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LETTER

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CO_2 Capturing Mechanism in Aqueous Ammonia: NH_3-Driven Decomposition−Recombination Pathway

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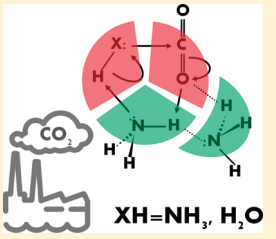
Supporting Information

ABSTRACT: Capturing CO_2 by aqueous ammonia has recently received much attention due to its advantages over other state-of-the-art CO_2-capture technology. Thus, understanding this CO_2-capturing mechanism, which has been causing controversy, is crucial for further development toward advanced CO_2 capture. The CO_2 conversion mechanism in aqueous ammonia is investigated using ab initio calculations and kinetic simulations. We show full details of all reaction pathways for the NH_3-driven conversion mechanism of CO_2 with the pronounced effect of microsolvation. Ammonia performs multiple roles as reactant, catalyst, base, and product controller. Both carbamic and carbonic acids are formed by the ammonia-driven trimolecular mechanism. Ammonia in microsolvation makes the formation of carbamic acid kinetically preferred over carbonic acid. As the concentration of CO_2 increases, the dominant product becomes carbonic acid. The conversion from carbamic acid into carbonic acid occurs through the decomposition−recombination pathway. This understanding would be exploited for the optimal CO_2 capture technology.



SECTION: Energy Conversion and Storage

Despite numerous debates it is widely accepted that the accumulation of greenhouse gases in the atmosphere causes an enhanced greenhouse effect, leading to climate change and global warming.[1,2] Hence, there is major scientific interest in preventing the release of CO_2 and lowering its concentration in the atmosphere. The development of technologies such as capturing and storing CO_2 for various commercial applications[3−7] provides a midterm solution to reduce environmental problems, allowing us to use carbon-based fuels until an alternative new energy source matures.[8−12] Currently, the amine scrubbing process is the leading technology for CO_2 capture, and this process is predicted to be the dominant technology for CO_2 capture from coal-fired power plants in 2030.[13,14] An alternative advanced technique, capturing CO_2 by aqueous ammonia (Scheme 1),[15−18] has recently received much attention due to its advantages over the conventional amine-based technique. However, few reports dealing with the ammonia process are available. Although there are papers that demonstrate the CO_2 conversion mechanism in the pure aqueous system,[19,20] there is no clear understanding of the reaction mechanism of CO_2 in aqueous ammonia solutions, while there are some incorrect speculations on this reaction mechanism. There is thus an urgency to detail the conversion mechanism of CO_2 in aqueous ammonia, with this study being the first to elucidate details of the mechanism. In both fundamental and applied points of view, this study provides important information about CO_2 capture for future green chemistry.

CO_2 in the aqueous phase exists almost entirely in the form of hydrated CO_2 and 1% H_2CO_3.[19] However, in the case of CO_2 in aqueous ammonia solutions, it exists primarily as a converted form of NH_2COOH or H_2CO_3, with these molecules primarily in ionic forms due to their acid−base behavior, with the dominant product depending on the ratio of reactants.[18] When the amounts of CO_2 and NH_3 are comparable, H_2CO_3 is the main product in solution; however, when an excess of NH_3 exists, NH_2COOH becomes the main product in solution.

For the formation of carbamates, originally, a two-step zwitterion mechanism had been suggested.[21,22] However, this mechanism was proved to be unlikely, and rather, a synchronous trimolecular mechanism was proposed.[23] When CO_2 reacts with NH_3 to form a carbamate in the aqueous phase, the bond formation between the C in CO_2 and the N in NH_3 takes place simultaneously with a proton transfer to a nearby base (B), $CO_2 + NH_3 + B \leftrightarrow NH_2COO^- + BH^+$. However, the previous investigations have been limited only to the formation of the carbamate species.[23−25] The function of the catalytic base is important, but its understanding remains uncertain. The role of microsolvation around the reaction core has never been considered in the past studies. The details of the reaction mechanism for CO_2 in aqueous ammonia, being dynamically controlled by the ratio of reactants, are not clearly understood. In this regard, we try to shed light on the comprehensive reaction mechanism of CO_2 in aqueous ammonia, using ab initio calculations and kinetic simulations. Finally, the NH_3-driven catalytic conversion processes of CO_2 with an effective perturbation by microsolvation are shown in full detail for all reaction pathways, which include the

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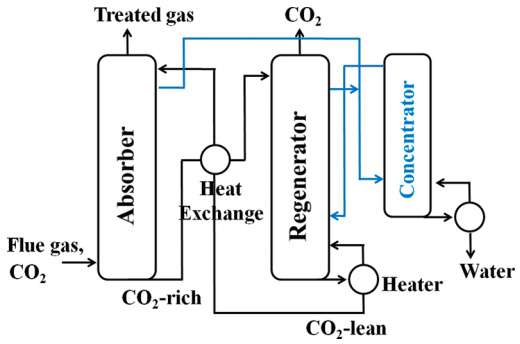
conversion processes of CO_2 into either carbamic or carbonic acids and between carbamic and carbonic acids.

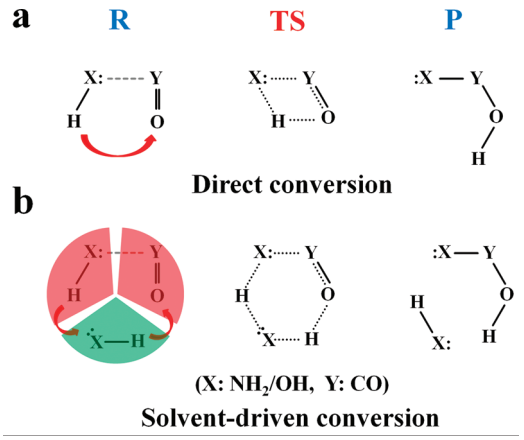
To properly model the nanoscopic nature of the reaction region of CO_2 in aqueous ammonia, we investigate the potential energy surfaces of reaction pathways from the decomposed combination of CO_2, NH_3, and H_2O to either NH_2COOH or H_2CO_3 with a varying number of active solvent molecules and with the change in molar ratio of NH_3/H_2O. Then, the catalytic efficiencies are compared. In bulk, the decomposed reactants exist primarily in molecular forms, while the products, NH_2COOH or H_2CO_3, are primarily in ionic forms due to their acid−base behavior. At the initial stage of the CO_2 conversion process, the reaction is like a gas-phase one at the interface between gas and solution because CO_2 is hardly soluble at the moment that the solution is spread over CO_2; thus, the transition state is also almost the gas-like state. Moreover, at the final stage of the reaction after passing the transition barrier, the product is much more stable than the reactant in solution. Thus, this CO_2 conversion takes place by overcoming an early transition state, which then should be similar to the gas-phase transition state. Therefore, our model calculation with molecular clusters successfully depicts the reactant mechanism in bulk systems. Figure S1 in Supporting Information and Figures 1 and 2 show the potential energy surface of the reactions, $H_2CO_3 + (m - n - 1)H_2O + nNH_3 \leftrightarrow CO_2 + (m - n)H_2O + nNH_3 \leftrightarrow$

Scheme 1. Schematic Flow Diagram of the POSCO/RIST Pilot Plant for CO_2 Capture Using Aqueous Ammonia[a]



[a] Flue gas containing CO_2 enters into the absorber. Aqueous ammonia selectively absorbs CO_2 and forms a CO_2-rich solution. The solution is then pumped to the regenerator and heated up to form pure CO_2. As a result, the pure CO_2 is released at the top of the regenerator. The CO_2-lean solution is recycled back to the absorber and reused. The concentrator is used for the ammonia vapor recovery. The POSCO/RIST Pilot Plant can treat flue gas at a rate of 1000 N m^3/h, producing 3000 tons of CO_2 annually (see Supporting Information).

Scheme 2. Schematic Views of Direct and Solvent-Driven Conversions into H_2CO_3 and NH_2COOH (P) from the Decomposed Reactants (R)[a]



[a] TS: transition state; X = NH_2/OH and Y = CO.

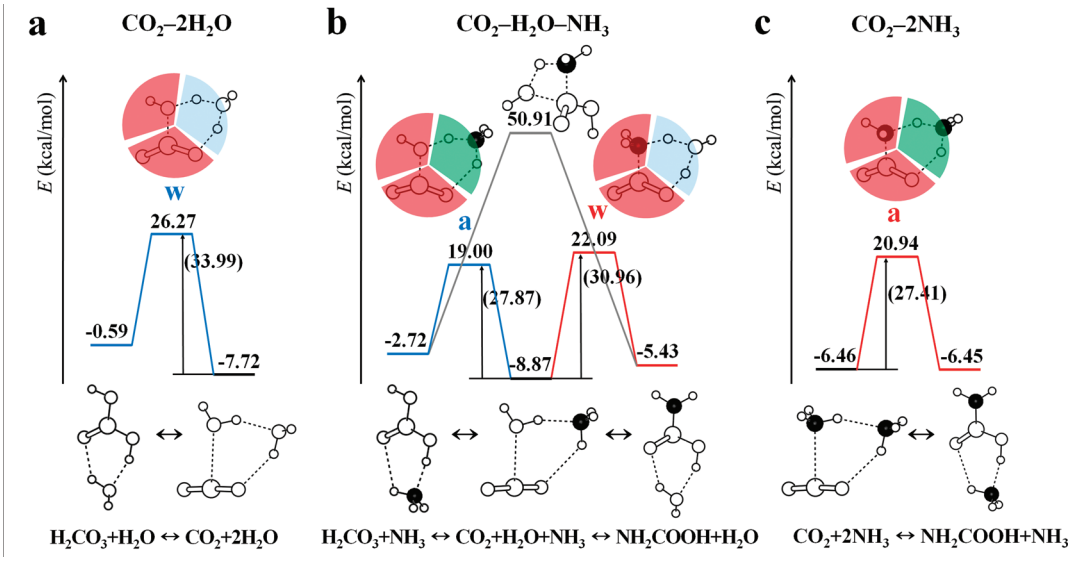


Figure 1. Potential energy surfaces of the reaction pathways for conversions between the decomposed reactants and the acidic products H_2CO_3 and NH_2COOH in complexes $CO_2-(2-n)H_2O-nNH_3$. The ratio of NH_3/H_2O is changed ($n = 0-2$ in a−c). The reactions occur along the single water or ammonia catalytic pathways (**w** or **a**). The energies along the pathways are obtained from CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ///MP2/aug-cc-pVDZ relative to the decomposed reactants (Supporting Information). Conversion into H_2CO_3 is represented by the blue line, and conversion into NH_2COOH is presented by the red line. The one-step exchange pathway between H_2CO_3 and NH_2COOH is represented by the gray line. A N atom is given in black, H by a small circle, O by a medium circle, and C by a large circle.

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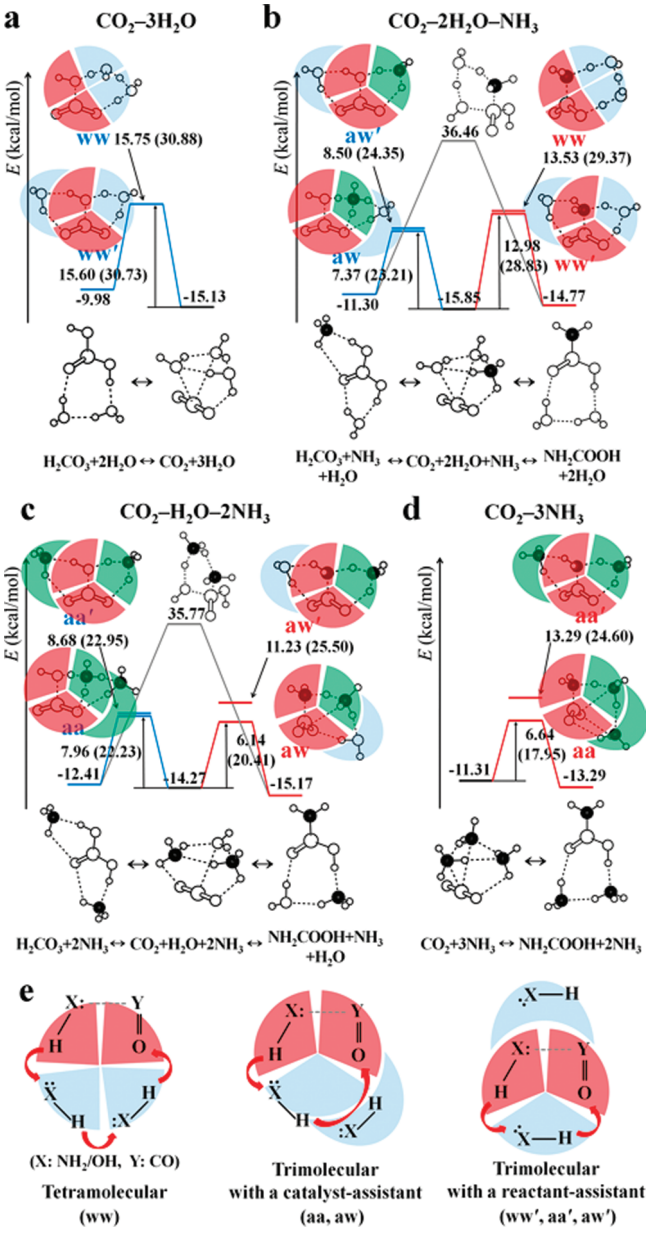

Figure 2. Potential energy surfaces of the reaction pathways for conversions between the decomposed reactants and the acidic products H_2CO_3 and NH_2COOH in complexes $CO_2-(3-n)H_2O-nNH_3$. The ratio of NH_3/H_2O ($n = 0-3$) changes in (a–d). The reactions occur along the double water/water, ammonia/water, or ammonia/ammonia catalytic pathways (**ww**/**ww**′, **aw**/**aw**′, or **aa**/**aa**′). The **ww**-type reaction occurs via a single-step tetramolecular mechanism, the **aa**- and **aw**-type reactions occur via a trimolecular mechanism with a catalyst assistant, and **ww**′-, **aa**′-, and **aw**′-type reactions occur via a trimolecular mechanism with a reactant assistant. Schematic views of these mechanisms are shown in (e). The relative energies are obtained from CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ///MP2/aug-cc-pVDZ. Conversion into H_2CO_3 is represented by a blue line, and conversion into NH_2COOH is presented by a red line. The one-step exchange pathway between H_2CO_3 and NH_2COOH is represented by a gray line. A N atom is given in black, H by a small circle, O by a medium circle, and C by a large circle.

$NH_2COOH + (m-n)H_2O + (n-1)NH_3$ ($n = 0-m$, where $m = 1-3$). The trends of activation energy (E_a) and reaction energy (ΔE) are presented in Figure 3. For each barrier on the reaction pathway, the microcanonical rate constant is obtained using Rice–Ramsperger–Kassel–Marcus (RRKM) theory,[26] with the microcanonical rate constant obtained being converted to the thermal rate constant (k). Tunnelling corrections are included by utilizing the Skodje and Truhlar approximations.[27]

Extremely Rare Direct Conversion. In $CO_2-(1-n)H_2O-nNH_3$ ($n = 0-1$), the conversion from $CO_2 + NH_3/CO_2 + H_2O$ to NH_2COOH/H_2CO_3 is a reversible process, as shown in Figure S1 (Supporting Information). Initially, the reactant $CO_2 + NH_3/CO_2 + H_2O$ is characterized by the interaction between $C^{\delta+}$ in CO_2 and $N^{\delta-}/O^{\delta-}$ in NH_3/H_2O. In the conversion to NH_2COOH/H_2CO_3, $CO_2 + NH_3/CO_2 + H_2O$ forms a C–N/O bond with a simultaneous proton crossing into an electron-rich O site in CO_2. However, without a catalyst, the ring strain of the transition state leads to quite a high energy barrier. The E_a's of the $CO_2 + NH_3 \rightarrow NH_2COOH$ and $CO_2 + H_2O \rightarrow H_2CO_3$ reactions are 51.7 and 47.2 kcal/mol, respectively. The k's at 300 K are 3×10^{-18} and 3×10^{-21} s^{-1}, respectively, indicating that these direct (**d**) conversion processes are extremely rare events. As illustrated in Scheme 2, the conversion process of CO_2 into either NH_2COOH or H_2CO_3 in an aqueous ammonia solution happens via the catalytic effect of solvent molecules.

Catalytic Base NH_3. The activation energy barrier for the reaction of CO_2 with H_2O/NH_3 drastically decreases with the inclusion of a single catalytic H_2O (**w**) or NH_3 (**a**) to the complexes of $CO_2-(2-n)H_2O-nNH_3$ ($n = 0-2$) (Figures 1 and 3). The catalytic solvent molecule acts as a proton shuttle, thereby forming a no-strain trimolecular transition state. Due to the higher basicity of NH_3 over H_2O, the **a**-type pathway has a lower energy barrier than the **w**-type pathway. An inclusion of one NH_3 molecule to the reactions $H_2O + CO_2 \rightarrow H_2CO_3$ and $NH_3 + CO_2 \rightarrow NH_2COOH$ yields E_a's of 27.9 and 27.4 kcal/mol, respectively. The energy barriers for the two reactions are lower than the **d** pathway by 23.8 (46%) and 19.8 kcal/mol (42%) respectively, while the rates are faster by a factor of 10^{11} and 10^7 at 300 K, respectively. The inclusion of one H_2O molecule reduces the energy barriers for the reactions by 34%. The conversion of hydrated CO_2 into H_2CO_3 occurs by the catalysis of water molecules in the aqueous phase.[19,20] However, in the case of the reaction of CO_2 in aqueous ammonia, the NH_3-driven pathway is favored.

Pronounced Effect of Microsolvation on the Formation of NH_2COOH. The effects of the inclusion of two active solvent molecules are investigated on the $CO_2-(3-n)H_2O-nNH_3$ ($n = 0-3$) complexes in Figures 2 and 3. The first solvent molecule acts as a proton shuttle, forming a trimolecular reaction. With the introduction of the second solvent molecule, two different types of reaction channels compete with each other.[20] First, the trimolecular reaction is aided by the second solvent molecule near the site of the proton transfer. Thus, depending on the ratio of NH_3/H_2O, three different types of H-bonded solvent networks are formed, (i) $H^+\cdots H_2O\cdots H_2O\cdots O^-$ (**ww**), (ii) $H^+\cdots NH_3\cdots H_2O\cdots O^-$ (**aw**), and (iii) $H^+\cdots NH_3\cdots NH_3\cdots O^-$ (**aa**). Second, the trimolecular reaction is aided by the second solvent molecule, denoted by a prime (′), *on the opposite side* to the site of the proton transfer forming two fused-trimeric ring structures, (iv) $H_2O\cdots XH^+\cdots H_2O\cdots O^-$ (**ww**′), (v) $H_2O\cdots XH^+\cdots NH_3\cdots O^-$ (**aw**′), and (vi) $NH_3\cdots XH^+\cdots NH_3\cdots O^-$ (**aa**′), where X = NH_2/OH. The second active solvent molecule can assist the reaction either as a direct participant forming a tetramolecular intermediate or as a spectator molecule around the reaction core.

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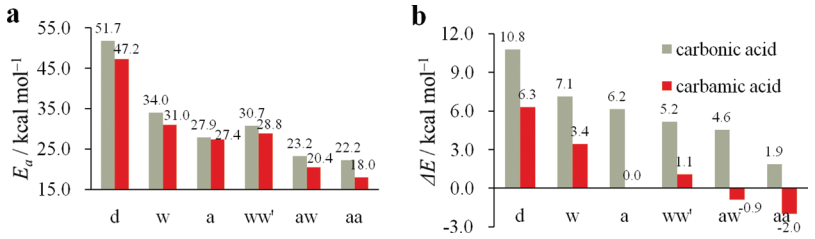

Figure 3. Activation energies (E_a) and reaction energies (ΔE) obtained from the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ///MP2/aug-cc-pVDZ level of theory for H_2CO_3 and NH_2COOH formation by the direct pathway (**d**), the one catalytically active solvent molecule pathway (**w**, H_2O; **a**, NH_3), and the two catalytically active molecule pathways (**ww′**, $2H_2O$; **aw**, $NH_3{-}H_2O$; **aa**, $2NH_3$).

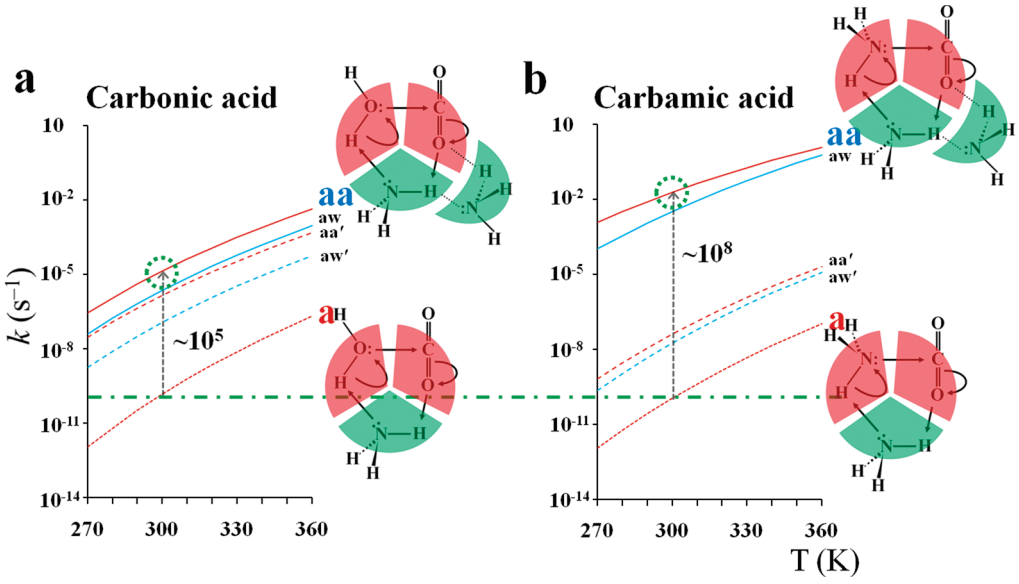

Figure 4. Rate constants for the formation of H_2CO_3 (a) and NH_2COOH (b) from the decomposed reactants. The **aa**-type pathway is dominant for both reactions. Along the **a**-type pathway, the formations of H_2CO_3 and NH_2COOH have similar reaction rates. Along the **aa**-type pathway, the formation of NH_2COOH becomes kinetically ~3 orders faster in magnitude than the formation of H_2CO_3. The contribution ratio of each **aa**/**aw**/**aa′**/**aw′** pathway ($k_{aa}/k_{aw}/k_{aa'}/k_{aw'}$ at 300 K) is 1:0.2:0.1:0.01 for the formation of H_2CO_3, while the contribution ratio of each **aa**/**aw** pathways (k_{aa}/k_{aw} at 300 K) is 1:0.2 for the formation of NH_2COOH, with the contributions of the **aa′** and **aw′** pathways being insignificant. These indicate that the catalytic effects of ammonia and water molecules in the first solvation shell in the conversion process for the carbonic and carbamic acids are very different from each other.

For the **ww**-type, triple proton transfer occurs simultaneously via the H-bonding chain of two catalytic H_2O molecules through a synchronous tetramolecular mechanism. However, for the **aa**- and **aw**-types, a proton in a transient NH_4^+ moves directly into an O site in CO_2, thereby not mediating the next NH_3 or H_2O molecule. This means that only the nearest NH_3 molecule participates directly in the proton shuttle reaction. The other NH_3 or H_2O molecule, which is H-bonded to a catalyst, assists the reaction by stabilizing transition states near the catalyst. This demonstrates the **a**-type trimolecular mechanism with a catalyst assistant. For the **ww′**-, **aa′**-, and **aw′**-types, only the nearest solvent molecule is directly involved in the proton shuttle reaction, in a way similar to that seen for **aa**- and **aw**-types. The other solvent molecule stabilizes the transition state on the opposite side of the proton transfer by being H-bonded to a reactant. This shows a trimolecular mechanism with a reactant assistant. Schematic illustrations of these mechanisms are presented in Figure 2e.

Among various pathways, the **aa**-type shows the lowest-energy pathway and the most accelerated rate constant. The E_a's of the **aa**-type pathway for the formation of H_2CO_3 and NH_2COOH are 22.2 and 17.9 kcal/mol, respectively; the k's at 300 K are 1×10^{-5} and 2×10^{-2} s^{-1}, respectively, showing an increase of a factor of ~10^5 and ~10^8 compared to the a pathway (Figure 4). This illustrates that microsolvation of the reaction core by NH_3 molecules effectively aids the **a**-type trimolecular reaction. By neglecting solvation, the NH_2COOH and H_2CO_3 formations show nearly isoenergetic activation barriers and similar reaction rates along the **a** pathway. Due to the substantial effect of microsolvation on the formation of NH_2COOH compared to that of H_2CO_3, the formation of NH_2COOH becomes kinetically faster than that of H_2CO_3.

Also, we should note that the **aw**-, **aa′**-, and **aw′**-types contribute to the conversion reaction into H_2CO_3 with $k_{aa}/k_{aw}/k_{aa'}/k_{aw'}$ = 1:0.2:0.1:0.01 at 300 K. The **aw**, **aa′**, and **aw′** pathways which form H_2CO_3 require ~1−2 kcal/mol higher activation energies than the **aa** pathway. On the other hand, only the **aw** pathway contributes to the conversion reaction into NH_2COOH (k_{aa}/k_{aw} = 1:0.2 at 300 K), while the contributions of the **aa′** and **aw′** pathways are insignificant. The **aa′** and **aw′** pathways which form NH_2COOH require ~6−7 kcal/mol higher energies than the **aa** pathway. In the case of H_2CO_3, the effect of microsolvating the trimolecular reaction both near the site and on the opposite side of the proton transfer are important. However, in the case of NH_2COOH, microsolvating the trimolecular reaction near the site

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of the proton transfer aids the reaction more effectively than that on the opposite side of the proton transfer.

Applying implicit solvents utilizing the self-consistent reaction field (SCRF) theory with the isodensity surface polarized continuum model (IPCM),[28] polar transition states are more stabilized, which leads to the lowering of the E_a's by ∼11 kcal/mol. This results in an enhancement of k's by an order of ∼8 in magnitude, where the $k_{\mathbf{aa}+\mathrm{IPCM}}$'s toward H_2CO_3 and NH_2COOH become $\sim 10^3$ and $\sim 10^6\ s^{-1}$, respectively. As the $k_{\mathbf{aa}+\mathrm{IPCM}}$ is the reaction rate in a unimolecular process, an overall reaction rate constant (k_{overall}) is obtained by multiplying the $k_{\mathbf{aa}+\mathrm{IPCM}}$ by the probability of the formation of an **aa** cluster in solution ($P_{\mathbf{aa}} \approx 10^{-2}$, Supporting Information). Then, the k_{overall}'s for H_2CO_3 and NH_2COOH are ∼10 and $\sim 10^4\ s^{-1}$, respectively. These results are in good agreement with the experimental rate constants for the reaction of CO_2 in aqueous ammonia solutions ($\sim 10^3\ s^{-1}$).[29] So far, no experimental comparison of kinetic rates between the formation of NH_2COOH and H_2CO_3 from the decomposed reactants has been made. From our calculations, we have shown that the formation of NH_2COOH is kinetically faster than that of H_2CO_3 due to a more pronounced effect of microsolvation.

From NH_2COOH to H_2CO_3 via the Decomposition−Recombination Pathway. While only a small fraction of hydrated CO_2 converts into H_2CO_3 (K_{eq} at 300 K = $\sim 10^{-3}$) in the aqueous phase, the majority of CO_2 converts into NH_2COOH or H_2CO_3 (K_{eq} at 300 K = $\sim 10^3$) in the aqueous ammonia phase. Basic ammonia, which acts as a catalyst in the conversion process, stabilizes the acidic product formed. With the addition of two active H_2O molecules, we observe the decreases of ΔE's in the formation of NH_2COOH and H_2CO_3 by ∼5 kcal/mol, while the addition of two active NH_3 molecules leads to the decreases of ΔE's by ∼8−9 kcal/mol, compared to the **d** pathway (Figure 3b). Treating the basic bulk implicitly, the SCRF/IPCM calculation for the **aa** pathway leads to the decreases of ΔE's by ∼12 kcal/mol. Then, the $\Delta E_{\mathbf{aa}+\mathrm{IPCM}}$'s for the formation of NH_2COOH and H_2CO_3 are ∼−6 and ∼−1 kcal/mol, respectively. This shows that the formation of NH_2COOH is both kinetically and energetically favored over that of H_2CO_3 from decomposed reactants.

Thus, when CO_2 enters into aqueous ammonia solutions, carbamic acid is the main species in the initial stage, while it exists primarily in its conjugate form, $NH_3 + NH_3 + CO_2 \rightarrow NH_4^+ + NH_2COO^-$. In this process, one NH_3 molecule acts as a reactant, and the other NH_3 acts as a catalytic base in the trimolecular reaction. NH_3 moleucles in the microsolvation shell effectively aid the reaction. When the molar ratio of CO_2 to NH_3 is greater than 1:2, the NH_3 reactant path is blocked, while the energetically favored NH_3 catalytic path is observed. As a result, the formation of bicarbonate species (conjugate form of carbonic acid) starts to accelerate via the reaction $NH_3 + H_2O + CO_2 \rightarrow NH_4^+ + HCO_3^-$, while at the same time, the formation of carbamate species starts to diminish. Thus, one molar equivalent of CO_2 is captured by one molar equivalent of NH_3 instead of two molar equivalents of NH_3. Regarding the ammonia scrubbing process of CO_2 capture in Scheme 1, the loading of CO_2 into the regenerator in the form of carbonic acid will be more beneficial than the loading in the form of carbamic acid in terms of loading capacity. Also, the less stable C−O bond in carbonic acid requires a lower energy to break than the C−N bond in carbamic acid during the thermal regeneration step.

Transformation from carbamate species to bicarbonate species can occur through two pathways, (i) via the decomposition−recombination path (red−blue line in Figures 1 and 2) or (ii) via the one-step exchange path (gray line in Figures 1 and 2). In the one-step path, NH_2COOH is transformed into H_2CO_3 through the process where the C in NH_2COOH is attacked by O in H_2O to form a C−O bond with a simultaneous dissociation of a C−N bond, producing NH_3 and H_2CO_3, with the bound O···C···N structure as the transition state. However, the very high energy barrier of this one-step pathway indicates that the conversion from NH_2COOH to H_2CO_3 takes place through the decomposition−recombination pathway.

In summary, we have detailed the comprehensive reaction mechanism of CO_2 in aqueous ammonia, showing several roles of NH_3. Regarding the formation of both carbamic and carbonic acids, the H_2O catalytic trimolecular pathway has been considered, while the bases play a certain role. However, we have shown that the reactions take place mainly along the NH_3 catalytic trimolecular pathway. However, via the NH_3-driven trimolecular reaction in the absence of solvation molecules, the formation of carbamic and carbonic acids requires similar activation energy barriers and reaction rates. Thus, a second active solvent molecule is considered. In our calculation, this solvent molecule does not participate in the proton shuttle reaction directly but instead effectively assists the trimolecular reaction in the microsolvation shell. The differences between the various microsolvation effects in the conversion processes were investigated. We predict that NH_3 molecules in the first microsolvation shell aid the conversion process of carbamic acid more effectively than that of carbonic acid, resulting in the formation of carbamic acid becoming kinetically faster than that of carbonic acid. When the concentration of carbon dioxide is low in aqueous ammonia solutions, the carbamate species is the main product due to its higher stability over the bicarbonate species. In this process, two molar equivalents of ammonia capture one molar equivalent of carbon dioxide, with one ammonia molecule acting as a reactant and the other ammonia molecule acting as a catalytic base. Thus, as the concentration of CO_2 increases, ammonium bicarbonate becomes the dominant species. In this process, one molar equivalent of ammonia captures one molar equivalent of carbon dioxide. The conversion process from carbamate into bicarbonate does not occur through the direct pathway but through the decomposition−recombination pathway. This has never been demonstrated before. This study provides useful information not only for the development of improved CO_2 capture by ammonia or amine scrubbing but also for the design of futuristic techniques for CO_2 capture and utilization[7,30,31]

■ ASSOCIATED CONTENT

Supporting Information. Computational methods, schematic flow diagram of the pilot plant for the CO_2 capture process using aqueous ammonia, and calculated IR Spectra for all transition states and minima. This material is available free of charge via the Internet at http://pubs.acs.org.

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