FTIR depend on the environment, particularly on the occurrence of stabilizing species. As for  $\text{CO}_2$  absorption in amine solutions, it is expected that dipolar species such as 1,6-zwitterions or ionic

species such as alkylammonium carbamate will be stabilized by polar solvent molecules, for example, water,<sup>5</sup> whereas neutral species such as carbamic acid occur particularly in polar organic solvents that promote hydrogen bonding.<sup>8</sup> As for amine-functionalized silica, occurrence of ammonium carbamate versus carbamic acid is strongly dependent on the amine surface density.<sup>19,24</sup> At high density, the nucleophilic attack of  $\text{CO}_2$  is typically assisted by a nearby amine, leading to ammonium carbamate, often stabilized by hydrogen bonding,<sup>13,14,18,19</sup> whereas hydrogen-bonded carbamic acid is favored at low amine loading.<sup>14,19,24</sup>

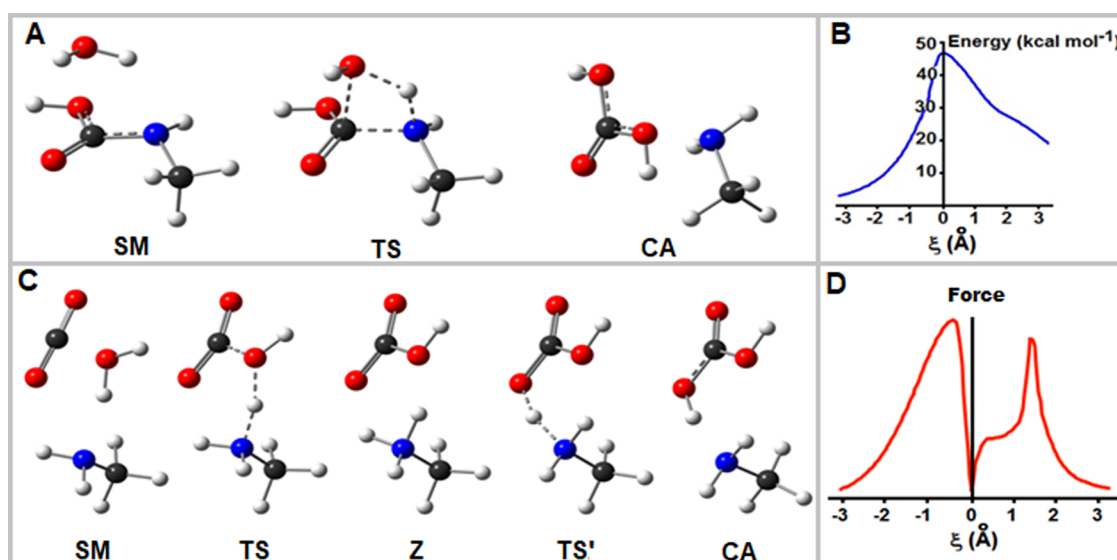
**Water-Assisted Formation of Carbamic Acid.** Another important question arises when  $\text{CO}_2$  adsorption takes place in the presence of moisture or in aqueous solvents is whether water assists the  $\text{CO}_2$ –amine reaction? Our calculations indicated that similar to amine, water may assist the formation of carbamic acid (Figure S2B). This is an elementary stage with simultaneous proton exchange between water and amine through a six-membered mechanism. The barrier was found to be 16.5 kcal mol<sup>−1</sup> (Table 1), indicating that from a kinetics point of view, the water-assisted pathway is less competitive than the amine-assisted formation of carbamic acid. Notice that in the presence of nonhindered protic amine aqueous solutions, the carbamate anion and ammonium cation form in equal amounts until amine depletion,<sup>5,52,53</sup> indicating that because such amines are stronger nucleophiles and stronger Brønsted bases than water, they play both roles.

As for solid-supported amines, because of the limited mobility of amine groups, it is surmised that water catalytic assistance becomes prominent for a low amine surface density, leading to carbamic acid or hydronium carbamate ( $\text{CO}_2/\text{N} = 1$ ), often stabilized by hydrogen bonding.<sup>15,19,24,25</sup> Notice that hydroxyl groups may play the same assisting role as water vapor.<sup>29</sup> This is consistent with experimental evidence as the enhancement of amine efficiency under humid conditions was found to be most pronounced for low amine surface coverage.<sup>24</sup>

**Experimental Evidence of Six-Membered Mechanism.** Catalytic assistance of a Brønsted base toward the formation of carbamic acid/carbamate was substantiated experimentally using  $\text{D}_2\text{O}$  as an assisting species. Figure 3 (Spectrum a) shows

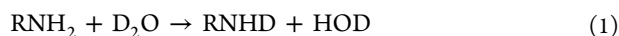


**Figure 3.** FTIR data in support of  $\text{CO}_2$ –amine reactions assisted by  $\text{D}_2\text{O}$ . (Spectrum a): thermally treated adsorbent, (Spectrum b): difference between the spectrum of the adsorbent exposed to  $\text{D}_2\text{O}$  and Spectrum a, (Spectrum c): difference between the spectrum of the adsorbent exposed to the  $\text{D}_2\text{O}/\text{CO}_2$  mixture and Spectrum a, and (Spectrum d): difference between Spectrum b and Spectrum c.



**Figure 4.** Carbonate/bicarbonate formation. (A) Calculated structures associated with hydrolysis of carbamic acid (CA); (B) corresponding energy profile; (C) calculated structures associated with the amine-assisted  $\text{CO}_2$  reaction with water; and (D) corresponding force profile.

the FTIR spectrum of propylamine-grafted silica after the initial thermal treatment. Figure 3 exhibits bands at  $3357\text{--}3159\text{ cm}^{-1}$  and  $1595\text{ cm}^{-1}$ , attributable to  $\text{NH}_2$  stretching and deformation, respectively. Difference spectra after exposure to the  $\text{CO}_2/\text{D}_2\text{O}$  mixture and  $\text{D}_2\text{O}$  vapor are shown in Figure 3 (Spectrum b and c), respectively. In both cases, at  $1595\text{ cm}^{-1}$  the characteristic band of  $\delta(\text{NH}_2)$  deformation disappeared, and two bands at  $3335$  and  $2096\text{ cm}^{-1}$  attributed to  $\nu\text{N}\text{--H}$  and  $\nu\text{N}\text{--D}$  stretching in  $\text{--NHD}$  developed. This indicates that an H/D exchange took place in both cases, but not to the same extent, because the different spectra are not strictly identical. Interestingly, as shown in Figure 3 (Spectrum d), subtracting spectrum 3b from 3c led to qualitatively the same spectrum as that of the starting material shown in Figure 3 (Spectrum a). This is a clear evidence that the H/D isotopic exchange due to  $\text{D}_2\text{O}$  is partial (eq 1) because spectrum 1c contains the characteristic bands of both  $\text{NH}_2$  and  $\text{NHD}$ , whereas upon regeneration of the material after exposure to  $\text{CO}_2/\text{D}_2\text{O}$  (eq 2), the deuteration was quantitative. This provides direct evidence that a D atom from  $\text{D}_2\text{O}$  was added to  $\text{CO}_2$  to form carbamic acid/carbamate (eq 2), which becomes bonded to the amine N atom upon regeneration (eq 3), leading to the observed  $\nu(\text{N}\text{--D})$  vibrations.



**Carbonate and Bicarbonate Formation. Carbamate Hydrolysis.** Numerous literature reports indicated the formation of ammonium bicarbonate/carbonate during  $\text{CO}_2$  capture by supported amines under humid conditions, mostly by inference, because the amine efficiency increases in the presence of moisture,<sup>48</sup> but in some cases, experimental<sup>11,20</sup> or theoretical<sup>13</sup> evidence was provided. Likewise, carbamate and ammonium bicarbonate were found to apparently occur stepwise in amine aqueous solutions.<sup>5,52,53</sup> It is widely believed that in the presence of primary and secondary amines, bicarbonate/carbonate originates from carbamate hydrolysis both in  $\text{CO}_2$  absorption or adsorption, mostly, because

bicarbonate/carbonate is observed<sup>5</sup> or presumed to occur<sup>54</sup> after the formation of ammonium carbamate. Hence, we investigated this process by optimizing the structures of the compounds involved and the transition state. As shown in Figure 4A, the formation of carbonic acid from carbamic acid (or bicarbonate from carbamate) follows a concerted one-step mechanism. The transition state is characterized by the simultaneous breakage of the O–H bond, elongation of the carbamic acid C–N bond, and nucleophilic attack of the  $\text{CO}_2$  carbon by water oxygen. Notice that the formation of carbonic acid is concerted but asynchronous, that is, the proton from  $\text{H}_2\text{O}$  attaches to nitrogen before oxygen binds to the  $\text{CO}_2$  carbon. However, the calculated barrier of  $47.3\text{ kcal mol}^{-1}$  is very high. Even when assisted by another water molecule (Figure S3), the energy barrier associated with the six-membered mechanism remains as high as  $38\text{ kcal mol}^{-1}$ .

In line with our data, Matsuzaki et al.<sup>55</sup> reported activation energies of 41 and  $37\text{ kcal mol}^{-1}$  for nonassisted and water-assisted hydrolysis of monoethanolamine carbamate. The high energy barriers indicate that the formation of carbonic acid/bicarbonate by this route is highly unlikely. Moreover, based on literature reports,<sup>5,52,53</sup> it is clear that in the presence of aqueous solutions of protic unhindered amines (strong Lewis bases), the formation of bicarbonate/carbonate starts only after the quantitative formation of ammonium carbamate. It is thus intriguing that as long as ammonium carbamate is accumulating at the expense of amine, no bicarbonate/carbonate formed.

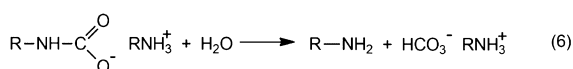
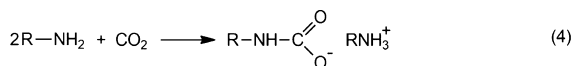
To gain further insights into the potential carbamate hydrolysis or the lack thereof, we exposed aqueous monoethanolamine to flowing  $\text{CO}_2$  and took samples before and after complete depletion of amine.  $^{13}\text{C}$  NMR analysis showed (Figure S4) that none of the species evolved over several days even though the sample solutions contained ammonium carbamate and water, indicating that the formation of bicarbonate/carbonate requires  $\text{CO}_2$ , but in the absence of significant amounts of protic amines. It is thus clear that the occurrence of bicarbonate/carbonate is not the direct result of carbamate hydrolysis. Similar argument can be made for  $\text{CO}_2$  adsorption over immobilized amines.<sup>54</sup>



### Amine-Assisted Formation of Ammonium Bicarbonate.

The formation of ammonium bicarbonate and carbonic acid due to the nucleophilic attack of CO<sub>2</sub> by a water molecule assisted by an amine group (Figure 4C) was investigated. The force profile (Figure 4D) is comparable to the already discussed CO<sub>2</sub> reaction with diamines (Figure 2C). Furthermore, the activation barrier was found to be about 21.0 kcal mol<sup>-1</sup> (Table 1). It is proposed here that in the presence of aqueous amines, the main route to bicarbonate/carbonate is the reaction of CO<sub>2</sub> and water.

In the presence of unhindered primary and secondary amines, the CO<sub>2</sub> reaction generates primarily ammonium carbamate (eq 4) because such amines are more basic and



more nucleophilic than water. However, provided that the CO<sub>2</sub> pressure is maintained, when the amine is almost depleted, ammonium bicarbonate/carbonate starts forming according to eq 5. This in turn leads to the gradual decomposition of ammonium carbamate (opposite eq 4). Notice that combining eq 5 and opposite eq 4 represents the apparent hydrolysis of ammonium carbamate (eq 6).

In the presence of tertiary amines<sup>5</sup> or weak amine nucleophiles such as sterically hindered amines,<sup>7,56</sup> water becomes a competitive nucleophile, attacking the electrophilic CO<sub>2</sub> and generating ammonium bicarbonate/carbonate concurrently with, or at the exclusion of, ammonium carbamate, depending on the severity of the steric hindrance. This mechanism is actually not limited to water. It was shown, for example, that in nonaqueous solvents, the hindered amino alcohol such as *N*-*t*But-ethanolamine reacts with CO<sub>2</sub>, exclusively through the hydroxyl group with assistance of the amine group, leading to 1,6-zwitterionic carbonate species.<sup>57</sup>

It is clear that, conceptually, CO<sub>2</sub> capture by amines whether in solutions or in solid adsorbents under dry or humid conditions follows similar reaction mechanisms, depending on the nature of the nucleophile (Lewis base), the assisting species (Brønsted base) and other stabilizing components. Figure 5 captures the mechanisms of all possible reactions of CO<sub>2</sub> with amines and water, depending on the actual conditions. As for CO<sub>2</sub> adsorption by supported nonhindered primary or secondary amines, the mechanism depends on the amine surface density and on whether the feed gas is dry or humid. At high amine loading under dry conditions, the nucleophilic attack of CO<sub>2</sub> by amines is primarily assisted by a neighboring amine (X = N, Y = N), leading to a 1,*n*-zwitterion (n > 3) or to alkylammonium carbamate, depending on whether the two

amines involved are linked or separate. At low amine loading, the nucleophilic attack of CO<sub>2</sub> by isolated amines may be assisted by hydroxyl groups (X = N, Y = O), leading to carbamic acid or hydronium carbamate. Under humid conditions, water may also assist the nucleophilic attack of CO<sub>2</sub> by amines (X = N, Y = O) to form hydronium carbamate or play the role of a nucleophile assisted by amines to form ammonium bicarbonate (X = O, Y = N) at the expense of carbamate. The latter mechanism applies also for tertiary and hindered amines, regardless of their surface density.<sup>20,58</sup>

The most common CO<sub>2</sub> absorption processes use nonhindered protic amines, where the amine plays both the role of a nucleophile and Brønsted base (X = N, Y = N),<sup>5</sup> leading to ammonium carbamate or carbamic acid, depending on existing stabilizing species. The assisting species could also be a non-nucleophile, strong Brønsted base, such as guanidines.<sup>6,8</sup> In aqueous solutions, when the amine is almost depleted, water acts as a Lewis base attacking CO<sub>2</sub> with the catalytic assistance of the trace amine (X = O, Y = N), leading to the formation of ammonium bicarbonate and the decomposition of carbamate, until equilibrium is reached. Such equilibrium was found to depend on the nature of the amine and the absorption conditions;<sup>5–7</sup> however, in the presence of increasingly hindered amines (i.e., weaker Lewis bases) or tertiary amines, water becomes a more and more competitive Lewis base, giving rise to increased formation of ammonium bicarbonate (X = O, Y = N) in comparison with carbamate.<sup>7</sup>

## CONCLUSIONS

In summary, the four-membered mechanism leading to 1,3-zwitterions often reported in the literature was found to be systematically associated with high activation barriers, greater than 30 kcal mol<sup>-1</sup>. Instead, a unified six-membered mechanism involving the nucleophilic attack of CO<sub>2</sub> by a Lewis base assisted by a Brønsted base for hydrogen transfer/exchange is proposed. Depending on the conditions, different Lewis bases such as amines, water, or alcohol and different Brønsted bases such as amines, water, guanidine, or OH groups may compete, leading to a variety of end-products. The role of nonpolar aprotic solvents such as CCl<sub>4</sub> was limited to slightly decreasing the reaction energy barriers but without any change in the reaction mechanisms, whether synchronous or asynchronous. However, in the presence of water as a solvent, the shape of the energy profiles associated with synchronous mechanisms remains unchanged, whereas for asynchronous mechanisms, the energy profiles indicate that they are no longer concerted with a single transition state but become a characteristic of two-step reactions.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c03727>.

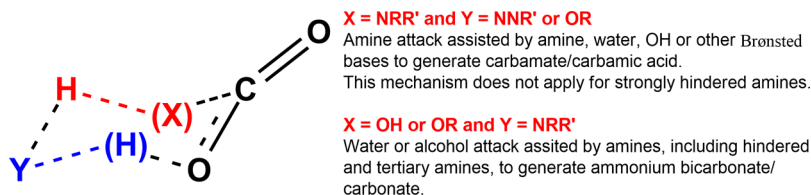


Figure 5. Unified schematic mechanism for CO<sub>2</sub>-amine-water interactions.

Schematic of FTIR setup (Figure S1); CO<sub>2</sub> reaction with a primary amine (Figure S2); hydrolysis of carbamic acid assisted by another water molecule (Figure S3); <sup>13</sup>C NMR spectra (Figure S4); activation energy and Gibbs activation energy (Tables S1–S2); selected bond lengths of the 1,6-zwitterion for ethylenediamine (Table S3); and optimized XYZ and total energy at B3LYP/6-311++G(d,p) (Table S4) (PDF)

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### Notes

The authors declare no competing financial interest.

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