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CO$_2$ Absorption in an Alcoholic Solution of Heavily Hindered Alkanolamine: Reaction Mechanism of 2-(*tert*-Butylamino)ethanol with CO$_2$ Revisited

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S Supporting Information

ABSTRACT: To advance the optimal design of amines for postcombustion CO$_2$ capture, a sound mechanistic understanding of the chemical process of amines with good CO$_2$ capture performance is advantageous. A sterically hindered alkanolamine, 2-(*tert*-butylamino)ethanol (TBAE), in ethylene glycol (EG) solution was recently reported to have better CO$_2$ capture performance and unusual reactivity toward CO$_2$, in comparison with those of the prototypical alkanolamines. However, the reaction mechanism of TBAE with CO$_2$ in EG solution is unclear. Here, various quantum chemistry methods were employed to probe the reaction mechanism of TBAE with CO$_2$ in EG and aqueous solution. Six reaction pathways involving three kinds of possible reactive centers of TBAE solution were considered. The results indicated that the formation of anionic hydroxyethyl carbonate by the attack of $-$OH of EG on CO$_2$ is the most favorable, which is confirmed by complementary high-resolution mass spectrum experiments. This clarified that the speculated zwitterionic carbonate species is not the main product in EG solution. The reaction process of TBAE in aqueous solution is similar to that in EG solution, leading to bicarbonate, which agrees with experimental observations. On the basis of the unveiled reaction mechanisms of TBAE + CO$_2$, the role of the key *tert*-butyl functional group of TBAE was revealed.
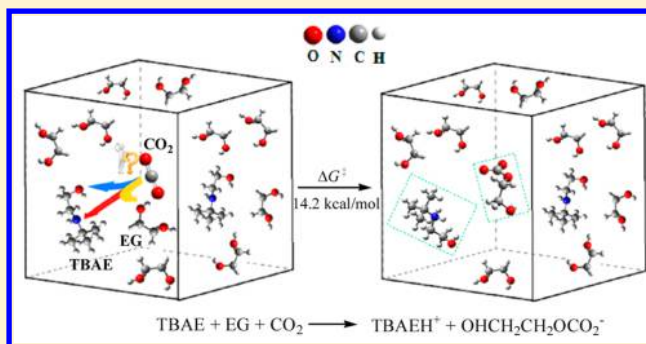
INTRODUCTION

Among numerous targets for the reduction of runaway atmospheric CO$_2$ emissions, the coal-fired power generation sector has been identified as the most logical one.[1] Currently, postcombustion capture (PCC), where aqueous amine solvents are employed to enable reversible capture of CO$_2$, is the frontline technology for separating and capturing CO$_2$ from the flue gas of coal-fired power generation.[2−7] Among the amines used in PCC, aqueous monoethanolamine (MEA) is a benchmark solvent, which has been used for more than 60 years in natural gas purification and food-grade CO$_2$ production[3,4] and has recently received attention as a candidate for the capture of CO$_2$ from flue gas.[8−13] Although PCC with aqueous MEA as a solvent is able to effectively capture CO$_2$ from flue gas, it has several drawbacks, including high energy costs during regeneration of MEA and poor cyclic capacity due to the formation of thermally stable carbamate species, all of which reduce the otherwise ideal properties of MEA for PCC applications.[1,12,14−17] There has therefore been a significant effort to identify other amine-based solvents with better performance.[1,16,18−24]

To advance the optimal design of amines toward PCC applications, a sound knowledge and understanding of the fundamental reaction mechanism involved in the capture of CO$_2$ is very advantageous. Up to now, mechanistic studies have

been mainly performed on the reactions of prototypical systems, including MEA, 2-amino-2-methyl-1-propanol (AMP), and diethanolamine (DEA) with CO$_2$.[25−34] Two typical reaction mechanisms have been identified: one is the carbamate reaction mechanism, where the reaction of amine with CO$_2$ proceeds via a zwitterion intermediate to form carbamate (eq 1)

$$RNH_2 + CO_2 \rightarrow \text{zwitterion} \xrightarrow{RNH_2} RNHCOO^- + RNH_3^+ \tag{1}$$
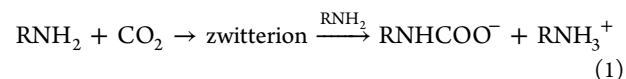
where R represents a substituent group. The other reaction is the bicarbonate reaction mechanism, where the reaction directly forms bicarbonate by the involvement of one water molecule via eq 2 or the unstable carbamate formed in eq 1 further reacts with water to form bicarbonate (eq 3). However, the reaction mechanism of novel amine solutions with good CO$_2$ capture performance has received little attention. In principle, the improvement in CO$_2$ capture performance and change of chemical processes of amines in CO$_2$ capture should be interlinked. Therefore, to facilitate amine design, the

absorption mechanism of novel amines with good capture performance deserves special investigation.

$$RNH_2 + CO_2 + H_2O \rightarrow RNH_3^+ + HCO_3^- \qquad (2)$$

$$RNHCOO^- + H_2O \rightarrow RNH_2 + HCO_3^- \qquad (3)$$
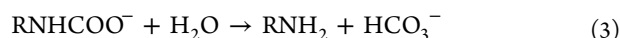
Recently, a sterically hindered alkanolamine, 2-(*tert*-butylamino)ethanol (TBAE), was reported to be able to reversibly interact with CO_2 in a 1/1 molar ratio exclusively through its −OH group, producing zwitterionic carbonate species in 30% ethylene glycol (EG) solution of TBAE via eq 4 but not carbamate or bicarbonate that can be produced by the prototypical amines[35]

$$2R'NHCH_2CH_2OH + CO_2$$
$$\rightarrow R'NH_2{}^+CH_2CH_2OH + R'NHCH_2CH_2OCO_2{}^- \qquad (4)$$
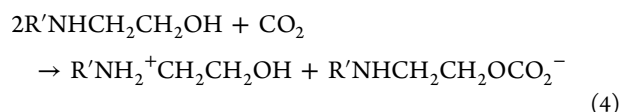
where R′ represents the *tert*-butyl group. More inspiringly, the formed zwitterionic carbonate species release CO_2 at temperatures considerably lower than those for the CO_2 adducts of other alkanolamines, including MEA and DEA. Another benefit from this system lies in its lower heat capacity of the ethylene glycol solvent in comparison to that of water, which could decrease energy requirements in the amine regeneration. Therefore, in comparison with prototypical amines such as MEA, AMP, and DEA, the EG solution of TBAE has better performance for CO_2 capture and could present a novel reaction mechanism. However, the reaction mechanism of TBAE with CO_2 in EG solution remains unclear, although some efforts have been made to clarify it.

The novel mechanistic result[35] of the reaction of TBAE with CO_2 in EG solution was speculated on the basis of the experimental results of the reaction of pure TBAE with CO_2, but not in EG solution. A computational mechanistic study based on gas-phase configurations of the molecules seems plausible to explain the novel reaction mechanism of TBAE with CO_2 in the study.[35] However, previous computational studies on the reaction of amines with CO_2 indicated that geometries of the intermediates and products are quite sensitive to the presence of a solvent,[26,28] which means that the results of the computational studies that did not consider the solvent effects in the optimization of geometries may not be completely reliable. More importantly, in view of the electronic structures, the speculated active center −OH of TBAE should have similar reactivity to −OH of EG solvent toward CO_2 if we hypothesize the long-range electronic effect (starting γ site of −OH) on −OH of both R′NHCH_2CH_2−OH and HO−CH_2CH_2−OH is ignored. Accordingly, −OH of EG solvent should have more chances to react with CO_2, due to the higher −OH concentration of EG solvent in comparison to that of TBAE (30%) in the EG solution. Therefore, on the basis of the above analysis, the experimental speculation on the reaction mechanism from pure TBAE to 30% TBAE in EG solution could be called into question. In addition, very recently, a direct experimental observation indicated that in a 30% aqueous solution of TBAE, CO_2 mainly reacts with −OH of water, rather than −OH of TBAE.[36] Although the physical properties of water such as dielectric constant and H-bond network could be different from those of EG, the reactivity of −OH of water could be similar to that of EG toward CO_2. Therefore, the study could further confuse the speculated reaction mechanism of TBAE with CO_2 in a 30% EG solution of TBAE.

To get a clearer picture of the reaction mechanism of TBAE with CO_2 in EG solution, we investigated this reaction mechanism using more reliable theoretical methods. Specifically, we included implicit solvent effects in both the geometry optimizations and frequency calculations in the ab initio calculations. A complementary high-resolution mass spectrum experiment was employed to identify the product of reaction of TBAE with CO_2 in EG solution to confirm the revealed reaction mechanism. As a comparison, the reaction mechanism of TBAE with CO_2 in aqueous solution was also investigated.

■ COMPUTATIONAL DETAILS

Ab Initio Electronic Structure Calculations. The Gaussian 09 package[37] was used for the reaction mechanism calculations. The optimized geometries and harmonic frequencies of reactants, products, isomers, and transition states were obtained at the B3LYP/6-311++G(d,p) level. Connections of the transition states between designated local minima were confirmed by intrinsic reaction coordinate (IRC) calculations at the B3LYP/6-311++G(d,p) level. Implicit solvent effects were taken into account for geometry optimizations, frequency calculations, and single point energy calculations by exploiting the SMD model[38] within the polarizable continuum model (PCM) formalism. We adopted EG as the solvent in the calculations with the dielectric constant of EG ($\varepsilon = 40.2$). To make a comparison, water ($\varepsilon = 78.4$) was also used as a solvent in the reaction mechanism calculations. Previous studies indicated that the combination of the B3LYP method with the SMD implicit solvent model is reliable to reveal the reaction mechanism of amines with CO_2.[25,39,40] In addition, for some important reaction pathways, the single point energy was calculated with the B3LYP-D/6-311++G(3df,2pd) and MP2/aug-cc-pVDZ methods on the basis of the geometries at the B3LYP/6-311++G(d,p) level. The symbol "D" of B3LYP-D designates dispersion correction introduced by Grimme.[41]

We estimated the Gibbs free energy (G) for each species at 298 K by combining the total energy calculation with the vibrational frequency calculation. G is given by

$$G = E_{SCF} + G_{corr} \qquad (5)$$

where E_{SCF} is the total energy including solvation free energy and G_{corr} is a correction term. G_{corr} is given by

$$G_{corr} = E + k_B T - TS \qquad (6)$$

where E is the internal thermal energy computed from the molecular partition function (translational, rotational, and vibrational degrees of freedom), k_B is the Boltzmann constant, T is the absolute temperature, and S is the entropy, also computed from the molecular partition function. For the reaction that involves a single TBAE molecule, the total G value of the reactants TBAE + CO_2 is taken as the reference state for the relative G calculation of elemental reactions. For the reaction that involves two molecules of TBAE or one TBAE and one solvent ethylene glycol molecule (or water), the total G value of the reactants TBAE-complex + CO_2 is taken as the reference state for the relative G calculation of elemental reactions because TBAE may form a precomplex with another TBAE or solvent molecules in the real system. "TBAE-complex" denotes a complex formed from TBAE and TBAE or solvent molecules.

Conformer Selection. TBAE and EG have conformational degrees of freedom that may influence their reactivity. The ab initio molecular dynamics computational scheme that we used

in our previous study[27,42] was adopted to search the global minimum. The computational details are presented in Supporting Information. The obtained global minimum of 2-(*tert*-butylamino)ethanol (TBAE) is presented in Figure 1. For EG, the reported most stable tGg′ conformer (Figure 1) was selected as the reactant.[43,44]
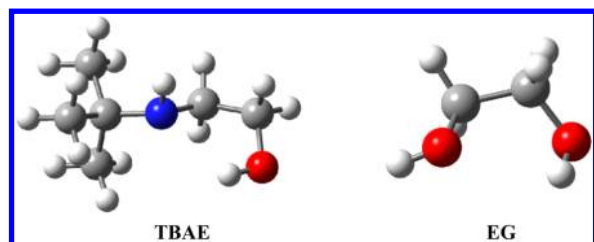

Figure 1. Global minimum of 2-*tert*-(butylamino)ethanol (TBAE) and ethylene glycol (EG). The red balls stand for O atoms, the blue ones for N atoms, the gray ones for C atoms and white ones for H atoms.

■ EXPERIMENTAL MATERIALS AND METHODS

Chemicals. TBAE with a purity of 98% was obtained from Tokyo Chemical Industry Co., Ltd. EG was of HPLC grade and was purchased from Kermel Chemical Reagent Co., Ltd. CO_2 with a purity of 99.995% was provided by Dalian (China) Special Gases Co., Ltd.

CO_2 Absorption Experiment. A 10 g portion of TBAE solution in EG (30 wt %) was prepared in a glass absorption tube. The tube was placed in a water bath to control the reaction temperature. N_2 was flowed into the absorption tube at 100 °C for 10 min to remove any volatile compounds. CO_2 gas was then introduced into the absorption tube at a rate of 20 mL min^{-1} at 40 °C for 60 min. Once the absorption was complete, the sample tube was sealed. The scheme for the absorption experiment of CO_2 is similar to that reported by Im et al.[35]

Absorption products were analyzed by a hybrid Fourier transform mass spectrometer combining a linear ion trap mass spectrometer and an Orbitrap mass analyzer (LTQ Orbitrap XL, Thermo Scientific). The electrospray ionization (ESI) source was operated in both positive and negative ion modes. The key optimized ESI parameters were as follows: scan range, m/z 50−220; source voltage, 3.5 kV; sheath gas (nitrogen), 30 L/min; auxiliary gas flow, 10 L/min; capillary voltage, −35.0 V; capillary temperature, 350.0 °C; tube lens, −110.0 V.

■ RESULTS AND DISCUSSION

Reaction of TBAE with CO_2 in EG Solution. For a 30% EG solution of TBAE, there are three types of possible reactive centers toward CO_2: the N atom of TBAE and O atoms of both TBAE and EG. Accordingly, three reaction pathways (A−C as shown in Figure 2) were first identified for the interaction of TBAE or EG with CO_2. Pathway A involves two steps: the first step is the attack of the N atom of TBAE on CO_2 to form a zwitterionic intermediate, and in the second step, the formed zwitterion reacts with another TBAE to finally form carbamate. Pathway B is a one-step process where the O atom of TBAE attacks CO_2 and the H connected to the O atom is intramolecularly transferred to the N atom of TBAE to form a zwitterionic carbonate. Pathway C is also a one-step process, in which the C atom of CO_2 is added to the O atom of EG via the O atom of EG attacking CO_2 and the H connected to the O atom is intermolecularly transferred to the N atom of TBAE to
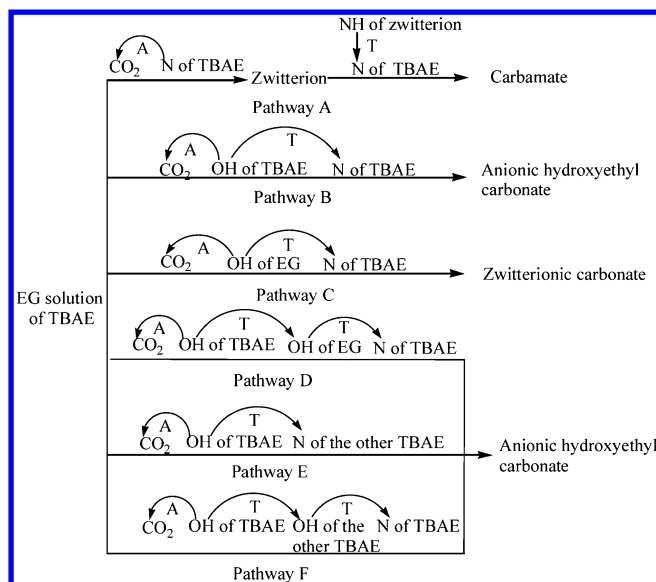

Figure 2. Six potential reaction pathways for the reaction of CO_2 with an EG solution of TBAE. The arrows denote the attack direction of the atom or the transfer direction of the proton. The symbols A and T represent attack and transfer, respectively.

form an anionic hydroxyethyl carbonate species. Figure 3 shows the schematic free energy surface for pathways A−C, and the corresponding optimized structures of complexes, transition states, and products are presented in Figure 4.

As shown in Figure 3, the overall activation free energies ($\Delta G^{\ddagger}$) for pathways A−C are 33.3, 19.9, and 14.2 kcal/mol, respectively (detailed in the Supporting Information), indicating that pathway C initiated by the attack of the O atom of EG at CO_2 is the most favorable. Therefore, CO_2 prefers to react with the O atom of the solvent EG, which is different from the experimental speculation that CO_2 exclusively reacts with the O atom of TBAE.[35] It deserves mentioning that the free energy of the zwitterionic intermediate is 10.3 kcal/mol higher than that of the reactants in pathway A, which means the zwitterionic intermediate either must overcome high activation free energy to form the carbamate or return back to the reactants, but not just remain as itself. To further investigate the possible competition of the pathways where the O atom of TABE attacks CO_2, we considered three more possible reaction pathways, D−F (Figure 2). The schematic free energy surfaces for reaction pathways D−F are presented in Figure 5, and the corresponding optimized structures of complexes, transition states, and products are presented in Figure 6.

In pathways D and F, the TBAE or EG molecule acts as a proton relayer to transfer a proton from the O atom of TBAE to the N atom of TBAE. The consideration of such pathways was inspired by previous studies that the proton relay by a H_2O molecule may reduce the reaction energy barrier for some reactions in aqueous solution.[45−47] The computed $\Delta G^{\ddagger\ddagger}$ values for pathway D (19.2 kcal/mol) and F (18.7 kcal/mol) are close to that of pathway B of the direct proton transfer (19.9 kcal/mol). Therefore, the involvement of TBAE or EG does not facilitate the proton transfer much from the O atom to the N atom of TBAE. It deserves mentioning that pathways D and F also still cannot kinetically compete with the most favorable pathway C due to their high $\Delta G^{\ddagger}$ values. In pathway E, CO_2 still reacts with the O atom of TBAE. However, the released proton is intermolecularly transferred to the N atom of another
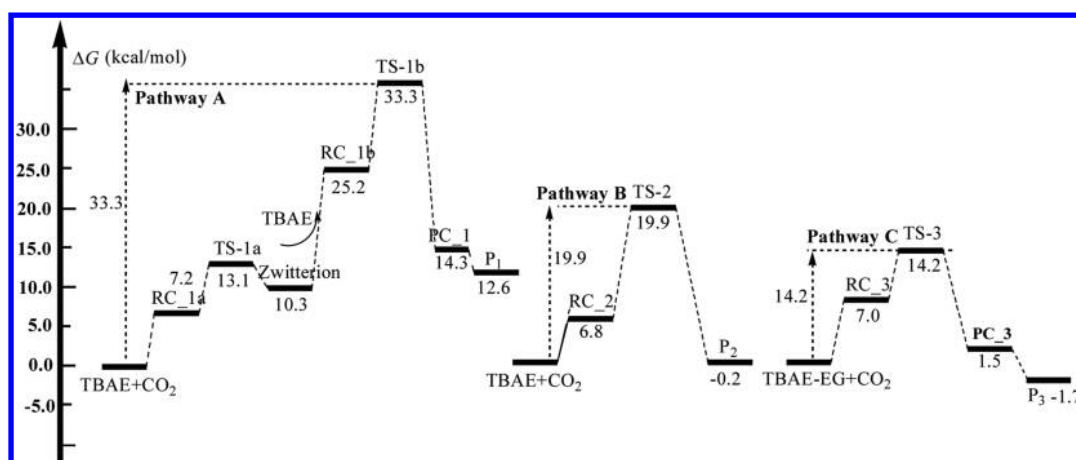
Figure 3. Schematic free energy surfaces for reaction pathways A−C in the reaction of CO_2 with TBAE in EG solution at the B3LYP/6-311+ +G(d,p) level. The symbols TBAE-EG, RC_m, TS-m, PC_m, and P$_m$ stand for the complex formed from TBAE and EG, prereactive complex, transition state, product complex, and product, respectively, and m denotes different species.
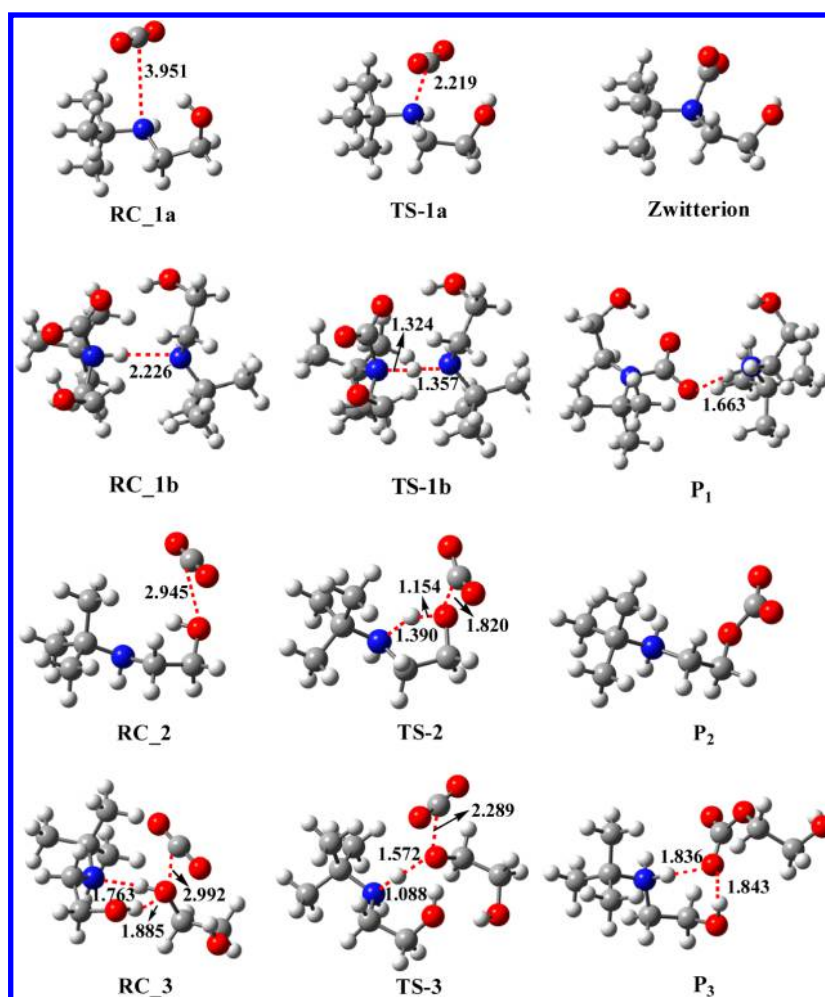

Figure 4. B3LYP/6-311++G(d,p)-optimized geometries for some important intermediates, transition states, and products for pathways A−C. The distances are given in Å. The red balls denote O atoms, the blue balls N atoms, the gray balls C atoms, and the white balls H atoms.

TABE. The $\Delta G^{\ddagger}$ value in pathway E is 16.2 kcal/mol, which is slightly lower than those of pathways B, D, and F that are all initiated by the attack of the O atom of TBAE on CO_2. In addition, it seems that the intermolecular proton transfer of TBAE (pathway E) is slightly more favorable than its intramolecular proton transfer (pathway B). A possible reason

is discussed in the Supporting Information. Still, pathway E is not as feasible as the most favorable pathway C. In view of the nature of the reaction and structures of transition states (TS-3 and TS-5), the reaction pathway E is similar to C because both pathways proceed via the attack of CO_2 at the O atom (of EG in pathway C and TBAE in pathway E) and the released proton
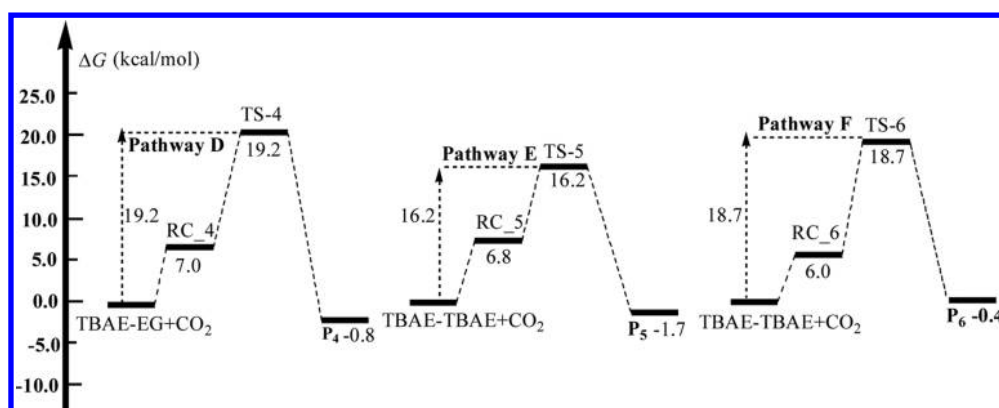
Figure 5. Schematic free energy surfaces for reaction pathways D−F in the reaction of CO_2 with TBAE in EG solution at the B3LYP/6-311++G(d,p) level. The symbols TBAE-TBAE, RC_m, TS-m, PC_m, and P$_m$ stand for the complex formed from TBAE and TBAE, prereactive complex, transition state, product complex, and product, respectively, and m denotes different species.
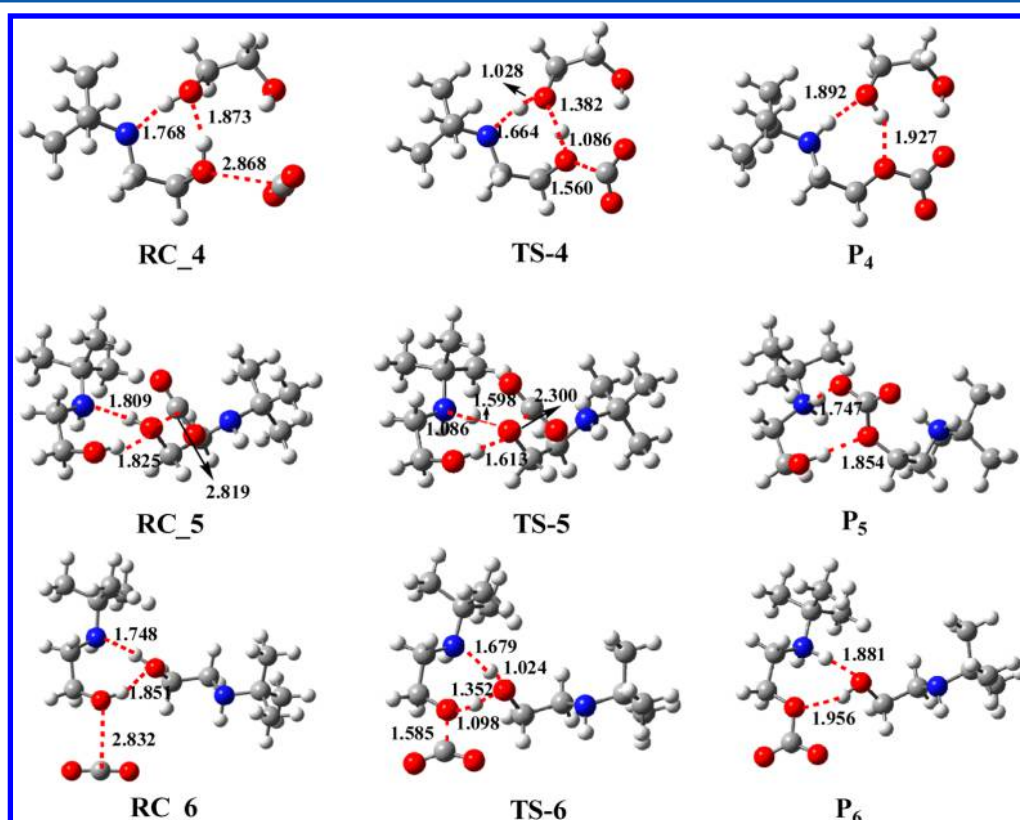

Figure 6. B3LYP/6-311++G(d,p)-optimized geometries for some important intermediates, transition states, and products for pathways D−F. Distances are given in Å.

is intermolecularly transferred to the N atom of TBAE. Therefore, the comparison of $\Delta G^{\ddagger}$ values between pathways C and E presents a more direct way to confirm that the O atom of EG has reactivity slightly greater than that of TBAE toward CO_2, which could be explained by a slightly higher O−H bond energy (102.2 kcal/mol at B3LYP/6-311++G(d,p) level) of TBAE in comparison to that of EG (101.0 kcal/mol).

High-level quantum chemical methods, including B3LYP-D/6-311++G(3df,2pd) and MP2/aug-cc-pVDZ, and the conductor-like polarizable continuum model (CPCM)[48,49] were further used to test the reliability of the B3LYP/6-311++G(d,p) level with the SMD solvent model for predicting the reaction mechanism of TBAE with CO_2. The results (presented in the Supporting Information) indicated that the theoretical method

and solvent model used here can reliably reveal the reaction mechanism of the title reaction. With our reliable computational scheme, we confirm that CO_2 prefers to react with EG to form anionic hydroxyethyl carbonate species. The similar carbonation process of saturated alcohols has also been found in the reaction of alcoholic solutions of amidine or guanidine with CO_2.[50] However, our finding is inconsistent with the previous experimental and computational expectation that CO_2 exclusively react with the O atom of TBAE.[35] It deserves mentioning that the gas-phase configuration in the computational study could not reasonably describe the interaction between amines and CO_2 as reported by some previous studies.[26,28] In addition, experimental mechanistic speculations from pure TABE to 30% EG solution of TBAE lack a direct

verification that EG has no competition toward CO_2 with TBAE.

As the formation of carbamate is the most favorable for primary and secondary amines,[26,28,51] it is interesting to discuss the formation pathways of carbamate from TBAE, although they are prohibited due to the extremely high $\Delta G^{\ddagger}$ values. Here, the carbamate is formed by a two-step reaction mechanism via a zwitterionic intermediate, which has been widely accepted for the reaction of amines with CO_2 in aqueous solution.[26] The $\Delta G^{\ddagger}$ value in the second step is higher than that in the first step for the reaction of TBAE with CO_2 in EG solution. This is different from the case for the prototypical amines of MEA and AMP, where the $\Delta G^{\ddagger}$ value for the second step is lower than that in the first step for forming carbamate.[25,26,28] Therefore, the *tert*-butyl group attached to the amino group of TBAE may block the proton transfer from the zwitterionic intermediate to TBAE in the second step. This conclusion is different from that of the previous study that the *tert*-butyl group attached to the amino group of TBAE blocks the approach of CO_2 to the N atom.[35]

CO_2 Absorption Experiment in EG Solution. TBAE, EG, and their CO_2 absorption products were detected and identified by a high-resolution mass spectrometer. Table S3 (Supporting Information) and Figure 7 show the accurate masses of the molecules and fragments measured by a LTQ Orbitrap instrument, the proposed formulas, theoretical masses, and double bond equivalents (DBEs) calculated by the associated software. In most cases, the errors between accurate mass

Figure 7. Mass spectral fragmentation patterns for TABE, EG, and their CO_2 absorption products: (A) positive ion mode full MS; (B) negative ion mode full MS; (C) negative ion mode full MS^2 for CO_2 absorption products.

measurements and theoretical masses of the proposed formulas were <6 ppm (Table S3), indicating a high degree of certainty in the identification.

As shown in Figure 7A, a molecular ion signal at m/z 118 ($C_6H_{15}NO$) was detected in positive ion mode, which could correspond to TBAEH$^+$ or unreacted TBAE. In the negative ion mode (Figure 7B), EG ($C_2H_6O_2$, m/z 61) and a CO_2 absorption product ($C_3H_6O_4$, m/z 105) were determined. On the basis of the mass spectral fragmentation pattern shown in Figure 7C, the CO_2 absorption product was proposed to be 2-hydroxyethyl carbonate. In addition, we did not find any ion signal for the CO_2 addition product of TBEA ($C_7H_{15}NO_3$, m/z 162 in positive ion mode or m/z 160 in negative ion mode). This indicates that the reaction of CO_2 with −OH of TBEA can be ignored. Thus, CO_2 prefers to react with the solvent EG rather than TBAE, which is consistent with our computational results.

Reaction of TBAE with CO_2 in Aqueous Solution. As a comparison, we also investigated the reaction of CO_2 with an aqueous solution of TBAE, which is observed experimentally to form bicarbonate.[36] Similar to the case for the EG solution of TBAE, there are three possible reactive centers: the N atom and O atoms of both TBAE and H_2O toward CO_2 in aqueous solutions of TBAE. Accordingly, six reaction pathways, designated by pathways A′−F′, corresponding to those in EG solution of TBAE, were considered. The structures of transition states are presented in Figure S1 (Supporting Information). The $\Delta G^{\ddagger}$ values for pathways A′−F′ are 33.8, 20.2, 16.5, 21.5, 18.5, and 22.0 kcal/mol, respectively. Similar to the case for an EG solution of TBAE, pathway C′ for forming bicarbonate is the most favorable and pathway A′ for forming carbamate is the most unfavorable. This finding is consistent with the experimental observation that bicarbonate is a main product in the reaction of CO_2 with a 30% aqueous solution of TBAE.[36] Therefore, our computational results are in line with the experimental observation for the reaction of CO_2 with a 30% aqueous solution of TBAE,[36] which in turn verifies that the current computational method is reliable to treat the reaction of CO_2 with TBAE. It deserves mentioning that this is the first attempt to unveil the reaction mechanism of TBAE with CO_2 in aqueous solution.

Comparison with Previous Experiment and Implications. This study found that the reaction of CO_2 with −OH of EG is the most favorable pathway for the reaction of CO_2 with an EG solution of TBAE, clarifying that the anionic hydroxyethyl carbonate species is a main product. The formation of hydroxyethyl carbonate was also confirmed by complementary high-resolution mass spectrum experiments. Also, in aqueous solution, the reaction of CO_2 with −OH of water is the most favorable, leading to bicarbonate species, which agrees well with the experimental finding that bicarbonate species is the main product in the reaction of CO_2 with 30% aqueous solution of TBAE.[36] In addition, this study also indicates that the various reaction pathways producing zwitterionic carbonate species through the attack of −OH of TBAE on CO_2 are more favorable than that forming carbamate. Therefore, we can speculate in the pure TBAE, without competition of solvent molecules EG or water for CO_2, the formation of zwitterionic carbonate species is the most favorable, which also agrees with the direct experimental observation that the zwitterionic carbonate species is an exclusive product for the reaction of pure TBAE with CO_2.[35]
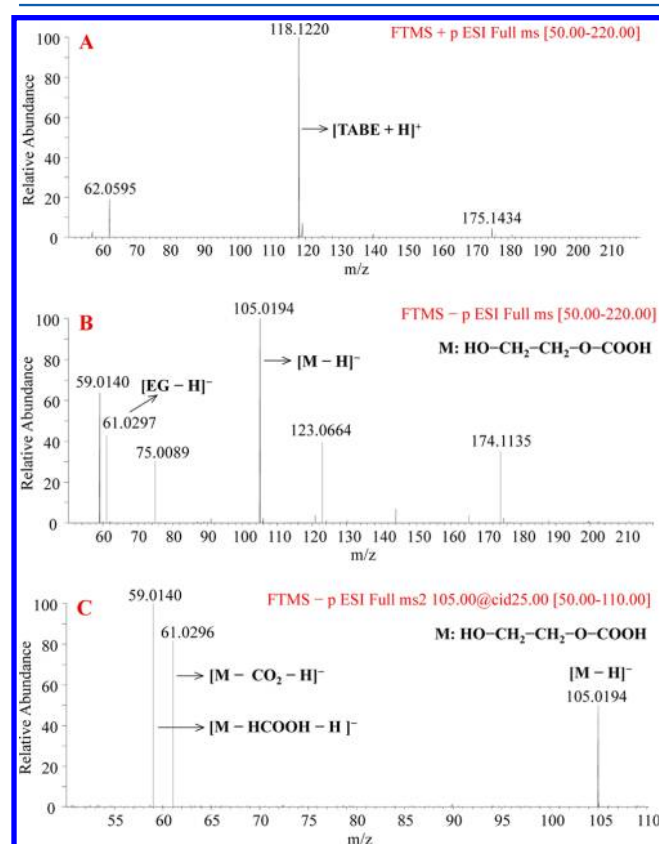
With the new reaction mechanism of CO_2 with an EG solution or aqueous solution of TBAE, we can unveil the role of the heavily hindered *tert*-butyl group in the reactivity of TBAE toward CO_2. First, the *tert*-butyl group of heavily hindered TBAE greatly blocks the formation of carbamate. More importantly, the block strength of the *tert*-butyl group for the formation of carbamate is greatly higher than that of two $-CH_3$ in the hindered amine AMP by comparing their $\Delta G^{\ddagger}$ values for carbamate formation (33.3 and 9.6 kcal for TBAE and AMP, respectively).[25] Second, our computed $\Delta G^{\ddagger}$ values of the prototypical amines MEA (20.8 kcal/mol) and AMP (19.6 kcal/mol) for the pathway involving the attack of the O atom of alkanolamine on CO_2, which is similar to pathway B of TBAE, are close to that (20.2 kcal/mol) of TBAE. This indicates that the *tert*-butyl group does not activate the activity of $-OH$ of alkanolamine. Therefore, the main role of the *tert*-butyl group in the chemical process of CO_2 capture of amine is to block the formation of carbamate but not activate the activity of the $-OH$ group of alkanolamines. The *tert*-butyl group could be used as an inhibitor of carbamate formation in future amine design for PCC applications.

◼ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving computational details for global minimum searches, overall activation free energy calculations for carbamate mechanisms, a discussion of the possible reasons that the intermolecular proton transfer of TBAE (pathway E) is slightly more favorable than its intramolecular proton transfer (pathway B), details of reliability evaluation calculations, B3LYP/6-311++G(d,p)-optimized geometries for the transition states of pathways A′−F′ for the reaction of CO_2 with TBAE in aqueous solution, and accurate mass measurements for TABE, EG, and their CO_2 absorption products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b02520.

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Notes

The authors declare no competing financial interest.

◼ ACKNOWLEDGMENTS

◼ REFERENCES

(1) Conway, W.; Wang, X.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Toward the Understanding of Chemical Absorption Processes for Post-Combustion Capture of Carbon Dioxide: Electronic and Steric Considerations from the Kinetics of Reactions of CO_2(aq) with Sterically hindered Amines. *Environ. Sci. Technol.* **2012**, *47* (2), 1163−1169.

(2) Dai, N.; Shah, A. D.; Hu, L.; Plewa, M. J.; McKague, B.; Mitch, W. A. Measurement of Nitrosamine and Nitramine Formation from NOx Reactions with Amines during Amine-Based Carbon Dioxide Capture for Postcombustion Carbon Sequestration. *Environ. Sci. Technol.* **2012**, *46* (17), 9793−9801.

(3) Veawab, A.; Tontiwachwuthikul, P.; Chakma, A. Corrosion Behavior of Carbon Steel in the CO_2 Absorption Process Using Aqueous Amine Solutions. *Ind. Eng. Chem. Res.* **1999**, *38* (10), 3917−3924.

(4) Liu, Y.; Zhang, L.; Watanasiri, S. Representing Vapor−Liquid Equilibrium for an Aqueous MEA−CO_2 System Using the Electrolyte Nonrandom-Two-Liquid Model. *Ind. Eng. Chem. Res.* **1999**, *38* (5), 2080−2090.

(5) Nielsen, C. J.; Herrmann, H.; Weller, C. Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS). *Chem. Soc. Rev.* **2012**, *41* (19), 6684−6704.

(6) da Silva, E. F.; Booth, A. M. Emissions from Postcombustion CO_2 Capture Plants. *Environ. Sci. Technol.* **2013**, *47* (2), 659−660.

(7) Rochelle, G. T. Amine Scrubbing for CO_2 Capture. *Science* **2009**, *325* (5948), 1652−1654.

(8) Reguia, S.; Rochelle, G. T. Modeling of CO_2 capture by aqueous monoethanolamine. *AIChE J.* **2003**, *49* (7), 1676−1686.

(9) Abu-Zahra, M. R. M.; Niederer, J. P. M.; Feron, P. H. M.; Versteeg, G. F. CO_2 capture from power plants: Part II. A parametric study of the economical performance based on mono-ethanolamine. *Int. J. Greenhouse Gas Control* **2007**, *1* (2), 135−142.

(10) Abu-Zahra, M. R. M.; Schneiders, L. H. J.; Niederer, J. P. M.; Feron, P. H. M.; Versteeg, G. F. CO_2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine. *Int. J. Greenhouse Gas Control* **2007**, *1* (1), 37−46.

(11) Soosaiprakasam, I. R.; Veawab, A. Corrosion and polarization behavior of carbon steel in MEA-based CO_2 capture process. *Int. J. Greenhouse Gas Control* **2008**, *2* (4), 553−562.

(12) McCann, N.; Maeder, M.; Attalla, M. Simulation of Enthalpy and Capacity of CO_2 Absorption by Aqueous Amine Systems. *Ind. Eng. Chem. Res.* **2008**, *47* (6), 2002−2009.

(13) Plaza, J. M.; Van Wagener, D.; Rochelle, G. T. Modeling CO_2 capture with aqueous monoethanolamine. *Int. J. Greenhouse Gas Control* **2010**, *4* (2), 161−166.

(14) Sartori, G.; Savage, D. W. Sterically hindered amines for carbon dioxide removal from gases. *Ind. Eng. Chem. Fundam.* **1983**, *22* (2), 239−249.

(15) Idem, R.; Wilson, M.; Tontiwachwuthikul, P.; Chakma, A.; Veawab, A.; Aroonwilas, A.; Gelowitz, D. Pilot Plant Studies of the CO_2 Capture Performance of Aqueous MEA and Mixed MEA/MDEA Solvents at the University of Regina CO_2 Capture Technology Development Plant and the Boundary Dam CO_2 Capture Demonstration Plant. *Ind. Eng. Chem. Res.* **2005**, *45* (8), 2414−2420.

(16) Liu, A.-H.; Ma, R.; Song, C.; Yang, Z.-Z.; Yu, A.; Cai, Y.; He, L.-N.; Zhao, Y.-N.; Yu, B.; Song, Q.-W. Equimolar CO_2 Capture by N-Substituted Amino Acid Salts and Subsequent Conversion. *Angew. Chem., Int. Ed.* **2012**, *51* (45), 11306−11310.

(17) Lee, A. S.; Kitchin, J. R. Chemical and Molecular Descriptors for the Reactivity of Amines with CO_2. *Ind. Eng. Chem. Res.* **2012**, *51* (42), 13609−13618.

(18) Puxty, G.; Rowland, R.; Allport, A.; Yang, Q.; Bown, M.; Burns, R.; Maeder, M.; Attalla, M. Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines. *Environ. Sci. Technol.* **2009**, *43* (16), 6427−6433.

(19) Conway, W.; Wang, X.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Toward Rational Design of Amine Solutions for PCC Applications: The Kinetics of the Reaction of CO_2(aq) with Cyclic and Secondary Amines in Aqueous Solution. *Environ. Sci. Technol.* **2012**, *46* (13), 7422−7429.

(20) Gurkan, B. E.; de la Fuente, J. C.; Mindrup, E. M.; Ficke, L. E.; Goodrich, B. F.; Price, E. A.; Schneider, W. F.; Brennecke, J. F. Equimolar CO2 Absorption by Anion-Functionalized Ionic Liquids. *J. Am. Chem. Soc.* **2010**, *132* (7), 2116−2117.

(21) Vaidhyanathan, R.; Iremonger, S. S.; Dawson, K. W.; Shimizu, G. K. H. An amine-functionalized metal organic framework for

preferential CO_2 adsorption at low pressures. *Chem. Commun.* **2009**, 35, 5230−5232.

(22) Wang, C.; Mahurin, S. M.; Luo, H.; Baker, G. A.; Li, H.; Dai, S. Reversible and robust CO_2 capture by equimolar task-specific ionic liquid-superbase mixtures. *Green Chem.* **2010**, 12 (5), 870−874.

(23) Wang, C.; Luo, H.; Jiang, D.-e.; Li, H.; Dai, S. Carbon Dioxide Capture by Superbase-Derived Protic Ionic Liquids. *Angew. Chem., Int. Ed.* **2010**, 49 (34), 5978−5981.

(24) Hussain, M. A.; Soujanya, Y.; Sastry, G. N. Evaluating the Efficacy of Amino Acids as CO_2 Capturing Agents: A First Principles Investigation. *Environ. Sci. Technol.* **2011**, 45 (19), 8582−8588.

(25) 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_2. *Ind. Eng. Chem. Res.* **2014**, 53 (8), 3363−3372.

(26) Xie, H.-B.; Zhou, Y.; Zhang, Y.; Johnson, J. K. Reaction Mechanism of Monoethanolamine with CO_2 in Aqueous Solution from Molecular Modeling. *J. Phys. Chem. A* **2010**, 114 (43), 11844−11852.

(27) Xie, H.-B.; Johnson, J. K.; Perry, R. J.; Genovese, S.; Wood, B. R. A Computational Study of the Heats of Reaction of Substituted Monoethanolamine with CO2. *J. Phys. Chem. A* **2010**, 115 (3), 342−350.

(28) da Silva, E. F.; Svendsen, H. F. Ab Initio Study of the Reaction of Carbamate Formation from CO_2 and Alkanolamines. *Ind. Eng. Chem. Res.* **2004**, 43 (13), 3413−3418.

(29) Arstad, B.; Blom, R.; Swang, O. CO_2 absorption in aqueous solutions of alkanolamines: mechanistic insight from quantum chemical calculations. *J. Phys. Chem. A* **2007**, 111 (7), 1222−8.

(30) 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 (5), 612−616.

(31) 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 (4), 2172−2178.

(32) 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 (6), 522−526.

(33) Orestes, E.; Ronconi, C. M.; Carneiro, J. W. de M. Insights into the interactions of CO_2 with amines: a DFT benchmark study. *Phys. Chem. Chem. Phys.* **2014**, 16, 17213−17219.

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

(35) Im, J.; Hong, S. Y.; Cheon, Y.; Lee, J.; Lee, J. S.; Kim, H. S.; Cheong, M.; Park, H. Steric hindrance-induced zwitterionic carbonates from alkanolamines and CO_2: highly efficient CO_2 absorbents. *Energy Environ. Sci.* **2011**, 4 (10), 4284−4289.

(36) Choi, Y.-S.; Im, J.; Jeong, J. K.; Hong, S. Y.; Jang, H. G.; Cheong, M.; Lee, J. S.; Kim, H. S. CO_2 Absorption and Desorption in an Aqueous Solution of Heavily Hindered Alkanolamine: Structural Elucidation of CO_2-Containing Species. *Environ. Sci. Technol.* **2014**, 48 (7), 4163−4170.

(37) Frisch, M. J.; Trucks, G. W.; H.B, S.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R., et al. *Gaussian 09*; Gaussian, Inc., Wallingford, CT, 2009.

(38) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, 113 (18), 6378−6396.

(39) 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 (14), 3079−3086.

(40) Matsuzaki, Y.; Yamada, H.; Chowdhury, F. A.; Higashii, T.; Onoda, M. Ab Initio Study of CO_2 Capture Mechanisms in Aqueous Monoethanolamine: Reaction Pathways for the Direct Interconversion of Carbamate and Bicarbonate. *J. Phys. Chem. A* **2013**, 117 (38), 9274−9281.

(41) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132 (15), 154104.

(42) Miller, M. B.; Chen, D.-L.; Xie, H.-B.; Luebke, D. R.; Karl Johnson, J.; Enick, R. M. Solubility of CO_2 in CO_2-philic oligomers; COSMOtherm predictions and experimental results. *Fluid Phase Equilib.* **2009**, 287 (1), 26−32.

(43) Vital de Oliveira, O.; Gomide Freitas, L. C. Molecular dynamics simulation of liquid ethylene glycol and its aqueous solution. *J. Mol. Struct.: THEOCHEM* **2005**, 728 (1−3), 179−187.

(44) Gubskaya, A. V.; Kusalik, P. G. Molecular Dynamics Simulation Study of Ethylene Glycol, Ethylenediamine, and 2-Aminoethanol. 1. The Local Structure in Pure Liquids. *J. Phys. Chem. A* **2004**, 108 (35), 7151−7164.

(45) Hollóczki, O.; Terleczky, P.; Szieberth, D.; Mourgas, G.; Gudat, D.; Nyulászi, L. Hydrolysis of Imidazole-2-ylidenes. *J. Am. Chem. Soc.* **2010**, 133 (4), 780−789.

(46) Bayse, C. A. DFT Study of the Glutathione Peroxidase-Like Activity of Phenylselenol Incorporating Solvent-Assisted Proton Exchange. *J. Phys. Chem. A* **2007**, 111 (37), 9070−9075.

(47) Cox, R. A. A Greatly Under-Appreciated Fundamental Principle of Physical Organic Chemistry. *Int. J. Mol. Sci.* **2011**, 12 (12), 8316−8332.

(48) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, 102 (11), 1995−2001.

(49) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* **2003**, 24 (6), 669−681.

(50) Heldebrant, D. J.; Yonker, C. R.; Jessop, P. G.; Phan, L. Organic liquid CO_2 capture agents with high gravimetric CO_2 capacity. *Energy Environ. Sci.* **2008**, 1, 487−493.

(51) Versteeg, G. F.; Swaaij, W. P. M. v. On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions?I. Primary and secondary amines. *Chem. Eng. Sci.* **1988**, 43 (3), 573−585.