# Semicontinuum Solvation Modeling Improves Predictions of Carbamate Stability in the CO<sub>2</sub> + Aqueous Amine Reaction

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Supporting Information

**ABSTRACT:** Quantum chemistry computations with a semicontinuum (cluster + continuum) solvation model have been used to cure long-standing misprediction of aqueous carbamate anion energies in the industrially important  $CO_2$  + aqueous amine reaction. Previous errors of over 10 kcal mol<sup>-1</sup> are revealed. Activation energies were also estimated with semicontinuum modeling, and a refined discussion of the competing hypothetical mechanisms for  $CO_2$  + monoethanolamine (MEA) is presented. Further results are also presented to demonstrate that the basicity of an amine (aqueous proton affinity) correlates only with  $CO_2$  affinity within an amine



class: secondary amines have an extra CO<sub>2</sub> affinity that primary amines do not have.

# 1. INTRODUCTION

Aqueous solutions of primary and secondary alkanolamines are able to perform the important  $CO_2$ -capture<sup>1-4</sup> reaction

$$B + HXYN + CO_2 \rightarrow BH^+ + XYNCOO^-$$
(1)

where HXYN is a primary or secondary amine, and B = any base (HXYN, H<sub>2</sub>O, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, ...).<sup>5</sup> If the CO<sub>2</sub> is not immediately recovered via reverse reaction, degradation of carbamate to bicarbonate occurs as a second stage, with the delay (on the order of 1 h at typical conditions) dependent upon the pH and the particular amine.<sup>6,7</sup>

Meaningful rate constant data for carbamate formation requires agreement about the rate law used to fit to the experimental data. Two different mechanisms (the zwitterion<sup>5,8,9</sup> and termolecular  $^{10}$  mechanisms, here  $\rm Z$  and  $\rm T)$  have resulted in competing formalisms and impede understanding, and a third mechanism (via acid intermediate, here A) was proposed in 2009.<sup>11</sup> Quantum chemistry studies of the CO<sub>2</sub> + amine reaction might be able to assist in clarifying the reaction mechanism, but to date the geometry-optimization-based studies<sup>12-18</sup> have underestimated the stability of carbamate anions, to such an extent that optimized minima could not be found at moderate pH (single-amine) conditions. The reason for this failure is their inadequate treatment of solute-solvent hydrogen bonding. Herein we present a semicontinuum<sup>19</sup> (or "cluster + continuum") approach that properly demonstrates the relative stability of carbamate ions. We then use the improved activation energies to re-evaluate the relative importance of the competing mechanisms for the case of monoethanolamine (MEA).

In the Appendix we present results from simplified modeling that revealed an important difference between aqueous proton affinity and  $CO_2$  affinity.

# 2. MECHANISMS STUDIED

Consider a solution of primary or secondary amine HXYN, with a typical conjugate-acid  $pK_a = 9.5$  at room temperature. In a 1 M (mol L<sup>-1</sup>) solution, the pH would be 11.75 if the solution were ideal, and thus the dominant species are H<sub>2</sub>O (54 M) and HXYN (0.994 M), with OH<sup>-</sup> and H<sub>2</sub>XYN<sup>+</sup> concentrations near 0.006 M. Before CO<sub>2</sub> addition, all molecules and ions in the solution are in a dynamic hydrogen-bonded network.

Under optimal conditions and before the onset of bicarbonate production, up to 0.5 mol of  $CO_2$  can be dissolved into a liter of this solution,<sup>20,21</sup> forming predominantly<sup>21</sup> carbamate ions as per eq 1. At the instant that a  $CO_2$  molecule bonds to the nucleophilic amine nitrogen atom, the nitrogen atom becomes 4-coordinate and prone to losing an H atom to the hydrogen-bonded network. The network could conceivably do one of several things at that instant (Figure 1), giving rise to the competing mechanisms:

(i). Zwitterion (Z) Mechanism. Leave the H atom on the N initially (result:  $H^+XYNCOO^-$  zwitterion intermediate), later removing it via proton relay to form carbamate anion (and eventually protonate a second HXYN molecule). This is a representation of the zwitterion mechanism of Danckwerts,<sup>9</sup> favored by Versteeg;<sup>5</sup> it was a two-step simplification of a three-step mechanism originally proposed by Caplow for  $B = H_2O.^8$  The two steps are

$$HXYN + CO_2 \rightleftharpoons_{k_{-1}}^{k_1} HXYNCOO^{+-}$$
(2)

$$HXYNCOO^{+-} + B \xrightarrow{k_B} XYNCOO^{-} + HB^{+}$$
(3)

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**Figure 1.** Two-dimensional examples of proton relays upon chemisorption of  $CO_2$  to amine (step a, upper left). Caplow:<sup>8</sup> a or a + b is the initial step. Danckwerts:<sup>9</sup> a is the initial step. Crooks and Donnellan:<sup>10</sup> a + b is the initial step, and b could be amine-to-amine transfer. Generalized Crooks/Donnellan (T): sequences abcdef and abcg are examples of possible concerted single steps. Generalized Caplow/ Danckwerts (Z): sequences abcdef and abcg occur in two steps, with a being the first step. Generalized McCann/Maeder (A):<sup>11</sup> sequence abhij is an example of a possible concerted single step.

Modern understanding of proton transfer in aqueous media allows for the generalization that the second step may involve a concerted Grotthuss-style multimolecular proton relay.<sup>22</sup>

(ii). Termolecular (T) Mechanism. Instantly remove the H atom via proton relay (result: XYNCOO<sup>-</sup> carbamate product), to protonate a third molecule, either a second HXYN molecule nearby, or an  $H_2O$  or  $OH^-$  further into the bulk water and stabilized by other water molecules. Eventually an H<sup>+</sup> transfer into the bulk water would result in later protonation of a second HXYN molecule. This is a generalization (i.e., allowing for multimolecular proton relays) of the termolecular mechanism of Crooks and Donnellan;<sup>10</sup> their claim was that eq 1 is itself an elementary step. The criticism of Maeder and co-workers,<sup>11</sup> that a termolecular elementary step requires rare simultaneous collision of three entities, is not valid here because of hydrogenbond complexation; the reaction is effectively B·HXYN + CO<sub>2</sub>. The criticism of Versteeg,<sup>5</sup> that it cannot explain broken-order kinetics seen in alcohol solutions of amines,<sup>23</sup> is significant.

(iii). Acid (A) Mechanism. Instantly remove the H atom and protonate the carboxyl group on the same molecule (result: XYNCOOH carbamic acid intermediate), either directly or via concerted proton relay. Later this acid intermediate would lose its  $H^+$  via proton relay to form carbamate anion (and eventually protonate a second HXYN molecule). This would be the likely scenario behind the newer acid-intermediate mechanism of Maeder and co-workers,<sup>11</sup> as these authors did not specify how the carbamic acid could be generated in the initial step. The two steps are thus

$$HXYN + CO_2 \stackrel{k_1}{\underset{k_{-1}}{\rightleftharpoons}} XYNCOOH$$
(4)

$$XYNCOOH + B \xrightarrow{k_{B}} XYNCOO^{-} + HB^{+}$$
(5)

and differ from the zwitterion mechanism only in the identity of the intermediate.

*Bicarbonate mechanisms.* It is known that ordinary basic solutions can convert  $CO_2$  directly to bicarbonate in small

amounts. In amine solutions, two possible mechanisms are

$$OH^- + CO_2 \rightarrow HCO_3^-$$

or

$$XYZN + CO_2 + H_2O \rightarrow XYZNH^+ + HCO_3^-$$
(7)

In amine solutions, eq 6 was deemed to be of little importance.<sup>24</sup> eq 7, a base-catalyzed bicarbonate mechanism proposed by Donaldson and Nguyen,<sup>25</sup> is believed to be operative in the case of tertiary amines, which cannot form carbamates, but is likely negligible for other amines where the onset of carbamate far outpaces that of bicarbonate.<sup>7</sup> The eq 7 mechanism is, like the Crooks/Donnellan carbamate mechanism, a "termoleculecular" single-step mechanism, in which two bonds are broken and two bonds are formed in a concerted step among the three molecular entities within an encounter complex. While this is not a carbamate-forming reaction, it was deemed useful to add it to this study as a test of the accuracy of our methods, by seeing if our predicted activation energies for this reaction were lower than for the carbamate-forming mechanisms. It was also useful as a control for demonstrating the phenomenon of CO<sub>2</sub> affinity of amines.

# 3. TESTING MECHANISMS WITH RATE LAWS

For the zwitterion mechanism Z, during steady-state-intermediate conditions, the rate of reaction of  $CO_2$  ( $r_{CO.}$ ) is

$$r_{\rm CO_2} = -k_{\rm obs}[\rm CO_2] = \frac{-[\rm HXYN]}{\frac{1}{k_1} + \frac{1}{\sum_{\rm B} K_{\rm B}[\rm B]}}[\rm CO_2]$$
(8)

where

$$K_{\rm B} = \frac{k_1 k_{\rm B}}{k_{-1}} \tag{9}$$

Here B denotes any proton-accepting species present; if one considers {H<sub>2</sub>O, OH<sup>-</sup>, HXYN}, then one has elementary rate constants  $k_{\rm B} = \{k_{\rm w}, k_{\rm OH-}, \text{ and } k_{\rm HXYN}\}$  and the corresponding composites  $K_{\rm B}$  in eq 9. Fitting eq 8 to experimental data for aqueous amines would give values for the three  $K_{\rm B}$ 's as well as  $k_1$ , but this 4-parameter function often has indeterminacy problems. To cure such problems, many workers (a) ignore  $B = OH^{-}, {}^{5,26,27}, \text{ and/or (b) apply}^{26,28}$  one of two limiting cases: if  $k_{-1} \ll \Sigma_{\rm B}k_{\rm B}$ [B] (Caplow's weak-amine limit), eq 10 arises, while if  $k_{-1} \gg \Sigma_{\rm B}k_{\rm B}$ [B] (Caplow's strong-amine limit), eq 11 arises.

$$r_{\rm CO_2} = -k_1 [\rm CO_2] [\rm HXYN] \tag{10}$$

$$r_{\rm CO_2} = -\sum_{\rm B} K_{\rm B}[{\rm B}][{\rm CO_2}][{\rm HXYN}]$$
(11)

eq 10 gives a rate law that is first order in amine, and has only one constant to fit. Equation 11 allows for fractional orders of amine between 1 and 2, and has up to three constants to fit.

For the acid mechanism A, the rate law is eq 8, but with a different identity for the intermediate (acid, not zwitterion). Hence, a test of the A versus Z mechanisms would be to do ab initio modeling of the A vs Z reaction paths in Figure 1. The modeling must be good enough to treat the relative stabilities of the acid and the zwitterion forms properly, and the semicontinuum method should do the job.

For the termolecular mechanism T, the rate law is eq 11 but with the composite rate constants  $K_{\rm B}$  interpreted as elementary

(6)

rate constants. Hence the termolecular mechanism is the strongamine limit of the zwitterion mechanism. It does not require the complete absence of a zwitterion, as some computational chemists have assumed. It only requires that  $k_{-1} \gg \Sigma_{\rm B} k_{\rm B} [{\rm B}]$ , i.e., that the zwitterions lose CO<sub>2</sub> much more often than they deprotonate. Hence, a test of the T versus Z mechanisms would be to predict whether  $k_{-1} \gg \Sigma_{\rm B} k_{\rm B}$ [B]. While some computational chemists consider it sufficient to predict the  $E_a$  values inside  $k_{-1}$  and  $k_{\rm B}$ , it would be better to compare  $k_{-1}$  with  $\Sigma_{\rm B}k_{\rm B}[{\rm B}]$ . Recently, two of us used ab initio Eyring-formula rate constant predictions to analyze competing mechanisms in hydroboration in ether solutions; this required new expressions for the entropy-damping effect of solvation.<sup>29</sup> To date only Xie and co-workers<sup>15,30</sup> have tried predicting ab initio Eyringformula rate constants for the  $CO_2$  + amine reaction; we discuss their results with our own reanalysis in Section 6.4.

# 4. THE NEED FOR SEMICONTINUUM MODELING

Obtaining realistic mechanistic results using theoretical molecular models depends on a number of factors, one being the use of a proper molecular model capable of representing the essential chemistry of the real liquid solution. For liquid phase reactions involving ions, one important modeling aspect is the stabilization of ions by polar solvents: polar solvents will lower the energy of ionic intermediates and transition states dramatically, thus affecting the rate and even course of reactions. For this effect, a continuum solvation model (CSM), such as PCM,<sup>31</sup> SMx,<sup>32</sup> and COSMO,<sup>33</sup> can be used. A second aspect, important in the current case of aqueous amines, is the effect of local hydrogen-bonding solvation. For this effect, adding explicit solvent molecules to the model (with or without CSM) can be of benefit.

Previous computational chemistry studies of eq 1 have tried both of these modeling strategies. The dominant problem with these studies is that they consistently underestimate carbamate anion stability. It has been known since 1925 that the dominant initial product upon reacting  $CO_2$  with aqueous amines is carbamate anion.<sup>34,35</sup> To date, however, single-amine models have been unable to produce anions as intermediates at all (Table 1). These same researchers,<sup>12,13,15–17</sup> plus others,<sup>30,36</sup>

# Table 1. Reaction Pathways Observed in Single-Amine Modeling

reference	level of modeling	results <sup>a</sup>
ref 12 (2007)	Gas phase +2 $H_2O$	$CO_2$ +MEA+ $H_2O \rightarrow acid$
		$CO_2$ +DEA+ $H_2O \rightarrow acid$
ref 13 (2009)	IEFPCM	$CO_2$ +MEA+H <sub>2</sub> O $\rightarrow$ zwitterion
ref 14 (2009)	COSMO	$CO_2$ +AMP+H <sub>2</sub> O $\rightarrow$ acid
ref 15 (2010)	CPCM	$CO_2$ +MEA+H <sub>2</sub> O $\rightarrow$ zwitterion $\rightarrow$ acid
ref 16 (2011)	COSMO	$CO_2$ +MEA+ $H_2O \rightarrow acid$
ref 17 (2011)	IEFPCM-SMD	$CO_2$ +AMP+H <sub>2</sub> O $\rightarrow$ zwitterion $\rightarrow$ acid
ref 18 (2015)	IEFPCM	MEA zwitterion $\rightarrow$ acid
<sup><i>a</i></sup> MEA = HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ; DEA = $(HOCH_2CH_2)_2NH$ ; AMP = $HOCH_2C(CH_3)_2NH_2$ .		

have resorted to two-amine (complexes of neighboring amine) models to produce carbamate anions. The drawback to these neighboring-amine models is that they jeopardize mechanism integrity, as these models inherently assume that the zwitterion-deprotonating species B is another amine molecule, rather than  $H_2O$ . As we will show, the main problem with all these  $CO_2$  + amine studies is insufficient water molecules in the

model; more are needed to allow for proper relative stabilization of the anion.

Recently we published a report on our exploratory DFTbased molecular dynamics simulations of the various hypothesized stages of the  $CO_2$  + amine reaction in water.<sup>37</sup> On <100 ps time scales, interconversions between zwitterion, anion, and acid states were observed, often involving multimolecular proton relays, and that helped steer the current study toward models with multiple water molecules. Interestingly, the reverse reaction to amine + CO<sub>2</sub> was not observed in any of the simulations. This suggests that, for most amines, the zwitterion (a) is fleetingly stable and (b) finds a lower barrier for moving forward in the reaction (deprotonation) than moving in reverse (losing  $CO_2$ ). This would place these amines more toward Caplow's "weak-amine" regime than his "strong-amine" regime, at least when in low concentrations, and thus speaks against the termolecular mechanism. This observation became a point of focus for the follow-up static geometry-optimization-based study presented here.

#### 5. METHODS

All calculations were done using the Gaussian09<sup>38</sup> computational chemistry software program. The level of theory for geometry optimization was B3LYP/6-31G(d)/IEFPCM; B3LYP<sup>39,40</sup> is a common density-functional theory, 6-31G(d) denotes the basis set used for molecular orbitals,<sup>38</sup> and IEFPCM is the default version of the continuum solvation method in Gaussian09 (e.g., with UFF atomic radii used for overlapping-sphere solute cavity construction within the continuum).<sup>41</sup> Reported energies are "raw" (without zero-point and thermal-correction energies), and are from MP2/aug-cc-pVDZ/IEFPCM single-point runs (justified in the Supporting Information) using B3LYP/6-31G(d)/ IEFPCM geometries; MP2 is a common ab initio method.<sup>38</sup> Most results employ methylamine (MeNH<sub>2</sub>) or monoethanolamine (MEA) as the amine HXYZ. Calculations were performed with a semicontinuum model,<sup>19</sup> i.e., varying numbers of explicit H<sub>2</sub>O (W) molecules were included in a hydrogen-bonded cluster around the solutes inside the PCM continuum. The intent of the additional W molecules was twofold: to allow multimolecular proton relays as seen in our simulations (hence our 5W models), and to saturate H-bonding around solutes (hence our 18W and 20W models).

To investigate the various mechanisms, reaction paths were pursued with transition state (TS) optimizations, performed with the Gaussian09 algorithm opt = (ts, calcfc, noeigentest).<sup>42</sup> TS searches were made in regions of configuration space that were chosen based on observations we made in simulations of the various proposed intermediates;<sup>37</sup> in particular, multiple H<sub>2</sub>O molecules were considered in proton-transfer relays. Transition states were confirmed by vibrational frequency computation (one imaginary frequency needed) and by two energy minimization runs, each starting from the TS geometry but with some atoms displaced according to the direction shown in the imaginary-frequency normal mode.

# 6. RESULTS AND DISCUSSION

**6.1. Carbamate-Anion Stability Study.** A series of computations were performed, using methylamine as a test amine, to determine the energies of the anion-producing reactions R1-R4 as functions of the number of water molecules explicitly used to solvate the solute species in the semicontinuum model.

Single-amine  $(B = H_2O)$  model:

$$MeNH_{2}COO \cdot (nH_{2}O) + H_{2}O \cdot (nH_{2}O)$$
  

$$\rightarrow MeNHCOO^{-} \cdot (nH_{2}O) + H_{3}O^{+} \cdot (nH_{2}O)$$
(R1)

 $MeNHCOOH \cdot (nH_2O) + H_2O \cdot (nH_2O)$ 

$$\rightarrow \text{MeNHCOO}^{-} \cdot (nH_2O)) + H_3O^{+} \cdot (nH_2O)$$
(R2)

Two-amine (B = amine) model:

$$MeNH_{2}COO \cdot (nH_{2}O) + MeNH_{2} \cdot (nH_{2}O)$$

$$\rightarrow \text{MeNHCOO}(n\text{H}_2\text{O}) + \text{MeNH}_3^{+}(n\text{H}_2\text{O}) \qquad (\text{R3})$$

 $MeNHCOOH \cdot (nH_2O) + MeNH_2 \cdot (nH_2O)$ 

$$\rightarrow \text{MeNHCOO}^{-}(n\text{H}_2\text{O}) + \text{MeNH}_3^{+}(n\text{H}_2\text{O}) \qquad (\text{R4})$$

The  $nH_2O$ 's were added systematically to each solute molecule, with geometry reoptimization (Supporting Information, Figure S1). The raw  $\Delta E$  results for these reactions were plotted against *n* (Figure 2). As *n* increases from 0 to 3, an



Figure 2. Lowering of predicted B3LYP/6-31G(d)/IEFPCM  $\Delta E$  values for carbamate anion formation, due to adding explicit H<sub>2</sub>O molecules to the model. See Figure S1 for optimized-geometry conformers used.

enormous lowering of  $\Delta E$  (20–45 kcal mol<sup>-1</sup> !) occurs for all four reactions, due to improved solvation of the two created ions. Without explicit waters (n = 0), errors are 40–45 kcal mol<sup>-1</sup> for carbamate + hydronium, and 20–25 kcal mol<sup>-1</sup> for carbamate + protonated amine.

**6.2. Single-Amine Reaction Paths.** The  $CO_2$  + amine (MEA) reaction was pursued through to the acid intermediate state, even though the carbamate anion state should occur earlier; this was to evaluate relative stabilities of all proposed intermediates. Results are presented for 1-H<sub>2</sub>O (1W), 5-H<sub>2</sub>O (5W), and 20-H<sub>2</sub>O (20W) models. The mechanisms observed appear in Figure 3, with energy plots in Figure 4. Clearly, mechanisms incorporating other numbers of H<sub>2</sub>O in the proton relay are also possible.

In 1-amine-1-H<sub>2</sub>O (1A1W) modeling, a two-step six-atom cycle was found. No carbamate was found; the path first formed zwitterion (no H transfers) and then carbamic acid (2 concerted H transfers). The barrier between zwitterion and acid is overly high as well. These are incorrect results arising from too few  $H_2O$  in the model.

In 1-amine-5- $H_2O$  modeling, a 3-step 10-atom cycle was found during B3LYP geometry optimization (ignoring cluster



**Figure 3.** Reaction mechanisms observed in the one-amine-molecule (1A) modeling of eq 1. Spectator water molecules are omitted in the figure.



**Figure 4.** Reaction-energy profiles from three single-amine models: 1  $H_2O$  (small-dashed) 5  $H_2O$  (dashed), 20  $H_2O$  (solid). Note the drop in stability of carbamate anion with added water. See Figure S2 for optimized-geometry conformers used.

relaxation steps), although it became 2-step after MP2 singlepoint computation (Figure 4). The first step again produces zwitterion (no H transfers), but this time we have enough  $H_2O$ in the modeling to see it combined with a solvent-displacement step, which causes a more noticeable 6 kcal mol<sup>-1</sup> barrier. The second B3LYP step produces carbamate via abstraction of the proton by another water molecule (one H transfer); the presence of additional explicit water molecules has considerably stabilized the carbamate anion, but not enough to confirm it as an intermediate. The third B3LYP step produces the acid form (3 concerted H transfers via proton relay), but is still predicted to be overly exothermic.

In 1-amine-20-H<sub>2</sub>O modeling, two of the three steps in a 12-atom cycle were found (involving 5 H transfers). The initial step of zwitterion formation could not be found, due to uncertainty in building in a solvent-displacement component with so many H<sub>2</sub>O molecules in the model. The second and third steps were formation of carbamate (and a Zundel ion,<sup>43</sup> from 2.5 H transfers) and acid (2.5 more H transfers). With the H<sub>2</sub>O molecules now properly surrounding the amino and carboxyl groups, and the addition of more explicit H<sub>2</sub>O, the carbamate anion (with hydronium) is now finally seen to be a proper intermediate, 3 kcal mol<sup>-1</sup> above the zwitterion and acid forms in relative energy. This 3 kcal mol<sup>-1</sup> estimate, relative to the zwitterion, is a significant improvement over the previous predictions of Hwang et al.<sup>18</sup> (9 with 2 waters, 15 with 1 water), Xie et al.<sup>15</sup> (13 with 2 waters, 35 with 0 waters), and Arstad et al.<sup>12</sup> (14 with 2 waters, 26 with 1 water), with all these previous predictions featuring carbamate (+ hydronium) as a transition state instead of an intermediate.

Experimentally, carbamate anions decompose; at neutral pH they dissociate quickly (milliseconds) to  $CO_2$  + amine,<sup>35</sup> whose energy could not be estimated with 1A20W modeling. At 1A1W and 1A5W modeling (Figure 4), the  $CO_2$  + amine state has similar raw energy to the zwitterion; if this is true in reality, then 1A20W modeling places all intermediates at similar raw energy to this dissociated state. This dissociated state



Figure 5. Reaction mechanisms observed in two-amine-molecule (2A) modeling of eq 1. Spectator water molecules are omitted in the figure.



Figure 6. Reaction-energy profiles from four two-amine models. Upper plots: neighbouring amines. Lower plots: separated amines. Note the drop in stability of carbamate anion with added water. See Figure S3 for optimized-geometry conformers used.

would then have the lowest Gibbs energy of all intermediates because of the entropy benefit of dissociation, making it the favored state, which agrees with the experimental observation.

6.3. Two-Amine Reaction Paths. Two-amine (2A) models are useful for two reasons. First, the abstracting base B in the proposed mechanisms could be a second amine molecule, so that this barrier height might be important. Second, in most CO<sub>2</sub>-capture experiments with aqueous amines, the proton released by the zwitterion, even if released initially to bulk water, relays quickly to a second amine molecule (inhibiting the reverse decomposition of carbamate back to  $CO_2$  + amine), and the reaction energy of this completed reaction  $(CO_2 +$ 2 amines) can be estimated this way. Results are presented for 2A0W, 2A1W, and 2A18W models. Examples of the mechanisms observed appear in Figure 5, labeled by the heavy atoms N and O in order of the observed proton relay (e.g., the NNOO path features proton transfers from N to N to O to O). As in the previous section, mechanisms incorporating other numbers of H<sub>2</sub>O in the proton relay are clearly also possible. We separate the cases into neighboring-amine and separatedamine ones.

For neighboring-amine examples, 2-amine-0-H<sub>2</sub>O modeling first produced a 2-step 6-atom cycle (Figure 5, NNO cycle), which features no carbamate anion at all. With this modeling we also found alternative 3-step pathways that feature a carbamate intermediate (by using gauche MEA instead of trans MEA, or with a 5-atom cycle in which the H<sup>+</sup> lost by the zwitterion is transferred back to the anion to make the acid), but these had higher energy barriers than the one presented. Most importantly, none of the three pathways had the anion + alkylammonium stage being lower in energy than the acid + amine stage, again demonstrating the poor level of modeling. With 2-amine-18-H<sub>2</sub>O modeling, the anion + alkylammonium stage is properly found to be the lowest-energy stage (Figure 6, upper plot).

Separated-amine examples were also considered, an idea first postulated (but not tested) by Shim et al.;<sup>13</sup> we tested it with a 2-amine-1-H<sub>2</sub>O model which placed the H<sub>2</sub>O between the two amines. We used 2-amine-1-H<sub>2</sub>O and 2-amine-18-H<sub>2</sub>O modeling (Figure 5). Again, there is a dramatic improvement in the relative energies of intermediates when adding more H<sub>2</sub>O to the model (Figure 6, lower plot).

Note that the proper inclusion of more spectator  $H_2O$  molecules improves the stability of not just the carbamate anion stage, but also the transition state leading to it, in accord with the Evans/Polanyi principle. This was demonstrated by taking an optimized zwitterion-to-carbamate TS from 2-amine-0- $H_2O$  modeling, reoptimizing it with one additional water stabilizing the COO<sup>-</sup> moiety, and then again with a second  $H_2O$  stabilizing the forming protonated amine at its  $NH_3^+$  end (Figure S3). The corresponding reactants (zwitterion+amine) and products (carbamate+alkylammonium) were also optimized. The results (Figure 7) show that the activation energy for this step is lowered from 1.8 to 1.3 to 0.2 kcal mol<sup>-1</sup> when adding the water molecules, in tandem with the increased ion stabilization (0.5 to -1.3 to -4.4 kcal mol<sup>-1</sup>).

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**Figure 7.** Lowering of  $E_a$  (and  $\Delta E$ ) values for carbamate anion formation (in a neighboring-amine case), due to adding explicit H<sub>2</sub>O molecules to the model: 0 H<sub>2</sub>O (small-dashed) 1 H<sub>2</sub>O (dashed), 2 H<sub>2</sub>O (solid). See Figure S4 for optimized-geometry conformers used.

**6.4. MEA Reaction Mechanism.** Here we use the best results from single-amine and two-amine modeling (dark solid curves in Figures 4 and 6) to properly assess the validity of the Z, T, and A mechanisms for MEA from an ab initio point of view.

The A (acid) mechanism is discarded immediately; in neither Figure 4 nor Figure 6 (nor our simulations<sup>37</sup>) do we see a carbamic acid forming before the carbamate anion.

The T (termolecular) mechanism requires that  $k_{-1} \gg$  $\Sigma_{\rm B} k_{\rm B} [{\rm B}]$  (see section 3), i.e., a zwitterion much more prone to losing  $CO_2$  than losing H<sup>+</sup>. One could try computing ab initio Eyring rate constants, as Xie et al.<sup>15,30</sup> have done. This "simply" requires computation of the relevant Gibbs energies of activation,  $\Delta^{\ddagger}G$ . However, sufficient accuracy for Gibbs energies in aqueous solution is very difficult to achieve. For instance, four of their  $\Delta^{\ddagger}G$  predictions (in kcal mol<sup>-1</sup>) for the first elementary step of  $CO_2$  + MEA were 12 (continuum with Pauling radii),<sup>15</sup> 7 (continuum with SMD radii),<sup>30</sup> 9 (from potential of mean force using B3LYP/TIP3P simulations),<sup>15</sup> and 11 (from potential of mean force using PM3-PDDG/TIP3P simulations).<sup>30</sup> This level of imprecision adversely affected comparisons: (i) their 2010 estimates produced  $k_{-1} < k_{am}$  ( $k_{B}$ for  $\hat{B}$  = amine), but 2014 modeling produced  $k_{-1} > k_{am}$ , which would give their rate law an effective reaction order of >1.5 in amine (experiment produces values close to 1); (ii) they concluded that the alternative amine AMP would form bicarbonate instead of carbamate,<sup>30</sup> when in fact AMP does initially form carbamate faster than it forms bicarbonate.44 Despite the imprecision of the estimates, their effort is commendable and a useful first step in progressing the field.

Xie et al. did not report activation energies  $E_{a}$ <sup>15,30</sup> so we could not directly compare their results to ours. Given our improved  $E_a$  values, and our distrust of gas-phase entropy calculations for solution-phase entropy,<sup>29</sup> we present here an alternative analysis. First we consider  $\Sigma_{\rm B}k_{\rm B}[{\rm B}]$  by itself (leaving the comparison to  $k_{-1}$  for later), and do not immediately assume that the sum is dominated by  $k_{\rm am}[{\rm HXYN}]$  (deprotonation by amine) as Xie et al. did. To assess whether  $k_{\rm w}[{\rm H}_2{\rm O}]$ (deprotonation by  ${\rm H}_2{\rm O}$ ) is competitive, we estimate the ratio of the two:

$$\frac{k_{\rm am}[\rm HXYN]}{k_{\rm w}[\rm H_2O]} = \frac{A_{\rm am}e^{-E_{\rm a}(\rm am)/RT}[\rm HXYN]}{A_{\rm w}e^{-E_{\rm a}(\rm w)/RT}[\rm H_2O]} = \frac{f_{\rm am}}{f_{\rm w}} \frac{e^{-E_{\rm a}(\rm am)/RT}}{e^{-E_{\rm a}(\rm w)/RT}} \frac{[\rm HXYN]}{[\rm H_2O]}$$
(12)

where we have invoked the Arrhenius equation for rate constants. We have also approximated the ratio of frequency factors  $A_{\rm am}/A_{\rm w}$  with the ratio of probabilities that the collisional

neighbor would be amine versus water  $(f_{\rm am}/f_{\rm w})$ , as deprotonation of the MEA zwitterion by bulk water is sufficiently fast  $(E_{\rm a} < 4 \text{ kcal mol}^{-1})$  that we think the only way  $k_{\rm am}$ [HXYN] could be competitive is if the second amine were right there beside the first at the time the CO<sub>2</sub> molecule arrived. (This disagrees with the 2014 Xie et al. paper where they assumed the zwitterion would live long enough for the second amine to diffuse to it.<sup>30</sup>) Hence eq 12 is a product of three ratios:

$$\frac{[\text{HXYN}]}{[\text{H}_2\text{O}]} = 0.12$$
$$\frac{e^{-E_a(\text{am})/RT}}{e^{-E_a(\text{w})/RT}} = 18$$
$$\frac{f_{\text{am}}}{f_{\text{w}}} = e^{-\Delta G/RT} \frac{[\text{HXYN}]}{c^\circ} = 0.09 \pm 0.08$$

The values for the three ratios were obtained as follows. The concentration ratio was 5 M/42 M, using  $[H_2O] = 55.4-1.3 n$  [HXYN], where *n* is the number of carbons in the amine; this approximate relation for  $[H_2O]$  fits DEA 298 K solution data<sup>45</sup> rather well. The activation energy terms used T = 298 K,  $E_a(am) = 0$ , and  $E_a(w) = 1.7$  kcal mol<sup>-1</sup>, from  $E_a = \Delta H^{\ddagger} + RT = \Delta E_{elec}^{\ddagger} + \Delta \Delta E_{thermal}^{\ddagger} + RT$ , where  $\Delta E_{elec}^{\ddagger}$  came from Figure 4 1A20W (for B = water) or Figure 6 2A18W (for B = amine), and  $\Delta \Delta E_{thermal}^{\ddagger}$  came from the B3LYP/6-31G(d) frequency runs. The  $f_{am}/f_w$  range arose from T = 298 K, standard concentration  $c^\circ = 1$  M, and  $\Delta G = 3 \pm 1$  kcal mol<sup>-1</sup> for the dimerization equilibrium

 $2HXYN \rightleftharpoons (HXYN)_2$ 

which is relevant because its equilibrium constant  $K = c^{\circ}$ [(HXYN)<sub>2</sub>]/[HXYN]<sup>2</sup>, so that  $f_{am}/f_w = [HXYN \cdot HXYN]/[H_2O \cdot HXYN] \approx [(HXYN)_2]/[HXYN] = [HXYN] K/c^{\circ}$ . The value of  $3 \pm 1$  for  $\Delta G$  was obtained from  $\Delta S = R \ln (\Omega_{am}/\Omega_w) = R \ln ([HXYN]/[H_2O]) = R \ln (5 M/42 M) = 4.2$  cal mol<sup>-1</sup> K<sup>-1</sup>, and  $\Delta H = 2 \pm 1$  kcal mol<sup>-1</sup> as obtained from calculations discussed in the Supporting Information.

Returning to eq 12, the three ratios produce  $k_{\rm am}[{\rm am}]/k_{\rm w}[{\rm H}_2{\rm O}] = (0.09 \pm 0.08)(18)(0.12) = 0.19 \pm 0.17 < 1$ . (This 0.19 ± 0.17 estimate has more uncertainty than indicated by the ±0.17, due to the uncertainty in the factor 18 from the  $E_{\rm a}$  estimates.) Therefore, at 5 M concentration of MEA, the base B that deprotonates the zwitterion is 3 to 50 times more likely to be H<sub>2</sub>O than MEA, predicting a rate law for CO<sub>2</sub> consumption that is first order (or close to it) in MEA. Experimental observations have firmly established the rate law to be first order in MEA.<sup>5</sup>

We move on to try to compare  $\Sigma_{B}k_{B}[B]$  to  $k_{-1}$  for the test of the termolecular mechanism. The activation energy in  $k_{-1}$ is likely as small as in  $k_{w}$  (~3 kcal mol<sup>-1</sup>). We obtained a 9 kcal mol<sup>-1</sup> barrier from 1-amine-5-water modeling (Figure 4) but it involved solvent displacement—an act that could be ascribed to the mutual-approach diffusion step instead, with its own effective activation energy,  $E_{a}$ (diffusion). Although we did not observe loss of CO<sub>2</sub> in our simulations of zwitterions in aqueous solution,<sup>37</sup> a large component of the barrier preventing CO<sub>2</sub> loss could simply be  $E_{a}$ (diffusion). The crude models with 0 or 1 H<sub>2</sub>O, which have no forces ascribable to  $E_{a}$ (diffusion), show barriers of less than 2 kcal mol<sup>-1</sup> (Figures 4 and 6). We do not see any evidence that the barrier would be any larger than typical  $E_{a}$ (diffusion) values (3–4 kcal mol<sup>-1</sup>).<sup>46</sup> Since the

 $k_{-1}$  and  $k_{w}$  have similar activation energies, we are forced to compare a unimolecular frequency factor,  $A_{-1}$ , to a bimolecular one,  $A_{w}$ . This challenge is the remaining hurdle if one wishes to use ab initio means to adjudicate between the zwitterion and termolecular mechanisms. Improved calculations of  $\Delta^{\ddagger}G$  in solution (for Eyring rate constants) might be a promising tack in this effort.

Although we did not pursue the mechanism question for other amines, we did find a distinction between proton affinity and  $CO_2$  affinity worthy of report; see the Appendix for details.

# 7. CONCLUSIONS

Quantum chemistry computations with a semicontinuum (cluster + continuum) solvation model have been used to cure longstanding misprediction of aqueous carbamate anion energies in the industrially important  $CO_2$  + aqueous amine reaction. They underscore the need for inclusion of several explicit water molecules for realistic modeling of the reaction pathways. This work is the first ab initio study to establish that the CO<sub>2</sub>+MEA+nH<sub>2</sub>O reaction proceeds as initial complex  $(IC) \rightleftharpoons$  zwitterion  $\rightleftharpoons$  carbamate + hydronium  $\rightleftharpoons$  carbamic acid. This 3-step pathway was only seen when n, the number of explicit water molecules, was increased beyond 1 (n = 5 and n =20 cases, Figure 4). Instances of IC  $\rightleftharpoons$  zwitterion  $\rightleftharpoons$  carbamic acid or IC  $\rightleftharpoons$  carbamic acid result from fewer water molecules, due to relative errors of over 10 kcal mol<sup>-1</sup>, and unfortunately such erroneous results have been presented in the literature often.

A comparison of three mechanisms (zwitterion Z, termolecular T, and acid A) was performed for  $CO_2 + MEA + nH_2O$ , using our best results for the potential energy surface and consideration of concentration effects. While the A mechanism is quickly ruled out, the evaluation of the Z versus T mechanisms requires better estimation of Arrhenius prefactors, since all chemical barriers are predicted to be on the order of 3 kcal mol<sup>-1</sup> or lower for this rapid reaction. At the moment the best ab initio evidence against the termolecular mechanism is the absence of  $CO_2$  loss in recent zwitterion simulations.<sup>37</sup> The new results presented here were sufficiently accurate to demonstrate the correct first-order dependence of  $CO_2$  consumption



Figure 8. Six-atom cycles tested for comparison of carbamate (left) and bicarbonate (right) mechanisms.

versus MEA concentration, using a kinetics analysis of proton abstraction from zwitterions.

As demonstrated in the Appendix, the  $CO_2$  affinity of an amine roughly correlates to its aqueous proton affinity ( $pK_a$ ), but only within an amine class; secondary amines have inherently more  $CO_2$  affinity than a primary amine of identical proton affinity, due to better inductive effects for stabilizing the created anionic charge.

#### APPENDIX

#### Basicity versus CO<sub>2</sub> Affinity

Effects of amine basicity were tested using nine different amines, with a simple 1-amine-1- $H_2O$  model and on both carbamate and bicarbonate formation pathways (Figure 8). The inclusion of the bicarbonate pathway reveals the important difference between  $H^+$  affinity and  $CO_2$  affinity for amines. Reaction paths of the six-atom cycles were pursued through to acid forms.

The initial MP2/aug-cc-pVDZ/IEFPCM//B3LYP/6-31G(d)/ IEFPCM results for MEA are plotted as reaction profiles in Figure 9. The crude 1-amine-1-water semicontinuum model correctly shows that the carbamic acid zwitterion is greatly favored over the "carbonic acid zwitterion," and conversely that bicarbonate is greatly favored over carbamate. (The step-to-step energy profiles suffer from the effects of poor modeling; see caption.)

The MP2/6-31G(d,p)/IEFPCM level of theory, which we preferred for  $pK_a$  prediction,<sup>47</sup> was employed for comparisons of nine different amines. The same two-step pathways were observed. The activation energy ( $E_a$ ) for the first step is of focus here; in the carbamate pathway, the amine attacks CO<sub>2</sub> to make zwitterion, while in the bicarbonate pathway the amine attacks H<sup>+</sup> (of H<sub>2</sub>O) to make protonated amine. Figure 10 displays typical transition states used in the  $E_a$  computation. This level of modeling (1-amine-1-water) will not produce accurate absolute values of  $E_a$ , but it will reveal qualitative trends in  $E_a$  versus pK<sub>a</sub> that should apply to the real systems. All optimized geometries appear in Figures S6 and S7.



**Figure 10.** Examples of optimized transition states used for  $E_a$  calculation for Figure 11. Left: TS for 2-amino-1-propanol attacking CO<sub>2</sub> in carbamate pathway. Right: TS for the same amine attacking H<sup>+</sup> of H<sub>2</sub>O in bicarbonate pathway.



Figure 9. Potential energy surfaces from 1-MEA-1-H<sub>2</sub>O modeling, contrasting bicarbonate formation (circles) versus carbamate formation (triangles). (The zwitterion energies are ~5 kcal/mol too high, and the anion energies are ~20 kcal/mol too high, due to insufficient H<sub>2</sub>O in the model; if these corrections are added, the bicarbonate route would reveal a zwitterion barrier but quite stable anion, in accord with experiments<sup>7</sup> that reveal delayed but dominant formation of bicarbonate vis-à-vis carbamate.).



**Figure 11.** Correlations of  $E_a$  (MP2/6-31G(d,p)/IEFPCM, for the first step of CO<sub>2</sub> + amine + H<sub>2</sub>O as in Figure 8) versus other properties: reaction step endothermicity (upper left), lateness of the transition state for amine approach (upper right), and amine p $K_a$  (lower plots). Diamonds: primary amines. Circles: secondary amines.

For amine attack of  $CO_2$ , the upper two plots of Figure 11 show expected trends: the activation energy increases as the endothermicity of the step increases (upper left), in accord with the Evans/Polanyi Principle, and as it increases with endothermicity the transition state becomes later (upper right), in accord with Hammond's Postulate. The more interesting plots are the lower two plots of  $E_a$  versus  $pK_a$  in Figure 11. In both of these plots, the activation energy generally falls with increasing basicity ( $pK_a$ ) of the amine, as expected. However, in the  $CO_2$  attack plot (bottom left) there are *two curves*, one for primary amines and one for secondary amines; this is not so for H<sup>+</sup> attack (bottom right).

These two curves reveal that secondary amines have inherently greater  $CO_2$  affinity than primary amines when comparing amines of the same H<sup>+</sup> affinity (pK<sub>a</sub>). The negatively charged COO<sup>-</sup> group of the product zwitterion is better stabilized in the secondary amine case because of the better inductive effects of having more alkyl groups on the nitrogen atom. We do not see two distinct curves in the H<sup>+</sup>-attack case (bottom right of Figure 11) because the amines in this mechanism are attacking H<sup>+</sup>, not CO<sub>2</sub>, and hence the pK<sub>a</sub> is the perfect property for correlating to the process involved.

Interestingly, if one plots the data of Crooks and Donnellan<sup>10</sup> for rate constants for carbamate formation versus amine  $pK_{av}$  one does not see these two curves, but a more complex variation that they thought was dominated by steric effects. In fact, they thought that secondary amines would have *lower* CO<sub>2</sub> affinity than primary amines. More work is needed to understand the trends in Crooks' data; apparently more factors than simply CO<sub>2</sub> affinity are involved.

# ASSOCIATED CONTENT

#### **Supporting Information**

Ninety-six pages of geometrical structures and Cartesian coordinates, and one page of  $\Delta H$  discussion for section 6.4.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b06076. (PDF)

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#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Rochelle, G. T. Amine Scrubbing for  $CO_2$  Capture (Perspective). *Science* **2009**, 325, 1652–1654.

(2) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058–6082.

(3) Wang, M.; Lawal, A.; Stephenson, P.; Sidders, J.; Ramshaw, C. Post-combustion  $CO_2$  Capture with Chemical Absorption: A State-of-the-art Review. *Chem. Eng. Res. Des.* **2011**, *89*, 1609–1624.

(4) Li, B.; Duan, Y.; Luebke, D.; Morreale, B. Advances in CO<sub>2</sub> Capture Technology: A Patent Review. *Appl. Energy* **2013**, *102*, 1439–1447.

(5) Versteeg, G. F.; Van Dijck, L. A. J.; Van Swaaij, W. P. M. On the Kinetics Between  $CO_2$  and Alkanolamines Both in Aqueous and Non-Aqueous Solutions. An Overview. *Chem. Eng. Commun.* **1996**, 144, 113–158.

(6) Meldrum, N. U.; Roughton, F. J. W. The State of Carbon Dioxide in Blood. *J. Physiol.* **1933**, *80*, 143–170.

(7) Yang, Q.; Bown, M.; Ali, A.; Winkler, D.; Puxty, G.; Attalla, M. A Carbon-13 NMR Study of Carbon Dioxide Absorption and Desorption with Aqueous Amine Solutions. *Energy Procedia* **2009**, *1*, 955–962.

(8) Caplow, M. Kinetics of Carbamate Formation and Breakdown. J. Am. Chem. Soc. 1968, 90, 6795–6803.

(9) Danckwerts, P. V. The Reaction of  $CO_2$  with Ethanolamines. *Chem. Eng. Sci.* **1979**, *34*, 443–446.

(10) Crooks, J. E.; Donnellan, J. P. Kinetics and Mechanism of the Reaction between Carbon Dioxide and Amines in Aqueous Solution. *J. Chem. Soc., Perkin Trans.* 2 1989, 331–333.

(11) McCann, N.; Phan, D.; Wang, X.; Conway, W.; Burns, R.; Attalla, M.; Puxty, G.; Maeder, M. Kinetics and Mechanism of Carbamate Formation from  $CO_2(aq)$ , Carbonate Species, and Monoethanolamine in Aqueous Solution. *J. Phys. Chem. A* **2009**, *113*, 5022–5029.

(12) Arstad, B.; Blom, R.; Swang, O. CO<sub>2</sub> Absorption in Aqueous Solutions of Alkanolamines: Mechanistic Insight from Quantum Chemical Calculations. *J. Phys. Chem. A* **2007**, *111*, 1222–1228.

(13) Shim, J. G.; Kim, J. H.; Jhon, Y. H.; Kim, J.; Cho, K. H. DFT Calculations on the Role of Base in the Reaction Between  $CO_2$  and Monoethanolamine. *Ind. Eng. Chem. Res.* **2009**, *48*, 2172–2178.

(14) Ismael, M.; Sahnoun, R.; Suzuki, A.; Koyama, M.; Tsuboi, H.; Hatakeyama, N.; Endou, A.; Takaba, H.; Kubo, M.; Shimizu, S.; Del Carpio, C. A.; Miyamoto, A. A DFT Study on the Carbamates Formation through the Absorption of  $CO_2$  by AMP. *Int. J. Greenhouse Gas Control* **2009**, *3*, 612–616.

(15) Xie, H.-B.; Zhou, Y.; Zhang, Y.; Johnson, J. K. Reaction Mechanism of Monoethanolamine with CO<sub>2</sub> in Aqueous Solution from Molecular Modeling. *J. Phys. Chem. A* **2010**, *114*, 11844–11852.

(16) Han, B.; Zhou, C.; Wu, J.; Tempel, D. J.; Cheng, H. Understanding  $CO_2$  Capture Mechanisms in Aqueous Monoethanolamine Via First Principles Simulations. J. Phys. Chem. Lett. **2011**, 2, 522–526.

(17) Yamada, H.; Matsuzaki, Y.; Higashii, T.; Kazama, S. Density Functional Theory Study on Carbon Dioxide Absorption into Aqueous Solutions of 2-Amino-2-Methyl-1-Propanol Using A Continuum Solvation Model. J. Phys. Chem. A **2011**, 115, 3079–3086.

(18) Hwang, G. S.; Stowe, H. M.; Paek, E.; Manogaran, D. Reaction Mechanisms of Aqueous Monoethanolamine with Carbon Dioxide: a Combined Quantum Chemical and Molecular Dynamics Study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 831–839.

(19) Rick, S. W.; Berne, B. J. The Aqueous Solvation of Water: A Comparison of Continuum Methods with Molecular Dynamics. *J. Am. Chem. Soc.* **1994**, *116*, 3949–3954.

(20) Wagner, M.; von Harbou, I.; Kim, J.; Ermatchkova, I.; Maurer, G.; Hasse, H. Solubility of Carbon Dioxide in Aqueous Solutions of Monoethanolamine in the Low and High Gas Loading Regions. *J. Chem. Eng. Data* **2013**, *58*, 883–895.

(21) Astarita, G.; Marrucci, G.; Gioia, F. The Influence of Carbonation Ratio and Total Amine Concentration on Carbon Dioxide Absorption in Aqueous Monoethanolamine Solutions. *Chem. Eng. Sci.* **1964**, *19*, 95–103.

(22) Lim, C.-H.; Holder, A. M.; Musgrave, C. B. Mechanism of Homogeneous Reduction of  $CO_2$  by Pyridine: Proton Relay in Aqueous Solvent and Aromatic Stabilization. *J. Am. Chem. Soc.* **2013**, 135, 142–154.

(23) Sada, E.; Kumazawa, H.; Han, Z. Q.; Matsuyama, H. Chemical Kinetics of the Reaction of Carbon Dioxide with Ethanolamines in Nonaqueous Solvents. *AIChE J.* **1985**, *31*, 1297–1303.

(24) Littel, R. J.; Versteeg, G. F.; van Swaaij, W. P. M. Kinetics of Carbon Dioxide with Primary and Secondary Amines in Aqueous Solutions. I. Zwitterion Deprotonation Kinetics for DEA and DIPA in Aqueous Blends of Alkanolamines. *Chem. Eng. Sci.* **1992**, *47*, 2027–2035.

(25) Donaldson, T. L.; Nguyen, N. Y. Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 260–266. (26) Chen, X.; Rochelle, G. T. Modeling of CO<sub>2</sub> Absorption Kinetics in Aqueous 2-Methylpiperazine. *Ind. Eng. Chem. Res.* **2013**, *52*, 4239–4248.

(27) Ume, C. S.; Ozturk, M. C.; Alper, E. Kinetics of  $CO_2$  Absorption by a Blended Aqueous Amine Solution. *Chem. Eng. Technol.* **2012**, *35*, 464–468.

(28) Littel, R. J.; Versteeg, G. F.; Van Swaaij, W. P. M. Kinetics of  $CO_2$  with Primary and Secondary Amines in Aqueous Solutions. II. Influence of Temperature on Zwitterion Formation and Deprotonation Rates. *Chem. Eng. Sci.* **1992**, *47*, 2037–2045.

(29) Sandbeck, D. J. S.; Kuntz, C. M.; Luu, C.; Mondor, R. A.; Ottaviano, J. G.; Rayer, A. V.; Sumon, K. Z.; East, A. L. L. Challenges in Predicting  $\Delta_{rxn}$ G in Solution: The Mechanism of Ether-Catalyzed Hydroboration of Alkenes. *J. Phys. Chem. A* **2014**, *118*, 11768–11779. (30) Xie, H.-B.; He, N.; Song, Z.; Chen, J.; Li, X. Theoretical Investigation on the Different Reaction Mechanisms of Aqueous 2-Amino-2-methyl-1-propanol and Monoethanolamine with CO<sub>2</sub>. *Ind.* 

*Eng. Chem. Res.* **2014**, *53*, 3363–3372. (31) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999–3093.

(32) Cramer, C. J.; Truhlar, D. G. A Universal Approach to Solvation Modeling. *Acc. Chem. Res.* **2008**, *41*, 760–768.

(33) Klamt, A.; Schuurmann, G. COSMO: A New Approach to Dielectric Screening in Solvents with Explicit Expressions for the Screening Energy and its Gradient. *J. Chem. Soc., Perkin Trans.* 2 1993, 799–805.

(34) Faurholt, C. Etudes sur les Solutions Aqueuses d'Anhydride Carbonique et d'Acide Carbonique. *J. Chim. Phys.* **1924**, *21*, 400–455. (35) Wang, T.-T.; Bishop, S. H.; Himoe, A. Detection of Carbamate as A Product of the Carbamate Kinase-Catalyzed Reaction by Stopped Flow Spectrophotometry. *J. Biol. Chem.* **1972**, *247*, 4437–4440.

(36) Davran-Candan, T. DFT Modeling of  $CO_2$  Interaction with Various Aqueous Amine Structures. J. Phys. Chem. A **2014**, 118, 4582–4590.

(37) Sumon, K. Z.; Henni, A.; East, A. L. L. Molecular Dynamics Simulations of Proposed Intermediates in the  $CO_2$  + Aqueous Amine Reaction. *J. Phys. Chem. Lett.* **2014**, *5*, 1151–1156.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

(39) Becke, A. D. Density-Functional Thermochemistry. III. The Role Of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(40) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(41) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Ab Initio* Study of Solvated Molecules: A New Implementation of The Polarizable Continuum Model. *Chem. Phys. Lett.* **1996**, 255, 327–335.

(42) Baker, J. An Algorithm for the Location of Transition-States. J. Comput. Chem. 1986, 7, 385–395.

(43) Reed, C. A. Myths about the Proton. The Nature of  $H^+$  in Condensed Media. Acc. Chem. Res. 2013, 46, 2567–2575.

(44) Alper, E. Reaction Mechanism and Kinetics of Aqueous Solutions of 2-Amino-2-methyl-1-propanol and Carbon Dioxide. *Ind. Eng. Chem. Res.* **1990**, *29*, 1725–1728. Also see ref 7 for explicit <sup>13</sup>C-NMR detection of early onset of carbamate for the reaction of the 1,3-diol version of AMP.

(45) Versteeg, G. F.; Oyevaar, M. H. The Reaction between  $CO_2$  and Diethanolamine at 298 K. *Chem. Eng. Sci.* **1989**, *44*, 1264–1268.

(46) Rice, S. A. Diffusion-Limited Reactions. In *Comprehensive Chemical Kinetics*; Elsevier: New York, 1985; Vol. 25.

(47) Sumon, K. Z.; Henni, A.; East, A. L. L. Predicting pK<sub>a</sub> of Amines for CO<sub>2</sub> Capture: Computer versus Pencil-and-Paper. *Ind. Eng. Chem. Res.* **2012**, *51*, 11924–11930.