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Ab Initio Study of CO$_2$ Capture Mechanisms in Monoethanolamine Aqueous Solution: Reaction Pathways from Carbamate to Bicarbonate

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Abstract

Ab initio calculations combined with the continuum solvation model have been conducted to obtain complete reaction pathways involved in the CO$_2$ capture into monoethanol (MEA) aqueous solution. We have investigated the reaction pathways for the decomposition of MEA carbamate into bicarbonate. Although the already known pathways invoke a generation of free CO$_2$(aq), we are concerned with another mechanism which does not involve such an intermediate. The neutral hydrolysis of the MEA carbamate was found to be a slow reaction that has an essentially two-step nature. We propose an alternative pathway that involves the carbamic acid as an intermediate that undergoes an alkaline hydrolysis leading to the formation of bicarbonate. Taking account of the novel reaction pathways elucidated here as well as the established routes for the formation of carbamate and bicarbonate may lead to a comprehensive understanding and a better prediction of the chemical CO$_2$ capture process under specific conditions including pH (concentration of amine) and partial pressure of CO$_2$.

Keywords: CO$_2$ capture; amine absorbent; monoethanolamine; carbamate; bicarbonate; reaction rate; quantum chemistry

1. Introduction

Chemical absorption is currently one of the most promising technologies to capture CO$_2$. In practical applications of amine-based CO$_2$ capture technology, it is highly demanded to reduce the capture cost. Since a large portion of the capture cost is raised by the absorbent regeneration energy, developing new

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absorbents with preferred features (high absorption rate, high absorption capacity, and low heat of reaction) would be a most effective way to overcome the current status. In order to achieve this, it is essential to understand complete reaction pathways involved in the CO_2 capture process.

Monoethanolamine (MEA) is the most common amine examined for CO_2 capture. Possible reaction pathways involved in the CO_2 capture into aqueous MEA solutions are illustrated in Figure 1. The direct reaction of dissolved CO_2 with MEA produces a carbamate anion as represented by eq. (1):

$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+, \tag{1}$$

where -R stands for the $-CH_2CH_2OH$ group. To date, there have been a number of experimental [1] and theoretical [2-6] studies on the mechanism for the reaction (1). The recent high-level theoretical studies [5] support the two-step zwitterion mechanism consisting of reactions (1a) and (1b) shown in Figure 1, in which (1a) is the rate-determining step. The reaction product can also be a bicarbonate that is known to be a dominant product for sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP). Bicarbonate can be formed via the following reactions:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{2}$$

$$CO_2 + H_2O + RNH_2 \leftrightarrow HCO_3^- + RNH_3^+ \tag{3}$$
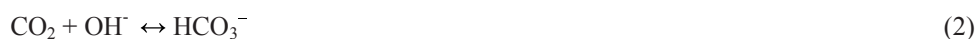
In the reaction (3), amine acts as a base-catalyst for the hydration of CO_2 as can be recognized from the transition-state structures obtained via the quantum chemical calculations [7,8].

In addition to the above mentioned reactions, the hydrolysis of carbamate (reaction (4)) is frequently invoked in the analyses of the CO_2 absorption processes[1]:

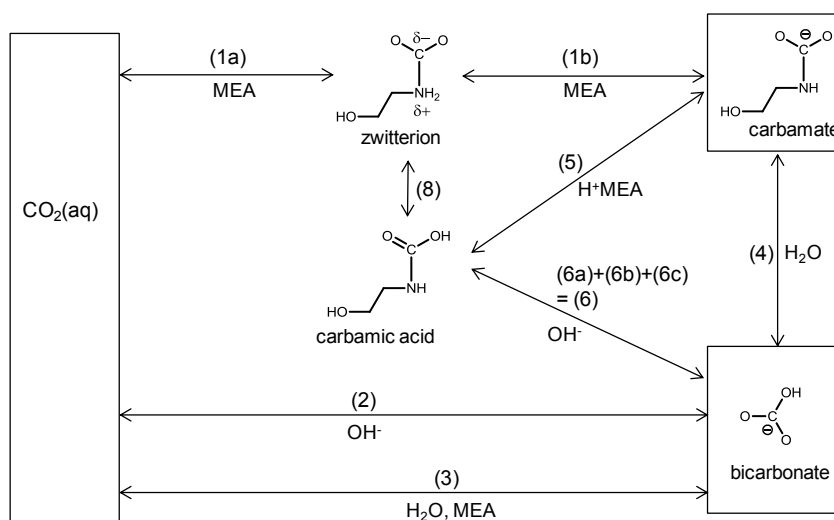$$RNHCOO^- + H_2O \leftrightarrow HCO_3^- + RNH_2. \tag{4}$$

Figure 1. Schematic representation of the reaction pathways involved in the CO_2 capture into aqueous MEA solutions.

Since the performance of the primary and secondary amines are closely related to the product ratio of bicarbonate to carbamate [9], it is essential to understand the mechanism of reaction (4) for the development of high performance absorbents. Recently, the kinetics of the formation and decomposition of MEA carbamate at high pH have been studied by the ^{1}H NMR spectroscopy [10]. These experiments provide an important contribution to the comprehensive understanding of CO_2 absorption reactions.

On the other hand, there are no theoretical studies on the mechanism for the reaction (4) except our preliminary one [8] in which we have reported the transition-state geometry of the reaction (4) for AMP as obtained by the DFT calculations. In this study, we perform a detailed analysis of the mechanism for this reaction of the MEA carbamate. Moreover, taking account of the relatively high concentration of the hydroxide ion in practical absorbents, we propose an alternative reaction pathway for the decomposition of the carbamate into the bicarbonate in which the OH^{-} ion plays a central role.

2. Computational Details

All of calculations were carried out using the Gaussian09 suite of program [11] in this study. The molecular geometries along reaction pathways were optimized by using the Møller-Plesset second-order perturbation (MP2) theory combined with the 6-311++G(d,p) basis set. The optimized transition states (TS) were confirmed to be connected with designated reactants and products by performing the intrinsic reaction coordinate (IRC) calculations. The geometries of reactants and products were fully optimized starting from those obtained by the IRC calculations. All of the optimized geometries were confirmed to be located as stationary points on the potential energy surfaces by performing normal vibration analyses. On the basis of the optimized geometries, single-point energy calculations were performed using the coupled-cluster theory with single, double, and non-iterative triple excitation (CCSD(T)) combined with the 6-311++G(2df,2p) basis set. All of the energy values reported in this article include the zero-point vibration energies. The activation energies were evaluated as an energy difference between reactants and TS.

In all the calculations, solvent polarization effects were incorporated by using the polarizable continuum model (PCM) with the dielectric constant of water (78.39). We used Pauling atomic radii to construct the PCM solvent cavity, since it provides a nice performance on the MEA/CO_2 system [5].

The conformational variations of the MEA and its derivatives such as carbamate anion and protonated cation may have significant effects on the kinetics and thermodynamics of CO_2 absorption reactions. Although alkanolamines are expected to be stabilized via the formation of intramolecular hydrogen-bonds, a preference for such conformers depends on the competition between intra- and inter-molecular interactions. In spite of the detailed analyses of the conformational distributions [12,13], this issue is now still on debate [6]. Since the purpose of the present study is to elucidate a general reaction mechanism, we discarded the conformers that form rigid intramolecular hydrogen bonds. Under such constraints, we have examined several conformers for the zwitterion, carbamic acid, and carbamate as well as the free MEA, and selected the gGg conformer (for the definition, see ref. [13]) throughout the present study because it was found to be main conformers in those species.

3. Results and Discussion

3-1. Neutral hydrolysis of carbamate

The results of our calculations on the neutral hydrolysis of MEA carbamate (reaction (4)) are displayed in Figure 2. The calculated activation energy (41.1 kcal/mol) is as high as that obtained for the corresponding reaction of AMP [8]. The IRC calculations starting from the **TS4** resulted in the designated

reactant (MEA carbamate in **RC4**) and the product (bicarbonate in **PC4**). However, as can be seen in Figure 2, the obtained reaction mechanism should be more properly interpreted as a two-step reaction rather than a concerted one; the first step is a proton transfer from the water molecule to the MEA nitrogen and the second step is an addition of the OH$^-$ ion to the zwitterion. On the basis of these features, it is worthwhile to examine in more detail the mechanisms for the decomposition of carbamate into bicarbonate in which the hydroxide ion plays a central role.
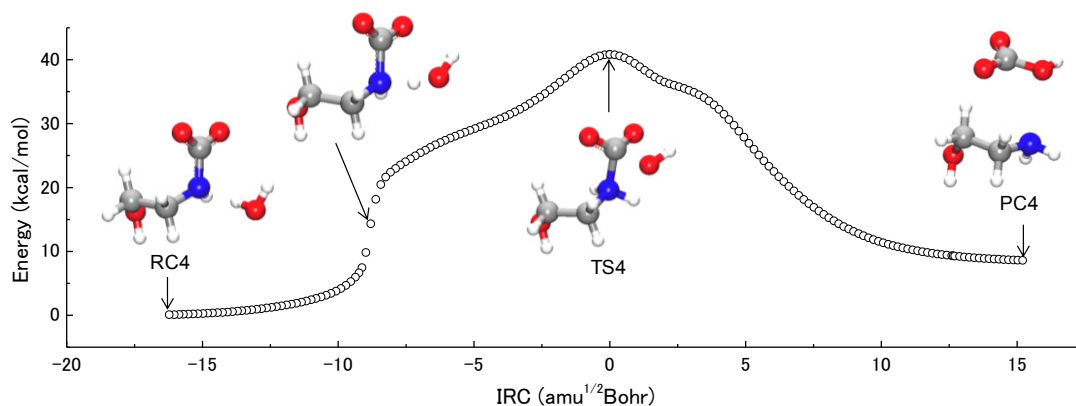

Figure 2. Potential energy profile along the IRC of reaction (4) as obtained by the PCM-MP2/6-311++G(d,p) calculations.

3-2. Alkaline hydrolysis of carbamic acid

At first, we point out that the OH$^-$ ion cannot attack MEA carbamate due to the electrostatic repulsion between negative charges as confirmed by the present calculations. Then, it is likely that the carbamate must become charge neutral via a protonation prior to the reaction with OH$^-$. Such a mechanism is consistent with the essentially two-step nature of the reaction (4) described above. Although, the proton is provided by H_2O in the reaction (4), more efficient proton donor would be a protonated MEA that has been produced in significant concentration via the direct CO_2 absorption reaction (reaction (1)). A protonation of the MEA carbamate yields either a zwitterion (reaction (1b)) or a carbamic acid:

$$RNHCOO^- + RNH_3^+ \leftrightarrow RNHCOOH + RNH_2. \tag{5}$$

The present calculations predict that the carbamic acid is more stable by 4.2 kcal/mol than the zwitterion, whereas the relative stability of these species may be altered in other amines.

We first investigate the nuclophilic attack of the OH$^-$ on the carbamic acid:

$$RNHCOOH + OH^- \leftrightarrow RNHCO(OH)_2^- \tag{6a}$$

As shown in Figure 3, the reaction product (**P6a**) is characterized by the tetrahedral carbon in the $CO(OH)_2^-$ group as in the case of the similar reactions of amide compounds [14,15]. The calculated activation energy (14.4 kcal/mol) is also close to the values predicted in those theoretical studies. As can be seen in Figure 1, the reaction (6a) competes with the reaction (8), which is a transformation of the
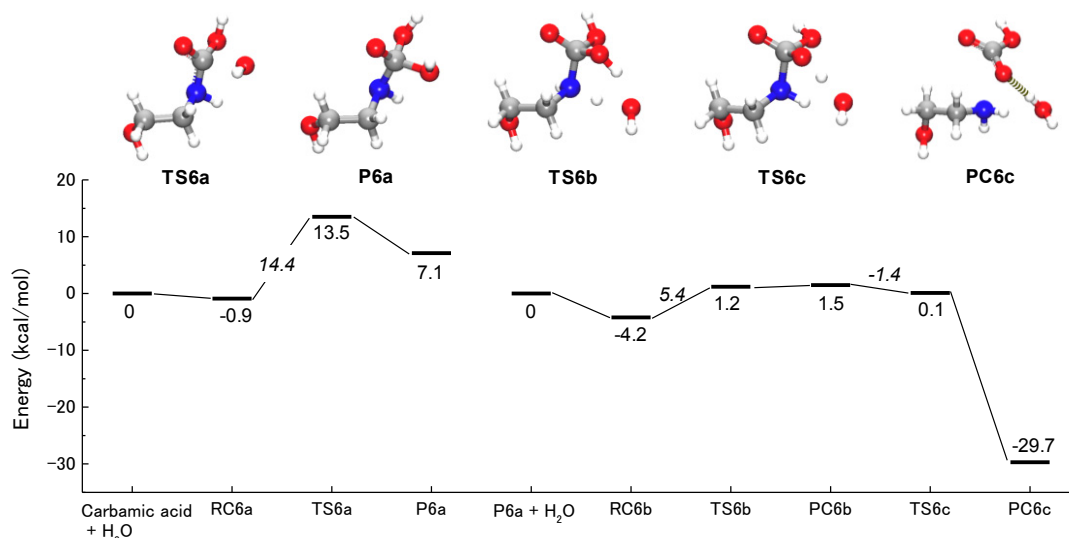
Figure 3. Schematic potential energy profile for the reaction (6) as obtained by the PCM-MP2/6-311++G(d,p) calculations. The values of activation energies (kcal/mol) are shown in italic.

carbamic acid into the zwitterion with the calculated activation energy of 13.6 kcal/mol, as well as the fast back transformation into the carbamate (MEA of OH^- act as a base).

The subsequent transformation of **P6a** into bicarbonate is also in analogy of the theoretically obtained pathways for the base-catalyzed hydrolysis of the *N*-methylacetamide [14]. Since **P6a** exhibits a basic character, it readily abstracts the proton from an adjacent water molecule:

$$RNHCO(OH)_2^- + H_2O \leftrightarrow RNH_2CO(OH)_2 + OH^-, \tag{6b}$$

with the calculated activation energy of only 5.4 kcal/mol. The product of this reaction can be characterized as a zwitterion consisting of the MEA and the carbonate (H_2CO_3). The OH^- ion, which is not necessarily the one generated by the reaction (6b), can abstract a proton from the hydroxyl group of the reaction intermediate, $RNH_2CO(OH)_2$:

$$RNH_2CO(OH)_2 + OH^- \leftrightarrow RNH_2 + HCO_3^- + H_2O. \tag{6c}$$
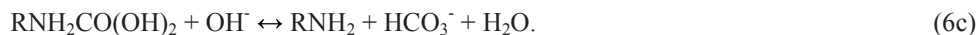
As can be seen in Figure 3, this reaction is almost barrier-less, and is associated with the cleavage of the C-N bond that results in the formation of the bicarbonate. It is noted that a combination of the reactions (6a), (6b), and (6c) results in an alkaline hydrolysis of the carbamic acid:

$$RNHCOOH + OH^- \leftrightarrow RNH_2 + HCO_3^-, \tag{6}$$

and the overall reaction consisting of the reactions (5) and (6) together with the generation of OH^-:

$$H_2O + RNH_2 \leftrightarrow OH^- + RNH_3^+, \tag{7}$$

gives rise to the hydrolysis of the MEA carbamate (i.e., (5) + (6) + (7) = (4)). Although the rate-determining step will be either (5) or (6a), a further discussion is prohibited by the lack of precision of the present methods in describing the reaction (5). The calculated activation energy for the reaction (5) is only 1.0 kcal/mol that is much smaller than that of the reaction (6a). However, for the backward reaction of (1b) which is similar to the reaction (5), the QM/MM real-solvent model predicts much higher energy barrier of 9.6 kcal/mol [5], while the corresponding value provided by the present method is 3.8 kcal/mol. This discrepancy is probably due to the underestimation of the solvation energies for the ionic species by the implicit solvent model.

A reaction of the zwitterion with OH^- similar to the reaction (6a) would be less probable, since the OH^- ion approaching the central carbon atom also points to the nearby N-H bond, and hence, the almost barrier-less proton abstraction leading to the carbamate formation overwhelms the addition of the OH^-. However, in the case of tertiary amines, the alkaline hydrolysis of zwitterions may contribute to the CO_2 absorption process, because there are no routes to carbamate species for the tertiary amines.

3-3. Mechanism for carbamate decomposition into bicarbonate

On the basis of the already known reactions, we obtain reaction pathways for the decomposition of carbamate that are different from those described above. They require the generation of free $CO_2(aq)$ via the backward reaction of (1). The free $CO_2(aq)$ can undergo reactions with either the OH^- (reaction (2)) or the H_2O and MEA (reaction (3)) to produce bicarbonates. The present calculations predict the activation energies for the reactions (2) and (3) to be 3.3 and 15.3 kcal/mol, respectively.

Consequently, there are at least four routes for the transformation of the carbamate into the bicarbonate: the pathways (4), (5)+(6), (1)+(2), and (1)+(3). The relative contributions of these pathways will vary depending on the actual experimental conditions such as pH and the partial pressure of CO_2.

At high pH (high amine concentration), the (5)+(6) and the (1)+(2) pathways will provide relatively large contributions. In the experimental study reported in ref [10], the decomposition of the MEA carbamate was initiated by adding OH^- ion to the solution containing MEA carbamate. It has been reported that with an increasing OH^- concentration, the reaction rate was decreased while the extent of carbamate decomposition was increased. These observations are consistent with both the (5)+(6) and the (1)+(2) pathways, since the OH^- ion transforms the relevant reaction intermediates (carbamic acid and zwitterion, respectively) back to the carbamates by abstracting protons from these species. On the other hand, at high CO_2 pressure, the contributions of the (1)+(2) and the (1)+(3) pathways will increase, since they involves the reactions of $CO_2(aq)$ despite the intrinsic low solubility of CO_2.

4. Conclusions

In order to reveal the comprehensive reaction pathways involved in the chemical CO_2 capture processes, we have theoretically investigated the mechanisms for the decomposition of the MEA carbamate into the bicarbonate. Although the already known pathways ((1)+(2) and (1)+(3)) invoke a generation free $CO_2(aq)$, we have been focused on another pathway which does not involve such an intermediate. The neutral hydrolysis of the MEA carbamate (reaction (4)) was found to be a slow reaction that has an essentially two-step nature. We propose an alternative pathway that involves the carbamic acid as an intermediate that undergoes the alkaline hydrolysis leading to the fomation of bicarbonate.

Taking account of the novel reaction pathways elucidated here as well as the established routes for the formation of carbamate and bicarbonate may lead to a comprehensive understanding and a better prediction of the chemical CO_2 capture process under specific conditions including pH (concentration of amine) and partial pressure of CO_2.

Acknowledgements

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