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Molecular Dynamics Simulations of Proposed Intermediates in the CO_2 + Aqueous Amine Reaction

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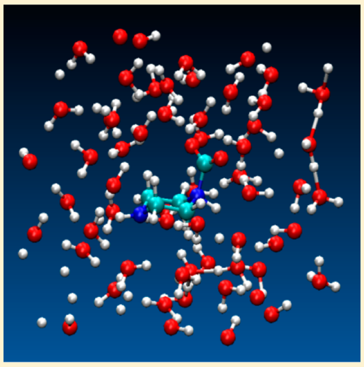
ABSTRACT: Ab initio molecular dynamics simulations of up to 210 ps have been performed on various aqueous intermediates postulated in the CO_2 + amine reaction, important for CO_2 capture. Observations of spontaneous deprotonation of aqueous carbamate zwitterions $R_1R_2NHCOO^{\pm}$ by bulk water (instead of additional amine, or via umbrella sampling) are reported apparently for the first time. Carbamic acid structures R_1R_2NCOOH were observed in some simulations, arising from zwitterions not via classical 1,3-H-shifts but via Grotthuss-style multiple-H^+ transfer pathways that involve bulk H_2O and require carbamate anions $R_1R_2NCOO^-$ as an intermediate stage along the way. H^+-bridging complexes, including not only Zundel ions $[\text{water}{\cdot}H^+{\cdot}\text{water}]^+$ but neutral carbamate complexes $[\text{carbamate}^-{\cdot}H^+{\cdot}\text{water}]$, were observed in simulation. These results should assist efforts in improving underlying mechanisms for kinetic modeling.



SECTION: Liquids; Chemical and Dynamical Processes in Solution

Aqueous amines are important for the separation of carbon dioxide from natural and flue gas streams.[1−4] Meaningful rate constant data for the important CO_2-capture reaction $CO_2 + HR_2N + B \rightarrow R_2NCOO^- + BH^+$ (B = any base, including H_2O; HR_2N = primary or secondary amine) requires agreement about the rate law used to fit to the experimental data. Two different mechanisms (the "zwitterion"[5−7] and "termolecular"[8,9] mechanisms, here Z and T) have resulted in competing formalisms and impede understanding, and a third mechanism (via acid intermediate, here A) was proposed in 2009.[10] Figure 1 summarizes the three.

Quantum chemistry studies of the CO_2 + amine reaction should be able to assist in clarifying the reaction mechanism. Unfortunately, traditional transition-state-optimization studies are susceptible to repeating the errors made during the study of the CO_2 + water reaction; there, the acid mechanism A was predicted by quantum chemistry models with limited numbers of water molecules,[11−14] but a molecular dynamics study[15] with complete and explicit solvation demonstrated (with metadynamics algorithms) that bicarbonate anion should form directly and the acid form would appear later in equilibrium with the anion (the "acid is last" idea). Therefore, our first step in trying to resolve the dispute regarding carbamate mechanisms is to report on our ab initio molecular dynamics (AIMD) simulations of hypothetical species postulated in the various competing mechanisms, to assess their relative importance. A followup full paper on the mechanisms is in preparation.

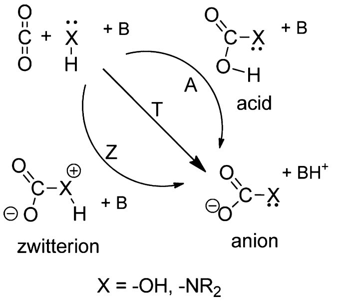


Figure 1. Debated carbamate-formation mechanisms ($X = -NR_2$, $B = HR_2N$, H_2O, OH^-) and analogous bicarbonate-forming mechanisms in water ($X = -OH$, $B = H_2O$, OH^-). Note that this scheme omits a dominant bicarbonate-forming mechanism $CO_2 + OH^-$, whose carbamate analogy would be $CO_2 + NR_2^-$, which is unlikely.

AIMD simulations are unfortunately limited in time scale (typically 10−100 ps), but potentially this could be long enough to see interconversion reactions in this system. Two other groups have already published results of simulations of this system, with different goals in mind. First, a 2011 study by Han et al.[16] presented results from four 6-ps simulations for 30 wt % aqueous MEA ($H_2NCH_2CH_2OH$), involving 16 H_2O molecules and two solute species in their simulation cell. Their {MEA,MEA}, {$MEAH^+$, $MEACOO^-$} and {$MEAH^+$, HCO_3^-} simulations showed stability (over 6 ps), while the {MEA, $MEAHCOO^{\pm}$} simulation achieved their goal of demonstrating rapid (0.4 ps) direct H^+ transfer from zwitterion to extra amine, forming $MEAH^+$ + $MEACOO^-$ with no further reaction. They did not test the zwitterion or acid forms for stability in bulk water. More recently a 2013 study by Guido et al.[17] did search for the fate(s) of an aqueous zwitterion, simulating a single

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Table 1. Summary of the Initial 8 ps Simulations

run	duration[a]	solute molecule	# H_3O^+	# H_2O	mol/L[b]	wt %[b]	results
A	8	CO_2	0	63	0	0	stayed as CO_2
B	8	$CO_2(OH_2)^{+-}$	0	62	0	0	0.02 ps: became CO_2
C	8	$CO_2(OH)^-$	1	61	0	0	stayed as anion
D	8	$CO(OH)_2$	0	62	0	0	4.7 ps: became anion
E	8	Me_2NHCOO^{+-}	0	60	0.86	4.0	stayed as zwitterion
F	8	Me_2NCOO^-	1	59	0.86	4.0	four H^+ exchanges[c]
G	8	Me_2NCOOH	0	60	0.86	4.0	6.5 ps: became anion

[a] Simulated time (ps). [b] Amine concentration. [c] H^+ exchanges with solvent occurred at t = 0.4 ps (became acid), 0.9 ps (became anion), 2.3 ps (became acid), and 5.3 ps (became anion).

Table 2. Summary of the Longer Zwitterion Simulations

run	duration[a]	solute molecule[b]	# H_2O	mol/L[c]	wt %[c]	t_{deprot}[d]	D_{anion}[e]	$D_{bridged}$[e]	D_{acid}[e]
H	100	Me_2NHCOO^{+-}	60	0.86	4.0	8.0	64.6	5.7	21.7
I trial 1	91	$MeNH_2COO^{+-}$	60	0.86	2.8	0.9	0.9	1.9	87.2
I trial 2	48	$MeNH_2COO^{+-}$	60	0.86	2.8	22.0	26.0	0	0
J	17	$MEACOO^{+-}$	59	0.86	5.4	0.6	16.4	0	0
K	210	$AMPCOO^{+-}$	59	0.83	6.6	148.1	0.4	0	61.5
L	110	$DEACOO^{+-}$	60	0.86	8.9	never	0	0	0
M	56	$PPZCOO^{+-}$	59	0.86	7.5	40.5	2.1	0.2	13.2
N	48	Me_2NHCOO^{+-} plus Me_2NH	57	1.72	8.1	28.0	20.0	0	0
O	27	$MeNH_2COO^{+-}$ plus $MeNH_2$	57	1.72	5.7	0.4	26.6	0	0

[a] Simulated time (ps). [b] MEA is $OHCH_2CH_2NH_2$; AMP is 2-amino-1-propanol; DEA is $(OHCH_2CH_2)_2NH$; PPZ is piperazine. [c] Amine concentration. [d] Time (ps) of zwitterion deprotonation. [e] Duration (ps) of particular postzwitterion state.

MEA carbamate zwitterion among 122 water molecules (3 wt % solution). In their study, a 15 ps unbiased simulation showed no reaction, and the ensuing application of umbrella sampling techniques to push the molecule out of the zwitterion potential well resulted in two pathways, (i) decomposition to CO_2 + amine, and (ii) deprotonation to anion, both characterized by free-energy barriers of 6−8 kcal mol^{-1} and thus competitive.

We hoped to build upon these two simulation studies by trying to observe "unaided" (i.e., no extra amine or umbrella sampling) interconversions, using longer simulations and trying six different amines. Evidence that such a study might be useful came from a second paper by Han et al.,[18] who reported in 2013 a liquid amine simulation which featured the conversions CO_2 → zwitterion (at 3.6 ps) → carbamate anion (at 16 ps), with the second step occurring via Grotthuss double-H^+ transfer through an OH group (NH···OH···N) to another MEA. Of our findings reported here, the most noteworthy are (i) the first reported observation of "unaided" proton transfer from carbamate zwitterion to bulk water, (ii) Grotthuss mechanisms for zwitterion → anion → acid, and (iii) the observance of a "Zundel" (H^+-bridged) neutral complex of carbamate anion with a water molecule.

The simulations were performed using the Vienna Ab Initio Simulation Package (VASP)[19,20] version 5.2.11 on the in-house supercomputer Dextrose. The following VASP specifications were used in all simulations: the potpaw GGA plane-wave basis sets;[21,22] standard precision (PREC=Normal); ENMAX = 350 eV; a Nosé thermostat for canonical (NVT) conditions[23] with 40 fs thermal oscillations (SMASS = 0), a Verlet velocity algorithm;[24] a temperature of 313 K (40 °C), and a time step of 1 fs. The sample cell was cubic in shape and replicated using periodic boundary conditions to mimic the bulk liquid. Cell width was 12.45 Å (except 12.59 Å for Run K), chosen to be appropriate for 64 H_2O molecules. The forces used in the simulations were computed with the PW91 approximation of density functional theory (DFT).[25]

Initial 8 ps Simulations. We began with short, exploratory 8 ps simulations of aqueous acids, zwitterions, anions, and CO_2, using for XH (Figure 1) the elementary amine Me_2NH (for carbamate formation) and, for comparison, H_2O (for bicarbonate formation). Starting geometries were built from "pseudo"-equilibrated water runs: (i) a pure water sample (64 water molecules randomly located) was simulated for 8 ps to moderate the temperature and allow a buildup of the hydrogen-bonding network, and the structure at 8 ps (Geometry 1) was then used to prepare Runs A-D (bicarbonate system) by substitution of solute for a small number of H_2O molecules; (ii) the 8 ps pure-water simulation was continued for an additional 24 ps, and its final structure (Geometry 2) was then used to prepare Runs E-G (carbamate system) by a similar substitution method. The results of Runs A-G are summarized in Table 1.

In runs A−D, for the better-known bicarbonate system (CO_2 + H_2O), only two interconversions were seen. In Run B, the hypothetical (not experimentally known) zwitterion decomposed "instantly" (<50 fs), in this case forming CO_2 + H_2O. In Run D, the carbonic acid lost H^+ to water after 4.7 ps, forming bicarbonate anion. Over infinite time, all of these runs would be expected to achieve a common equilibrium with interconversion of (primarily) $CO_2(aq)$, bicarbonate, and carbonic acid; $CO_2(aq)$ would feature most often based on known equilibrium constants. So, the A−D results are not unexpected. In runs E−G, for the carbamate system (CO_2 + Me_2NH), the anion and acid structures showed interconversions between those two forms (Runs F and G), while the zwitterion *stayed stable* for its 8 ps (Run E). While the lasting carbamate zwitterion differs from our carbonate zwitterion result, it does match that of Guido et al. for the monoethylamine zwitterion at lower concentration.[17] The 8 ps survival of the zwitterion (a

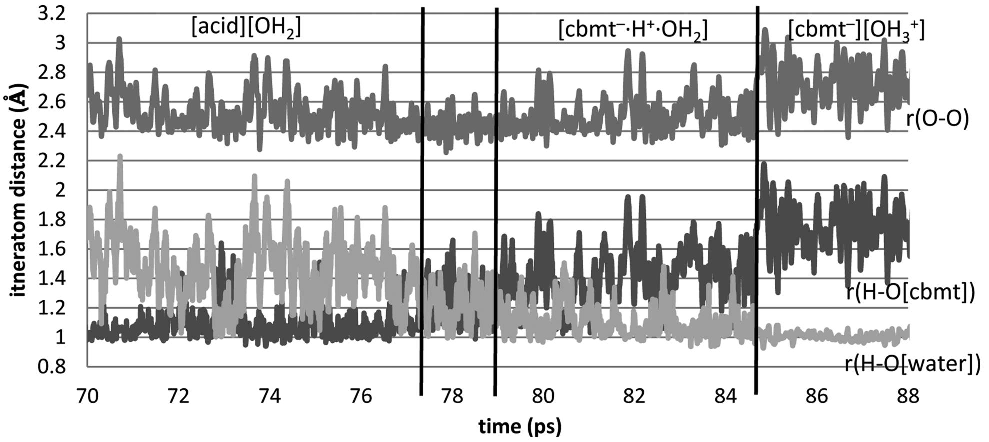


Figure 2. The H^+-bridged (Zundel-like) complex [carbamate$^-$·H^+·OH_2] in Run H: plots of the distance of the bridging H^+ to each of the involved O, as well as the O···O distance, versus time. The H^+-bridged complex existed between 79 and 85 ps. The unlabeled region between 77 and 79 ps involves extremely rapid interconversion of the acid and H^+-bridged complexes; the H^+-bridged complex stabilized for the next 6 ps.

species not spectroscopically detected) led us to explore, with longer simulations, various carbamate zwitterions.

Longer Zwitterion Simulations. These nine additional simulations are summarized in Table 2. The final geometry of Run E was used to build input structures for all the secondary amine zwitterion simulations (H, L, M, N), while the 64-H_2O Geometry 2 was used to build input structures for the primary-amine-zwitterion simulations (I, J, K, O).

We first discuss at length Runs H–M, runs of six different carbamate zwitterions in water at 0.86 mol L^{-1} concentration. In Run L the zwitterion persisted throughout the run, as in the shorter 15 ps MEACOO$^\pm$ run of Guido et al.,[17] but in the other five the zwitterion deprotonated, and in all five cases the system did not return to the zwitterion form during the simulation, but stayed past an apparent activation barrier and on the side of the anion/acid equilibrium. No instance of CO_2 loss was observed. Although this does not prove that zwitterions *must* be intermediate in the conversion of CO_2 to carbamate ions, this result combined with the Han 2011 observation (albeit in liquid amine) of CO_2 → zwitterion → carbamate lends more weight to the belief that the route to carbamate goes via zwitterion, and that the acid form would likely appear only after carbamate has been formed. This “acid-is-last” aspect would parallel what occurs in the bicarbonate case as well.[15] Hence, the step CO_2 + HX → XCOOH is unlikely to be elementary in either the bicarbonate (X = OH) or carbamate (X = NR_2) cases.

The zwitterion deprotonation times (t_{deprot}) varied from 0.6 to 148.1 ps, and did not correlate with amine pK_a. They are likely more dependent on the particular trajectories more or less dictated by how the zwitterion is initially placed in the water. The two trials of Run I differed only in the initial geometry; the deprotonation times showed a typical variation.

After deprotonation, limited oscillation between carbamate anion and carbamic acid was generally observed, and Table 2 reports the durations of the anion and acid states observed in each run. Large variations in relative durations are seen, most strikingly in the two trials of Run I. These large variations are due to the short time scale; unfeasibly long sampling times would be needed to see consistent equilibrium ratios in these durations. Since such equilibria depend on pH, one would not be able to obtain a meaningful equilibrium ratio even if long sampling times were possible, because the finite size of the simulation restricts the H^+ concentration to be either 0.86 M (carbamate anion state) or zero (zwitterion or carbamic acid state).

Along with the zwitterion, anion, and acid forms, a fourth state of the species was discovered for the first time: a *Zundel-like H^+-bridged neutral complex of carbamate anion with a single H_2O molecule.* The structural characteristic of this state is a distance of 1.3–1.5 Å from the bridging H to the carbamate oxygen, as the distance is 1.0–1.1 Å in the acid and 1.6–1.8 Å when only hydrogen-bonded to the carbamate. Figures 2 and 3 show two such observations.

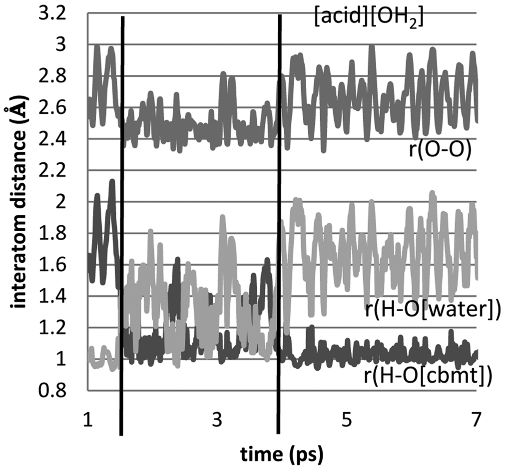
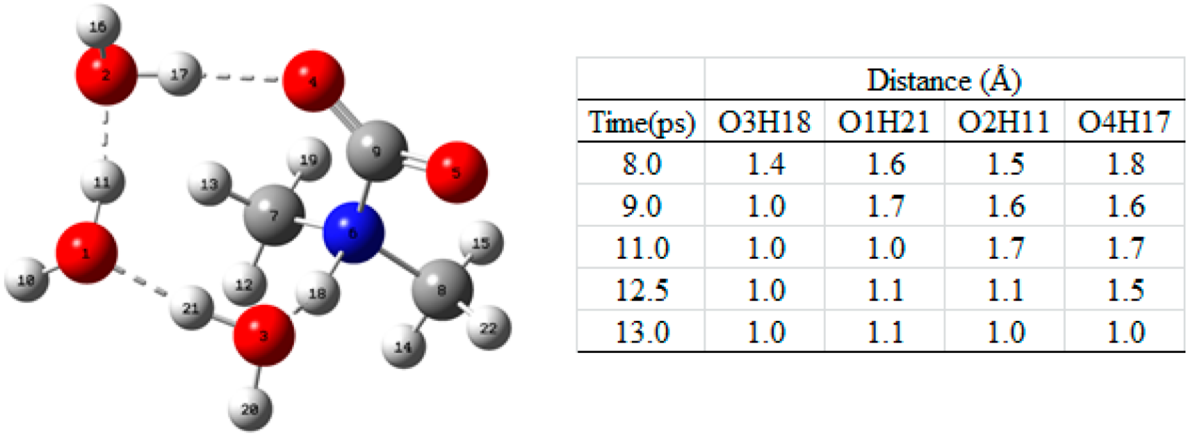


Figure 3. The H^+-bridged (Zundel-like) complex [carbamate$^-$·H^+·OH_2] in Run I trial 1: plots of the distance of the bridging H^+ to each of the involved O, as well as the O···O distance, versus time. The carbamate state at 0.9–1.5 ps changed to a time region of rapid interconversion of the acid and H^+-bridged complexes from 1.5 to 4.0 ps (similar to 77–79 ps in Run H) before stabilizing in the acid state.

As an aid for transition state searches, the interconversion mechanisms observed in Runs H–M are now described. In Run H (dimethylamine zwitterion), the zwitterion deprotonation by water may have been assisted by the basicity of the zwitterion’s COO^- moiety, via a hydrogen-bonded 10-atom cycle (Figure 4) that was fully set up prior to the deprotonation. In fact, this very cycle performed all four successive H^+ transfers (Grotthuss H^+ diffusion), along the dashed lines in the figure, to produce the first instance of the carbamic acid state 4.1 ps after the



	Distance (Å)			
Time(ps)	O3H18	O1H21	O2H11	O4H17
8.0	1.4	1.6	1.5	1.8
9.0	1.0	1.7	1.6	1.6
11.0	1.0	1.0	1.7	1.7
12.5	1.0	1.1	1.1	1.5
13.0	1.0	1.1	1.0	1.0

Figure 4. The 10-atom zwitterion deprotonation cycle (snapshot at *t* = 8.000 ps) observed in Run H (other H_2O molecules deleted for clarity), and a table of OH interatom distances detailing the four successive H^+ transfers along the dashed lines in the figure.

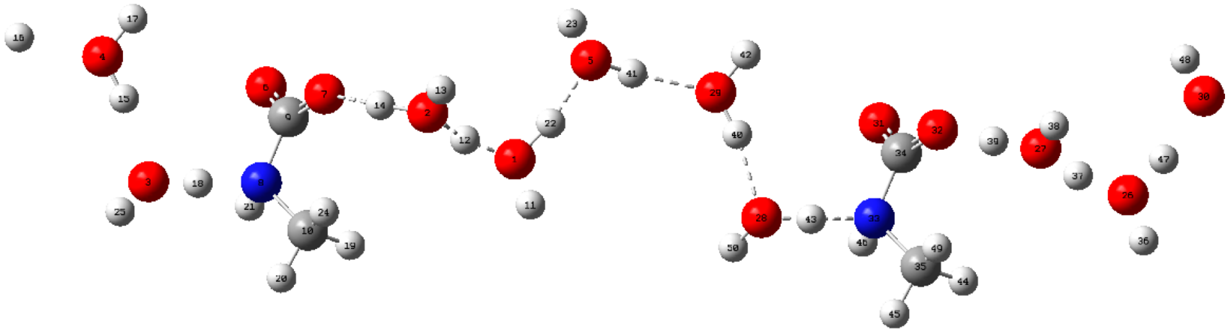


Figure 5. The 14-atom zwitterion-deprotonation chain (snapshot at *t* = 1.473 ps) observed in Run I (other H_2O molecules deleted for clarity).

initial deprotonation. However, these four H^+ transfers were not consecutive, as additional H^+ transfers occurred with H_2O molecules adjacent to this particular cycle between *t* = 8.0 and *t* = 12.1 ps. After the first formation of acid at 12.1 ps the system continued to oscillate between the acid and carbamate-anion states in the remainder of the simulation, with ensuing H^+ transfers at 14.4, 63.1, 79–85, and 96.5 ps. Protonation to the acid state for the first and third times (at 12.1 and 96.5 ps) involved H17 but for the second time (at 63.1 ps) it involved H153. The deprotonation at 79–85 ps required a 6 ps time range because of the pause at the Zundel-like H^+-bridged state (Figure 2).

In Run I trial 1 (methylamine zwitterion), and Run K (AMP zwitterion), the zwitterion deprotonation by water may have been assisted by the basicity of the COO^- moiety of the zwitterion *in a neighboring periodically replicated cell* (Figure 5) via a 14-atom H-bonded chain that was fully set up prior to the deprotonation. Furthermore, just as in Run H, this connection to the assisting group resulted in complete Grotthuss shuttling of H^+ atoms along this H-bonded multimolecule connection (6 H^+ transfers in the case of these chains) to the first instance of the carbamic acid state; the complete shuttling took 0.6 ps in Run I trial 1, and 0.4 ps in Run K. In both these runs, once this initial acid was formed, the H-bonded chain back to anion broke, and the systems stayed in the acid forms for essentially the remainder of the run. Only after 90 ps of its formation in Run I trial 1 did the acid form fully return the H^+ to the water, for the final 0.3 ps of the simulation.

In Run I trial 2 (methylamine zwitterion) and Run J (MEA zwitterion), there were no clear signs of deprotonation assistance by a COO^- moiety through an H-bonded chain or cycle. Deprotonation in Run I trial 2 occurred at a time when there was *both* one crude cycle and one crude chain in place, but neither as tight as the ones in the two previous runs. Deprotonation in Run J occurred without *any* crude chain or cycle being noticeable, but instead may have benefitted from beneficial local water structure, as the H^+ loss led instantly to a Zundel ion involving the abstracting H_2O and one of its neighbors. In neither of these runs was the acid form observed; this could be related to the absence of a tight H-bonded line to an acid form at time of deprotonation. With more time, eventually the excess H^+ in the water would find its way to a COO^- moiety via Grotthuss H^+ diffusion.

In Run M (PPZ zwitterion), zwitterion deprotonation again occurred without a good H-bonded chain to a COO^- moiety. However, unlike the two previous cases, this run did succeed in producing an acid form, and only 2.1 ps after deprotonation. First, a Grotthuss shuttling drew the charge 4 water molecules away in 0.7 ps, and after a further 1.2 ps as solvated H_3O^+, the same shuttling path (involving the same atoms) occurred in reverse in 0.2 ps, placing the abstracted H^+ onto the COO^- moiety of the original zwitterion. One might call this an "H_2O-catalyzed 1,3-H-shift," but due to the Grotthuss shuttling it would be wiser to call it a multistep process.

Finally, two simulations (Runs N and O, also in Table 2) were performed with an extra amine molecule with the carbamate zwitterion in the simulation box, in hopes of observing (as Han et al. did for aqueous[16] and liquid[18] MEA) a mechanism for proton transfer from zwitterion to amine that would occur during initial CO_2 loading (e.g., up to a 2:1 amine:CO_2 ratio). In Run N (dimethylamine), the neutral amine was placed at an N to N distance of 4.66 Å from the zwitterion, with the zwitterion N−H bond aimed roughly perpendicular to the extra amine. The zwitterion was deprotonated at 27.9 ps, starting a 14-atom 0.3-ps H-shuttling cycle stopping just short of forming a carbamic acid. Further H-shuttling occurred until t = 29.5 ps when the extra H^+ was finally deposited on the uncarboxylated amine molecule. This final state persisted for the remainder of the 48 ps simulation. In total, 11 water molecules were involved in the relay of proton from the zwitterion to the neutral amine, and the time required was 1.6 ps.

In Run O (methylamine), the neutral amine was placed at an N to N distance of 4.14 Å from the zwitterion, with the zwitterion N−H bond aimed roughly toward the extra amine. Deprotonation was fast (0.4 ps) and occurred in an essentially concerted (∼60 fs) double-proton-transfer from the zwitterion to one H_2O and that H_2O to the uncarboxylated amine (Figure 6). As in Run N, once the protonated amine was formed, it (and the carbamate anion) persisted for the remainder of the run. The NH−OH−N double-H^+-transfer of Run O also occurred in the Han et al. simulation with liquid MEA, although there the participating OH was a hydroxyl group of one of the two MEA molecules.[18]

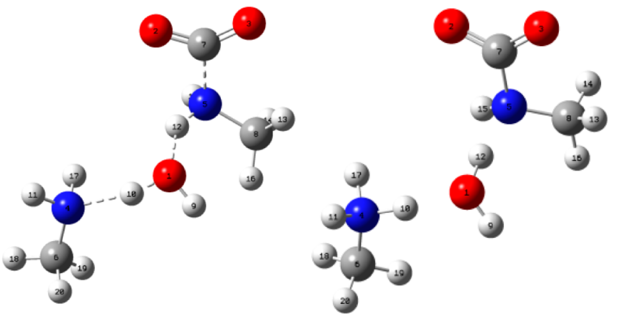


Figure 6. Snapshots at t = 0.32 ps (left) and 0.38 ps (right) of Run O, just before and after the double-proton transfer from zwitterion to amine.

In conclusion: (i) Aqueous carbamate zwitterions, and their deprotonation by water, can be observed in unbiased AIMD simulations. (ii) These zwitterions can live for 100 ps in water. (iii) For CO_2 capture at 40 °C, carbamic acid, like carbonic acid,[15] likely forms from its anion $XCOO^-$ rather than from CO_2 directly. Furthermore, the observed zwitterion → anion → acid conversions demonstrate that acid formation from the zwitterion can occur on <5 ps time scale via long 10−14-atom multimolecular H^+ relays, rather than unimolecular 1,3-H-shifts. A similar multimolecular Grotthuss mechanism was proposed (and transition states computed) by Lim et al.[26] for carbamic acid formation via GaP-catalyzed proton-coupled electron transfer. (iv) A Zundel-like neutral H^+-bridged complex of carbamate anion with a single H_2O molecule is predicted to exist transiently in aqueous solution. These complexes had a characteristic distance from H^+ to the carbamate O atom of 1.4 ± 0.2 Å in the 40 °C simulations. None lived longer than 6 ps, however, and during H^+ transfer they did not always occur. (v) During early CO_2 loading (i.e., with excess amine molecules present), the first carbamate zwitterions do not necessarily lose their excess H^+ directly or via concerted double-H^+-transfer to another amine molecule; Run N demonstrated that the bulk water may still take the H^+ initially and later transfer another H^+ to an amine.

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Notes

The authors declare no competing financial interest.

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