

The Fate of a Zwitterion in Water from *ab Initio* Molecular Dynamics: Monoethanolamine (MEA)-CO₂

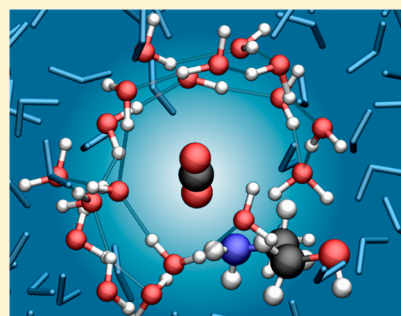
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S Supporting Information

ABSTRACT: Understanding the fundamental reactions accompanying the capture of carbon dioxide in amine solutions is critical for the design of high-performance solvents and requires an accurate modeling of the solute–solvent interaction. As a first step toward this goal, using *ab initio* molecular dynamics (Car–Parrinello) simulations, we investigate a zwitterionic carbamate, a species long proposed as intermediate in the formation of a stable carbamate, in a dilute aqueous solution. CO₂ release and deprotonation are competitive routes for its dissociation and are both characterized by free-energy barriers of 6–8 kcal/mol. Water molecules play a crucial role in both pathways, resulting in large entropic effects. This is especially true in the case of CO₂ release, which is accompanied by a strong reorganization of the solvent beyond the first coordination shell, leading to the formation of a water cage entrapping the solute (hydrophobic effect). Our results contrast with the assumptions of implicit solvent models.



INTRODUCTION

The need to develop innovative and/or improved technologies for the capture and sequestration of carbon dioxide (CO₂) has spurred a renewed interest in understanding the fundamental reactions involved in these complex multistep processes. In particular, the most mature technology for CO₂ capture, currently in use in the chemical industry, exploits a cyclic process, in which CO₂ is selectively and reversibly absorbed in an amine (aqueous) solution.¹ The related energy consumption is however too high, which explains the large empirical effort ongoing worldwide to reduce it, e.g., by proposing and screening new solvents.^{2–4}

Although there is undoubtedly need for a deeper understanding of the solute–solvent reaction mechanisms,^{5–9} attempts so far have been surprisingly limited and anchored to traditional and nonsophisticated methods; we still lack an understanding in terms of accurate modeling and simulations. For example, continuum models are still^{10–18} used to mimic water, namely, paradigms that are unable to describe the solute–solvent interaction at the molecular level and thus may fail to capture the role of the solvent in the reactions. In particular, the polarizable continuum model (PCM) has been successful in calculating solvation energies of a number of molecular systems in aqueous solutions.^{19–21} However, by missing geometrical degrees of freedom of the solvent, apart from a few added molecules, and including semiempirical parameters to adjust the size and shape of the molecular cavity,^{15,21} also PCM suffers from inherent limitations and may be inadequate to predict the development of a chemical reaction. It is indeed urgent to change strategy if progress has to be made in the field of carbon capture and sequestration with

input from theory and computations, and to exploit state-of-the-art advanced methods for the simulation of chemical reactions in aqueous solutions. The power and limitations of more simple efficient approaches^{21,22} will also become more clear.

The study we present here is intended to be a first step toward the understanding of the solute–solvent interaction in the amine solutions currently employed for carbon capture. It focuses on a carbamate, in its zwitterionic form, in water and characterizes two plausible routes for its decomposition: CO₂ release and deprotonation. As zwitterionic carbamate, we select the one formed by CO₂ with monoethanolamine (MEA; HOCH₂CH₂NH₂). This is the standard amine used in industrial small-scale applications and, as such, the mandatory reference for any search of a more cost-effective solvent. The zwitterion has long been postulated⁵ as a critical intermediate for the formation of a “stable” carbamate in amine solutions, also highly diluted. However, it has never been observed experimentally. The issue around the “stability” of the MEA–CO₂ zwitterion in water is thus a typical case for which atomistic simulations are required.

Our calculations were based on density-functional theory (DFT) molecular dynamics (MD) (Car–Parrinello MD)²³ augmented by metadynamics (MTD)²⁴ for sampling enhancement and for the reconstruction of the free-energy (FE) profile. We then used the umbrella sampling (US) method²⁵ especially to refine the evaluation of FE barriers. In this way, we could characterize quantitatively both dissociation reactions of the MEA–CO₂ zwitterion and thus start to investigate several so-far

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unanswered fundamental questions: (i) What is the specific role of water? (ii) Is the origin of the FE barriers enthalpic or entropic? (iii) To what extent are the two processes competitive? (iv) To what extent do these results depend on the exchange-correlation (xc) functional? In particular, ii is interesting also in a more extended perspective on the “stability” of zwitterionic conformers in water. Comparison will be drawn with the case of glycine, which is stable in water in its zwitterionic form and has been the subject of experimental investigation. Information on iv helps to monitor the validity of the predictions further. To this aim, we performed independent studies with two significantly different, but equally justified and commonly used, approximations for the DFT gradient-corrected xc functionals, PBE-D and BLYP-D, namely PBE²⁶ and BLYP^{27,28} with inclusion of Grimme’s empirical corrections for van-der-Waals interactions.^{29,30} Details on the computational scheme are given in the Supporting Information (SI).

RESULTS AND DISCUSSION

First, unbiased Car–Parrinello MD simulations were run at room temperature. Analysis of the trajectories accumulated over 15 ps showed that the zwitterionic carbamate visited three conformers, differing from each other in the position of the alcoholic tail relative to the carboxyl group (see SI, Table S1).

The one shown in Figure 1a was predominant (population about 70% in both PBE-D and BLYP-D); it is characterized by a larger separation between the alcoholic tail and the carboxylate group and by a dihedral angle OCCN fluctuating around -167° .

Figure 1b shows how the water molecules are distributed around the COO and NH₂ groups before MTD is switched on to drive the decomposition reactions. This figure refers to the PBE-D results; however, no relevant changes were found with BLYP-D (see SI, Figure S1).

Simple geometric coordinates could be used as collective variables for MTD simulations: the N–C distance for CO₂ release and the N–H distance for deprotonation. For the latter reaction, we also made an independent MTD simulation using the coordination number (CN) as a collective variable. This confirmed the previous results within 1 kcal/mol, the two variables being, as verified, strongly correlated (see SI, Figure S2).

Figure 2a illustrates the FE profile for the release of CO₂ obtained from MTD and US simulations at room temperature. The corresponding PBE-D FE barriers are the same within 1 kcal/mol, i.e., well within the accuracy of these calculations: 7 and 6 kcal/mol from MTD and US, respectively. BLYP-D MTD resulted in a FE of 8 kcal/mol, showing the independence on the xc functional for this quantity. As the CO₂ group moves away from the amine, the negative charge on it vanishes (Figure 2b) and the molecule becomes progressively linear as in the gas phase (bond angle from $\sim 140^\circ$ to 180°). An important reorganization of the water molecules takes place, accompanying the transformation of the COO(−) group to a nonpolar molecule, and ends up in a kind of “water cage” (Figure 2c). On the basis of the analysis of thousands of trajectories frames (see SI), we can provide a detailed description of the variation of the network of hydrogen bonds. The number of hydrogen bonds³¹ of CO₂ with the surrounding water molecules decreases from 3 ± 0.7 to 1 ± 0.7 in the TS to zero, and the average O_w–C distances increase by 0.5 Å. The water network changes significantly beyond the first

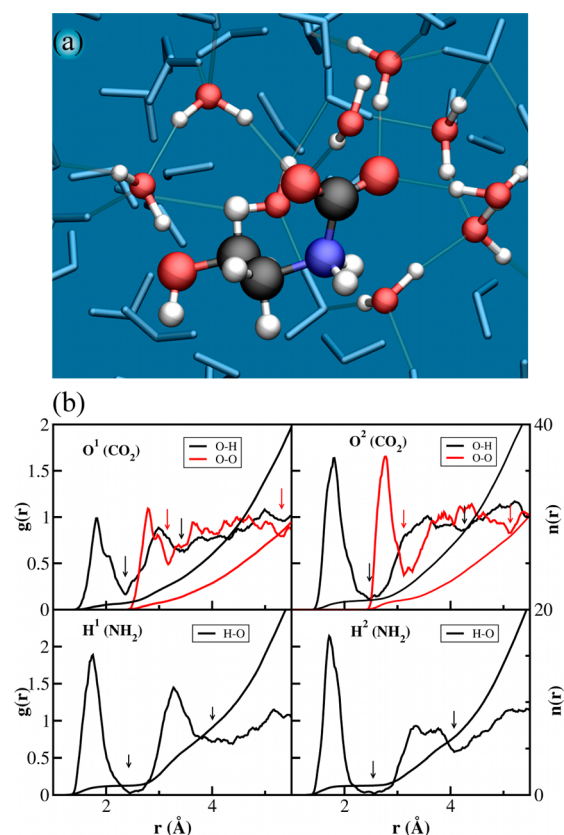


Figure 1. (a) Snapshot of the system: one zwitterion and 122 water molecules in a periodically repeated cubic cell. (b) Pair-correlation functions $g(r)$ and running integration numbers $n(r)$ showing the distribution of water molecules around the reactive sites (Os and Hs of the CO₂ and NH₂ groups). Arrows help to recognize the different “shells”: there are 1.2 (1.5) and 1.9 (1.9) Hs (Os) in the closest shell around O1 and O2, respectively. Two water molecules are hydrogen-bonded to the NH₂ site.

shell: the number of water–water H-bonds per molecule within the first shell increases from 0.4 ± 0.2 to 1 ± 0.1 , whereas it decreases from 2.3 ± 0.3 to 1.5 ± 0.2 between the first and second shell. The change in the orientation of the water molecules is in the variation of the angles θ and χ (tilt)³² defined in Figure 2d, on passing from the reactant (N–C distance: 1.5–1.7 Å) to the transition state (N–C distance: 2.3–2.5 Å; see also SI, Figure S3).

This behavior can be recognized as a manifestation of hydrophobic hydration as found to occur for small nonpolar solutes,^{32,33} in which the rearrangement of the solvent plays the major role in stabilizing it.

The effect of this strong water reorganization on the development of the reaction can be further seen in the entropy contribution to the FE barrier. We can derive it from a comparison of the FE barrier with an estimate of the enthalpy barrier obtained from the Kohn–Sham energies. The PBE-D value of the latter is 24 ± 3 kcal/mol, showing that the entropy term is indeed critical in reducing the reaction barrier.

For the deprotonation reaction, PBE-D and BLYP-D US simulations result in FE barriers of 6 and 8 kcal/mol, respectively (Figure 3a). In this case, the direct role of the solvent is evident, because one water molecule is the active agent of the reaction. In the process of accepting the proton, its H-bonds with the other water molecules reduce from 2.9 ± 0.7 to 2.2 ± 0.5 and strengthen (bond length decreasing from 1.82

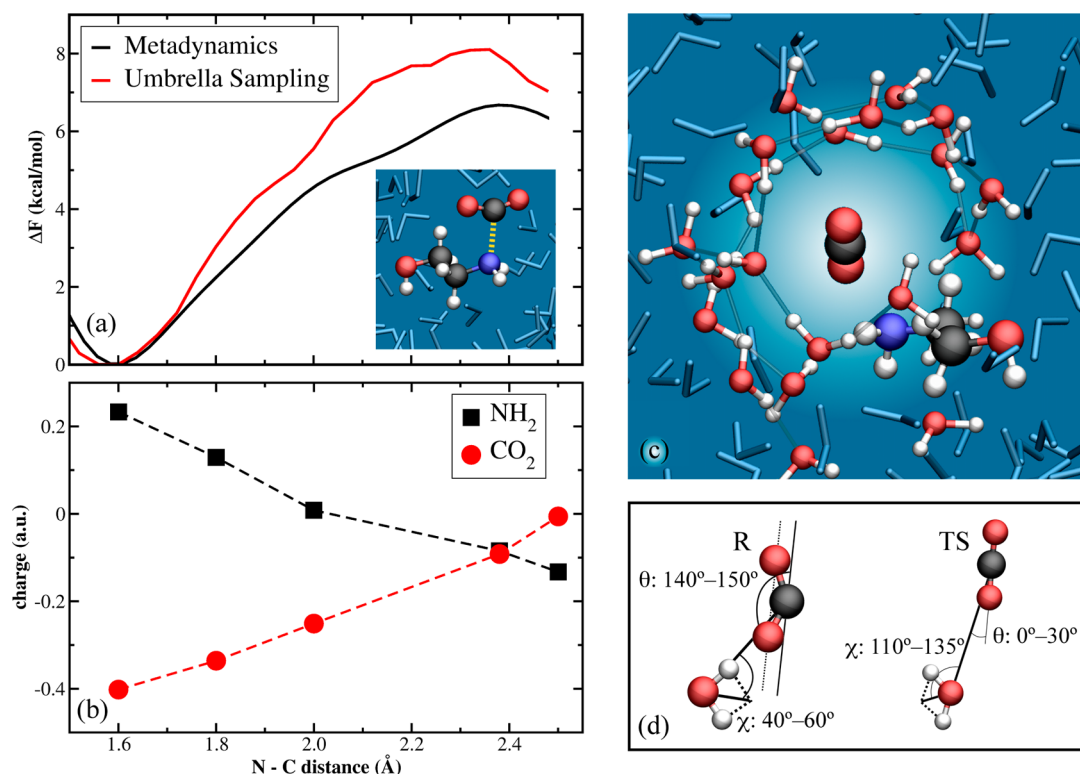


Figure 2. CO₂ release. (a) Free energy profile. The inset shows a snapshot of the system in the transition-state region. (b) Charge—calculated from a Mulliken population—at the two groups vs the N–C distance. (c) The “water cage”. (d) Angles describing the orientation of water molecules relative to CO₂ in the reactant (R) and the transition state (TS).

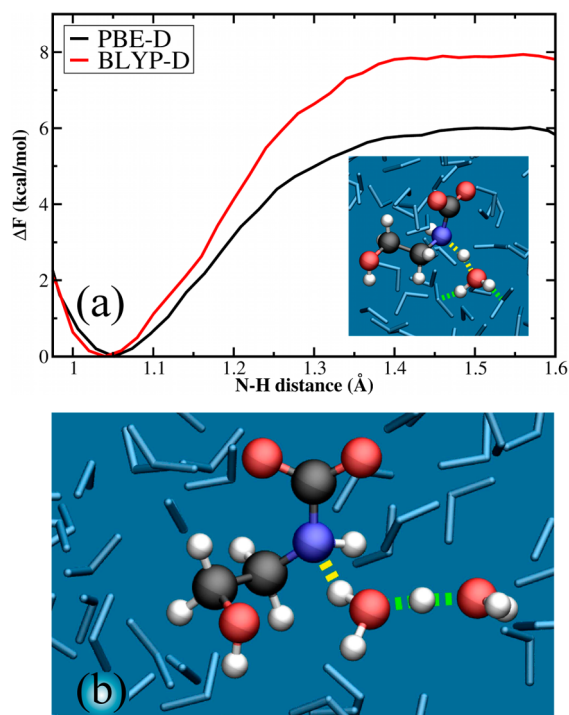


Figure 3. (a) Free-energy profile for deprotonation obtained with the umbrella sampling method. The inset shows a snapshot of the system in the transition-state region. (b) Snapshot showing proton diffusion in water.

Å to 1.62 Å). Therefore, the rest of the solvent does not behave as a passive spectator. The enthalpic barrier was estimated to be

13 ± 3 kcal/mol (PBE-D), which indicates again an important role of the entropy in reducing the reaction barrier.

Eventually, we observed the proton to diffuse through dissociation and subsequent reformation of the hydronium cation (Figure 3b). An accurate quantitative study of this process, as it was done for the water autoionization,³⁴ is beyond the scope of this paper.

One further question could be raised at this point: Do the two decomposition processes here considered mutually facilitate each other? Indeed, the opposite takes place. The loss of the COO group is accompanied by the shortening of both N–H bonds, from 1.06 Å to 1.02 Å on average; in turn, deprotonation induces a significant strengthening of the C–N bond, i.e., a bond-length decrease from 1.59 Å to 1.41 Å on average. This behavior along the reaction coordinates is shown in the SI (Figure S4).

Finally, as an independent validation of our calculations, we performed room-temperature MTD simulations of glycine in water, which is known to be more stable in the zwitterionic than in the neutral form, and for which both experimental data and previous DFT-MD simulations are available. We applied the same scheme and protocol used above, with the CN as a collective variable. The reaction investigated was the water-mediated intramolecular proton exchange leading to the transition from the zwitterionic to the neutral form. The PBE-D FE barrier calculated from the MTD reconstruction (see SI, Figure S4) was 12 kcal/mol. The experimental datum is 14.3 kcal/mol.³⁵ Our result closely agrees also with that of previous simulations³⁶ of a model hydrated glycine zwitterion with 52 water molecules, within BLYP and using the US procedure (12.7 kcal/mol). In contrast with the case of deprotonation of zwitterionic carbamate, the analysis of our

results for glycine showed that the entropy contribution to the FE barrier for proton intramolecular transfer is minor (10%) but still tends to decrease it.

CONCLUSIONS

In conclusion, our study of chemical reactions leading to the dissociation of a zwitterionic carbamate suggests that this is a metastable species in dilute aqueous solutions. Both CO₂ release and deprotonation are characterized by sizable free-energy barriers (6–8 kcal/mol). Being that those values are very close, these two routes are highly competitive. In both cases, the role of water, although different, is revealed to be crucial, and water molecules well beyond the first shell participate in the reaction. Therefore, the solvent cannot be represented either by an implicit model that ignores the specific solute–solvent interactions at the molecular level or by a hybrid scheme that includes only few explicit waters. Moreover, temperature effects cannot be neglected either. In particular, the entropic contribution is shown to be essential for a quantitative determination of the activation barriers and strongly reduces them. The use of an atomistic model with explicit solvent and of *ab initio* molecular dynamics is thus fully justified. However, given the slow dynamics of the hydrogen bonds, special care must be taken in the assessment of the statistical relevance of the results of liquid water simulations.

ASSOCIATED CONTENT

Supporting Information

Details on the calculations are reported and also further results for the structural characteristics of the various systems and for the glycine free energy profile. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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