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A Computational Study of the Heats of Reaction of Substituted Monoethanolamine with CO$_2$

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Various amines have been considered as materials for chemical capture of CO$_2$ through liquid-phase reactions to form either carbamate or carbamic acid products. One of the main challenges in these CO$_2$–amine reactions lies in tuning the heat of reaction to achieve the correct balance between the extent of reaction and the energy cost for regeneration. In this work, we use a computational approach to study the effect of substitution on the heats of reaction of monoethanolamine (MEA). We use ab initio methods at the MP2/aug-cc-pVDZ level, coupled with geometries generated from B3LYP/6-311++G(d,p) density functional theory along with the conductor-like polarizable continuum model to compute the heats of reaction. We consider two possible reaction products: carbamate, having a 2:1 amine:CO$_2$ reaction stoichiometry, and carbamic acid, having a 1:1 stoichiometry. We have considered CH$_3$, NH$_2$, OH, OCH$_3$, and F substitution groups at both the α- and β-carbon positions of MEA. We have experimentally measured heats of reaction for MEA and both α- and β-CH$_3$-substituted MEA to test the predictions of our model. We find quantitative agreement between the predictions and experiments. We have also computed the relative basicities of the substituted amines and found that the heats of reaction for both carbamate and carbamic acid products are linearly correlated with the computed relative basicities. Weaker basicities result in less exothermic heats of reaction. Heats of reaction for carbamates are much more sensitive to changes in basicity than those for carbamic acids. This leads to a crossover in the heat of reaction so that carbamic acid formation becomes thermodynamically favored over carbamate formation for the weakest basicities. This provides a method for tuning the reaction stoichiometry from 2:1 to 1:1.

Introduction

The capture (separation) and sequestration (long-term storage) of carbon dioxide is seen as a critical near-term strategy for mitigating the effects of greenhouse gas emissions. Generation of electricity from fossil fuels (coal, oil, and gas) accounts for approximately 25% of global CO$_2$ emissions.[1] Moreover, this fraction could increase drastically in the next 25 years.[2] The U.S. Department of Energy (DOE) has set a target for the capture and sequestration of 90% of the CO$_2$ in flue gas with a no more than 35% increase in the cost of electricity.[3] No technologies that achieve these targets are currently being implemented. Therefore, development of technologies that facilitate the cost-effective and energy-efficient capture of CO$_2$ from power plant flue gas is of paramount importance.

Postcombustion capture of CO$_2$ produced by conventional coal combustion in air presents technical challenges because the flue gas is at atmospheric pressure and the CO$_2$ concentration is 10–15 vol %, resulting in a low CO$_2$ partial pressure and a large volume of gas to be treated. One approach to postcombustion CO$_2$ capture is to use a regenerable solvent. Both physical and chemical solvents have been considered for CO$_2$ capture; however, chemical solvents (such as amines) are considered to be a more viable option for treating flue gases because of their ability to capture CO$_2$ at low partial pressures.[4–11]

Alkanolamine systems have been studied as possible materials for postcombustion capture of CO$_2$ from flue gas.[12–20] Among these alkanolamines, aqueous monoethanolamine (MEA) is the most widely used solvent, having been used for more than 60 years for natural gas purification and food-grade CO$_2$ production,[21–23] and has recently received attention as a candidate for the capture of CO$_2$ from flue gas.[4,5,7,9,24–33] However, there are several challenges associated with the use of aqueous MEA for capture of CO$_2$ from flue gas.[21,22] (1) The reaction of MEA with CO$_2$ to form carbamate is highly exothermic (approximately −17 kcal/mol), which means that more energy is required in the solvent regeneration step compared to what is optimal.[27,28,34] We note that a sizable fraction of the energy required to regenerate the solvent goes into vaporization of water in the aqueous solution.[35] (2) A non-negligible fraction of the MEA is lost due to vaporization and decomposition during regeneration.[29,30,36] (3) Aqueous MEA has been shown to be highly corrosive to carbon steels,[31,37] which increases the capital and maintenance costs of the process. As a result of these and other issues, the use of MEA to capture CO$_2$ is estimated to require an ~80% increase in the cost of electricity and a ~30% decrease in power plant efficiency,[3] making MEA not economically acceptable by the DOE standards.[3] There has therefore been a significant effort to identify other amine-based solvents that perform better than MEA.[1,38–45]

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TABLE 1: Electronegativities[69] of Substituent Groups

	H	CH$_3$	NH$_2$	OH	OCH$_3$	F
electronegativity	2.20	2.555	3.117	3.542	3.606	3.938

The generally expected reaction stoichiometry for the reaction between primary or secondary amines and CO$_2$ is 2:1, resulting in the formation of a carbamate anion and an ammonium cation as shown in eq 1:[46]

$$2RNH_2 + CO_2 \rightarrow RNH_3^+ + RNHCO_2^- \tag{1}$$
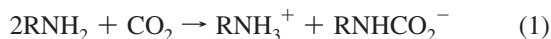
However, Mindrup and Schneider[47] used gas-phase quantum mechanical calculations to qualitatively predict that reactions between negatively charged amines in ionic liquids (i.e., the anions in the ionic liquid) and CO$_2$ could produce carbamic acid instead of carbamate

$$[RNH_2]^- + CO_2 \rightarrow [RNHCOOH]^- \tag{2}$$

Their calculations indicated that a 1:1 amine:CO$_2$ stoichiometry is achieved because the heat of reaction for the carbamic acid reaction is more exothermic than for the carbamate reaction. These predictions were later experimentally verified.[45]

We postulate that in general, the reaction of CO$_2$ with an amine will involve both reactions given in eqs 1 and 2. Moreover, the carbamate and carbamic acid species should be in thermodynamic equilibrium if the proton transfer step is facile, which could be the case for aqueous-phase reactions. Hence, carbamate will be the main product if its heat of reaction is more exothermic than that of carbamic acid, and vice versa. It may therefore be possible to change the reaction product distribution by modifying the relative heats of reaction for carbamate and carbamic acid products. Furthermore, we suggest that the relative heats of reaction may be changed via addition of substituent groups onto an amine.
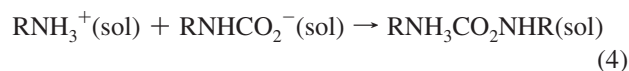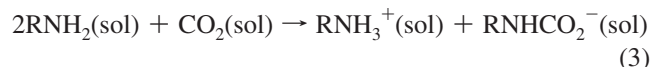
There has been limited computational work describing the effect of substituent groups on the heats of reaction of CO$_2$ with amines. The only study of which we are aware is that of Chakraborty et al.[48] They used molecular orbital theory to investigate how methyl substitution at the α-carbon of MEA decreased the basicity of MEA and therefore also decreased the heat of reaction for carbamate formation. The goal of this work is to investigate how substituent groups on the α- and β-carbons of MEA affect the heats of reaction for both carbamate and carbamic acid reactions. We have used the following substituent groups in this study: CH$_3$, NH$_2$, OH, OCH$_3$, and F (listed in Table 1, along with their electronegativities). Our shorthand notation for the substituted amines and the IUPAC chemical names are listed in Table 2. Our work provides general guidelines for tuning the heat of reaction for carbamate formation through the use of substituent groups. This could be useful for designing amines with heats of reaction more favorable than that of MEA. Lower heats of reaction should result in lower operating costs for CO$_2$ capture, although this is only one consideration.[35] We also investigate how substituents can be used to tune the reaction stoichiometry between amine and CO$_2$ by shifting the equilibrium from the carbamate 2:1 ratio toward the carbamic acid 1:1 ratio.

Methods

Heat of Reaction Calculations. We used a two-step approach to compute the heats of reaction for the various carbamates:

TABLE 2: Naming Conventions for Substituted MEAs Used in This Study

shorthand name	chemical name
MEA	2-aminoethanol
α-CH$_3$-MEA	2-aminopropan-1-ol
β-CH$_3$-MEA	1-aminopropan-2-ol
α-NH$_2$-MEA	2,2-diaminoethanol
β-NH$_2$-MEA	1,2-diaminoethanol
α-OH-MEA	1-aminoethane-1,2-diol
β-OH-MEA	2-aminoethane-1,1-diol
α-OCH$_3$-MEA	2-amino-2-methoxyethanol
β-OCH$_3$-MEA	2-amino-1-methoxyethanol
α-F-MEA	2-amino-2-fluoroethanol
β-F-MEA	2-amino-1-fluoroethanol

$$2RNH_2(sol) + CO_2(sol) \rightarrow RNH_3^+(sol) + RNHCO_2^-(sol) \tag{3}$$

$$RNH_3^+(sol) + RNHCO_2^-(sol) \rightarrow RNH_3CO_2NHR(sol) \tag{4}$$

This two-step approach uses a thermodynamic path to separate the chemical steps, involving bond breaking and formation as given in eq 3, from the process of bringing the two ions together to form a complex, given in eq 4. The second step involves electrostatic and dispersion interactions between solvated RNH$_3^+$ and RNHCO$_2^-$ species. The total heat of reaction, ΔH, is the sum of ΔH_1, the enthalpy change for eq 3, and ΔH_2, the enthalpy change for eq 4. We split the carbamate heat of reaction calculations for the sake of computational convenience. The carbamic acid heats of reaction are computed in a single direct step.

The reactants, intermediates, and products investigated in this work all have conformational degrees of freedom that may influence the calculated heats of reaction. We used ab initio molecular dynamics (AIMD) to generate reasonable gas-phase conformations for amines, RNH$_3^+$, RNHCO$_2^-$, and carbamic acids. We used density function theory (DFT) with the B88-PW86 functional[49] along with a triple-ζ valence polarized basis set (TZVP) within the RI approximation[50] to conduct the AIMD calculations. The temperature was set to 800 K to sample a large number of different configurations. A time step of 1.451 fs was used. The total length of each AIMD simulation was 7.256 ps (5000 time steps). Calculations were conducted using TUR-BOMOLE.[51] We selected configurations from the AIMD run and used these as starting points to obtain an average of 6 (range of 3−11) different local minimum structures for each species at the B3LYP/6-311++G(d,p) level using Gaussian 03.[52] Single-point energy calculations were then performed at the MP2/aug-cc-pVDZ//B3LYP/6-311++G(d,p) level to obtain accurate total energies for each of the sample configurations. In all geometry optimizations, harmonic vibrational frequency calculations, and single-point energy calculations, implicit solvent effects were considered by using the conductor-like polarizable continuum model (CPCM) formalism.[53,54] We used water as the solvent in these calculations even though the experiments were conducted in neat amines, because amines were not available as a solvent choice within Gaussian 03. However, additional test calculation using methanol and aniline as solvents gave results that were almost the same as those for the water solvent case, indicating that the heats of reaction are not dramatically dependent upon the solvent used, as long as the dielectric constant is high. The CPCM method was initially devised by Tomasi and co-workers[55−57] and extended for geometry optimizations to converge efficiently.

UAHF[58] atomic radii were used in the construction of the solute cavity for all calculations. A similar computational approach has successfully been used to calculate the kinetics of MEA–CO$_2$ reactions.[59] The enthalpy for each species in the liquid is calculated using the equation

$$H^s = H^s(g) + E_{sol} + ZPE \tag{5}$$

where H^s is the enthalpy of species s in the liquid phase, $H^s(g)$ is enthalpy of species s in the gas phase, ZPE is the zero-point energy, and E_{sol} is the solvation free energy of species s, which includes electrostatic interaction, cavitation, dispersion, and repulsion energies.[55–57]

To account for the different conformations in a physically reasonable way, we generated a Boltzmann-weighted distribution to compute the conformational averaged energy of each species s:

$$\bar{H}^s = \sum_i w_i H_i^s \tag{6}$$

where the Boltzmann weight w_i is given by

$$w_i^s = \frac{e^{-H_i^s/k_BT}}{\sum_i e^{-H_i^s/k_BT}} \tag{7}$$

and k_B is the Boltzmann constant and T is the absolute temperature, taken to be 298 K in our calculations. Note that it is not possible to sample conformations of the bound carbamate, [RNH$_3^+$][$^-$CO$_2$NHR], because it will transform to neutral species RNH$_2$ and RNHCOOH in our gas-phase AIMD simulations. Therefore, we used the configurations for RNH$_3^+$ and RNHCO$_2^-$ having the highest Boltzmann weight to evaluate electrostatic and dispersion interactions in eq 4.

As discussed in the Introduction, carbamate formation is expected to dominate for primary and secondary amines.[46] In addition, a small amount of a bicarbonate product can also be formed in aqueous solutions. We have not considered the bicarbonate product in our computations because the experiments were conducted in the absence of water (neat amine). However, we expect that our computational results will still be valid for aqueous amine solutions because bicarbonate is a minor product.

Relative Amine Basicity Calculations. In general, the basicity of a compound can be evaluated by calculating the pK_a value of the conjugate base of the compound using the reaction

$$BH^+(sol) \rightarrow B(sol) + H^+(sol) \tag{8}$$

The pK_a value can be calculated from

$$pK_a = \frac{1}{2.303RT}\Delta G \tag{9}$$

where ΔG is the Gibbs free energy of the reaction in eq 8, R is the gas contant, and T is the absolute temperature. According to this definition, the greater the pK_a value, the stronger the basicity of the amine and the more endothermic the reaction in eq 8. In this work, we are concerned only with the trends in basicity and not the absolute values. The free energy of the proton is constant for all amines, so one just needs to calculate the free energy difference between the protonated and unprotonated amine to calculate the relative basicity of an amine. The free energy calculation involves computing the solvation free energy for the cations. However, the implict solvent model is known to be inadequate for predicting the solvation free energy for cations.[60] We therefore used the cluster-continuum model in these solvation free energy calculations. This model has given execellent results for calculating pK_a values of acids and conjugate bases.[60–62] The solvation free energy of a cation is calculated in the cluster-continuum model as

$$\Delta G_{solv}^*(A^+) = \Delta G_{clust}^\circ(A^+(S)_n) + \Delta G_{solv}^*(A^+(S)n) + n\Delta G_{vap}(S) \tag{10}$$

where $\Delta G_{solv}^*(A^+)$ is the solvation free energy of A$^+$ at a concentration of 1 mol/L, $\Delta G_{clust}^\circ(A^+(S)_n)$ is the gas-phase clustering free energy at 1 atm, $\Delta G_{solv}^*(A^+(S)_n)$ is the solvation free energy of a cluster containing A$^+$ and solvent S, and $\Delta G_{vap}(S)$ is the vaporization free energy of the solvent. The computational details of the cluster-continuum model are given by Pliego and Riveros.[60] In this section, geometry optimizations in the gas phase were performed at the B3LYP/6-311++G(d,p) level of theory, and single-point energy calculations utilized the MP2/aug-cc-pVDZ level of theory. Solvation free energies were obtained at the MP2/aug-cc-pVDZ level within the CPCM model with UAHF radii. The idea of the cluster-continuum model is to represent the ion as a cluster formed by the ion and an optimal number of solvent molecules and then to solvate the cluster using the continuum model. The optimal number of solvent molecules is chosen in such a way as to achieve a minimum in the solvation free energy.[62] In Table S1 (see the Supporting Information), we show that the optimal number of water molecules is one for all amines except α-F-MEAH$^+$. The calculated Gibbs free energies for the unprotonated and protonated amines in aqueous solution are presented in Table S2 of the Supporting Information.

Experimental. Monoethanolamine, 2-aminopropanol (α-CH$_3$-MEA),and 2-hydroxypropylamine (β-CH$_3$-MEA) were purchased from Aldrich and used as received. Research grade CO$_2$ was purchased from Airgas Specialty Gases and used as received. The heats of reaction were measured using an OmniCal Inc. ReactMax-Z3-UL calorimeter. Hasteloy-C reactor vessels (25 mL) supplied by the calorimeter manufacturer that can withstand pressures of up to 34.5 bar were used. An additional stainless steel vessel was added adjacent to the calorimeter to supply heated CO$_2$ to the reactor vessel. This additional vessel was placed in a heated box fitted with a circulating fan. A Sierra Instruments Smart-Trak2Model C100L mass flow controller was installed between the reactor vessel and the additional stainless steel CO$_2$ storage vessel to measure the amount of CO$_2$ added to the reactor. This mass flow controller has an integrated totalizer to measure the total flow of a gas over a user-defined time.

The reactor vessel was filled with ~1.5 g of sample, and a magnetic stir bar was added. The exact volume of the sample was calculated using the exact weight and density of each sample. The total volume of the reactor system was 27.7 mL. The reactor was sealed and placed inside the calorimeter, with stirring set to ~530 rpm, and the temperatures of the calorimeter and the CO$_2$ storage vessel were set to 40 °C. The CO$_2$ storage vessel was filled with CO$_2$ from the supply tank. The system was then allowed to come to equilibrium for 1–2 h. When both

Heats of Reaction of Substituted MEA with CO$_2$

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TABLE 3: Relative Basicities (kilocalories per mole) of Substituted MEA

species	relative basicity	species	relative basicity
MEA	279.0	α-OH-MEA	275.5
α-CH$_3$-MEA	277.9	β-OH-MEA	281.3
β-CH$_3$-MEA	278.9	α-OCH$_3$-MEA	273.4
α-NH$_2$-MEA	277.8	β-OCH$_3$-MEA	278.7
β-NH$_2$-MEA	279.5	α-F-MEA	266.7
		β-F-MEA	275.9

the heat flow and the calorimeter temperature achieved steady state, the system was considered to be at equilibrium.

The totalizer on the mass flow controller was reset to zero, and the reactor was filled with approximately 430 standard cm^3 of CO$_2$. A large excess of CO$_2$ was added to the reactor to ensure complete reaction of the sample. The value on the mass flow controller totalizer was recorded, and the reaction was allowed to proceed until the heat flow returned to the baseline value. The total reaction time was approximately 100 min. The baseline value for the heat flow was established and subtracted from the raw data. The baseline-subtracted heat flow was then integrated over the reaction time to determine the total reaction heat. The total amount of CO$_2$ remaining in the headspace of the reactor was calculated from the pressure, temperature, and headspace volume. The total amount of CO$_2$ absorbed by the sample was calculated by subtracting the CO$_2$ remaining in the headspace at the end of the reaction from the total CO$_2$ added to the system initially. The heat of reaction was then calculated by dividing the total reaction heat by the amount of CO$_2$ absorbed by the sample.

Results and Discussion

Basicity of Substituted MEA. There is some debate in the literature about the exact details of the mechanism for the reaction between MEA and CO$_2$. Several different mechanisms have been proposed, including a single-step reaction mechanism,[46] a two-step mechanism that proceeds via zwitterion formation,[59,63,64] and a two-step mechanism involving carbamic acid as an intermediate.[65] However, there is general agreement that Lewis acid−base interactions between amine and CO$_2$ are important in both carbamate and carbamic acid reactions. Therefore, the basicity of an amine should have a significant influence on the heat of reaction. We have calculated the relative basicity of each of the substituted MEAs; these values are lited in Table 3. We note that the substitution site has an important influence on the change in basicity. The relative basicities of NH$_2$-MEA and OH-MEA for α site substitution are 277.8 and 275.5 kcal/mol, respectively, which is lower than that of the parent molecule MEA (279.0 kcal/mol). However, relative basicities of the corresponding β site substituted species are 279.5 and 281.3 kcal/mol, respectively, which are higher than the basicity of MEA. We have plotted the relative basicity of substituted MEA as a function of the electronegativity of the substituent group (taken from Table 1) in Figure 1. The α- and β-substituted compounds are plotted separately to avoid convolution with the site effects noted above. We see that α-substituted MEA shows a monotonic decrease in basicity with increasing electronegativity, but the decrease is highly nonlinear. Conversely, the basicity of β-substituted compounds initially increases and then decreases with increasing electronegativity. Hence, there is no simple relationship between electronegativity and basicity. Our findings are in agreement with the observation that several factors affect the basicity of a molecule in solution, including inductive or polarization effects, solvation free energy, the ability to form intramolecular hydrogen bonds, etc.[66]
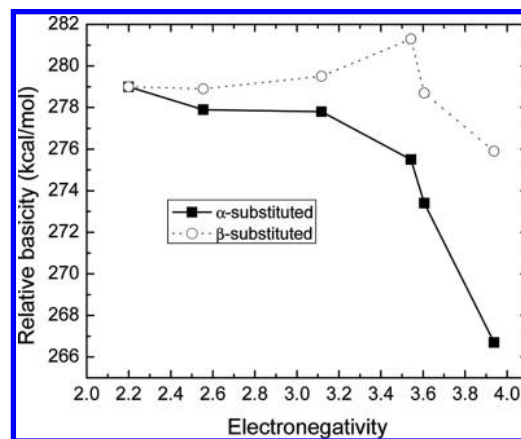

Figure 1. Relative basicity plotted as a function of the electronegativity of the subsitutient group for α-substituted (■) and β-substituted (○) MEA. Lines are drawn as a guide to the eye.

Heats of Reaction of Carbamic Acid. The geometries of the lowest-energy carbamic acid conformations are given in Figure 2, along with N−C bond lengths for the C atom of the COO group and some key intramolecular hydrogen bonds. The N−C bond length for the unsubstituted MEA is 1.34 Å. This bond length lies between typical N−C single (1.47 Å) and double (1.27 Å) bond lengths. We also note that the four atoms (NCOO) lie in the same plane. The bond length and the coplanarity of the NCOO group indicate that π conjugation is formed between the lone pair of electrons of N, the O atom of OH in COOH, and the CO π bond. We have examined the molecular orbitals to verify the existence of π conjugation in the carbamic acid product. Inspection of the orbitals revealed that the 10th highest occupied molecular orbital (HOMO-9) is the highest occupied orbital that has characteristics of π conjugation bonding between the COO group and the N atom. We have plotted the HOMO-9 orbitals in Figure 3. The formation of π conjugation orbitals increases the stability of the compound. In addition, an intramolecular hydrogen bond is formed between the H atom of the OH group connected to the CH$_2$ group and the O atom of the CO carboxylic acid group in the lowest-energy conformer. This hydrogen bond also increases the stability of the carbamic acid product. This is illustrated in Figure 2a. We have found that other higher-energy conformations typically have intramolecular hydrogen bonds with different groups of atoms. For example, an MEA carbamic acid conformer was found having a hydrogen bond involving the H atom of the OH group connected to the CH$_2$ group and the O atom of the OH group in COOH. The energy of this conformer is ~2 kcal/mol higher than that of the lowest-energy conformer. This indicates that there is a wide range of energies associated with intramolecular hydrogen bonds. The Boltzmann averaged heat of reaction for forming carbamic acid from MEA and CO$_2$ is calculated to be −8.9 kcal/mol at the MP2/aug-cc-pVDZ//B3LYP/6-311++G(d,p) level.

The lowest-energy conformers of carbamic acids formed from substituted MEA all share the same planar core among four atoms (COO and N) as discussed above for the parent compound. However, some of the substituted compounds do not have intramolecular hydrogen bonds discussed above and shown in Figure 2a for the parent compound as their lowest-energy conformers. See conformers e, f, and h−k in Figure 2. This may be a result of increased ring strain for the formation of seven-membered ring hydrogen bonds or a decrease in the formation energy of the hydrogen bond due to chemical effects. By way of illustration, the lowest-energy conformations in
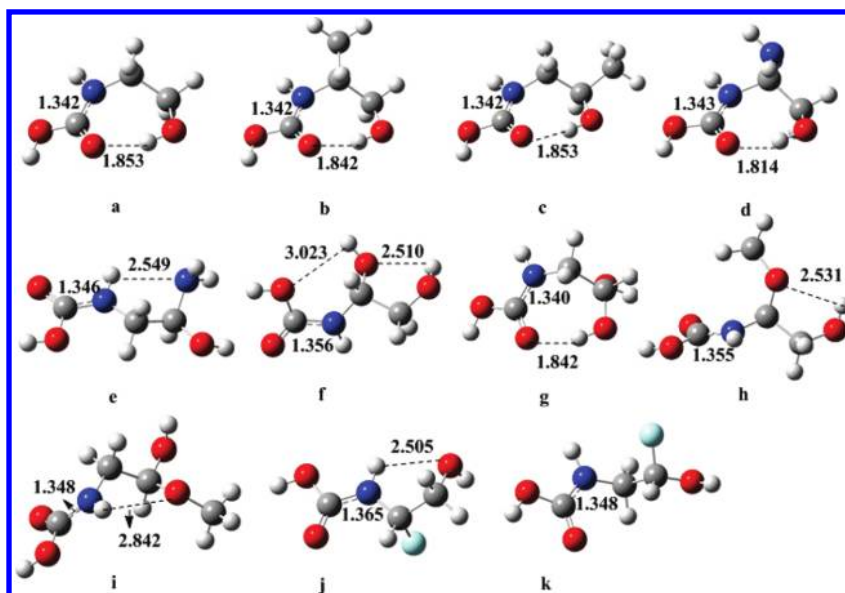
Figure 2. Lowest-energy conformers of carbamic acids formed from reactions of CO_2 with (a) MEA, (b) α-CH_3-MEA, (c) β-CH_3-MEA, (d) α-NH_2-MEA, (e) β-NH_2-MEA, (f) α-OH-MEA, (g) β-OH-MEA, (h) α-OCH_3-MEA, (i) β-OCH_3-MEA, (j) α-F-MEA, and (k) β-F-MEA. C–N bond lengths and hydrogen bond (dashed lines) lengths are given in angstroms. Red spheres denote oxygen, blue spheres nitrogen, gray spheres carbon, and white spheres hydrogen.
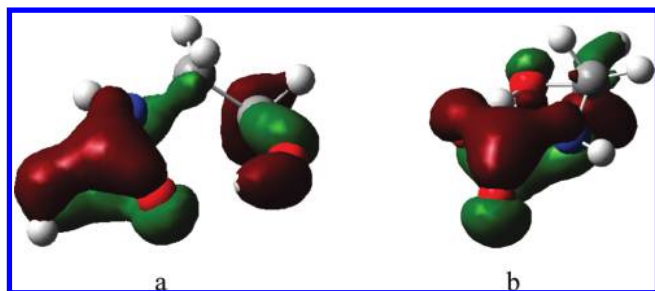

Figure 3. Tenth highest occupied molecular orbitals (HOMO-9) of the lowest-energy conformations of MEA-based carbamic acid (a) and MEA-based carbamate anion (b). The molecular obitals plotted are associated with π conjugation bonding between the lone pair of electrons of the N atom and the O atom of the COO group, and the CO π bond.

TABLE 4: Computed Heats of Reaction (kilocalories per mole) for Carbamic Acid

species	ΔH	species	ΔH
MEA	−8.9	α-OH-MEA	−6.7
α-CH_3-MEA	−7.6	β-OH-MEA	−9.8
β-CH_3-MEA	−8.8	α-OCH_3-MEA	−7.1
α-NH_2-MEA	−7.0	β-OCH_3-MEA	−9.0
β-NH_2-MEA	−8.9	α-F-MEA	−4.1
		β-F-MEA	−8.4

panels e, f, h, and i of Figure 2 involve intramolecular NH$\cdots$$NH_2$, HO$\cdots$HO$\cdots$HO, CH_3O$\cdots$HO, and NH$\cdots$$OCH_3$ hydrogen bonds, respectively. We see from inspection of Table 4 that the carbamic acid heats of reaction do not change a great deal as the substituent group is changed, except for α-F-MEA. The heat of reaction is 4.8 kcal/mol less exothermic for α-F-MEA than for MEA; the next largest change is a 2.2 kcal/mol less exothermic value for α-OH-MEA.

We have plotted the heat of reaction for carbamic acid as a function of amine basicity in Figure 4. We observe a roughly linear relationship between the heat of reaction and the relative basicity of the substituted amine with a correlation coefficient (R^2) of 0.85. Notwithstanding the scatter about the linear fit to the data, it is clear from inspection of the data that in general, the stronger the base the more exothermic the heat of reaction.
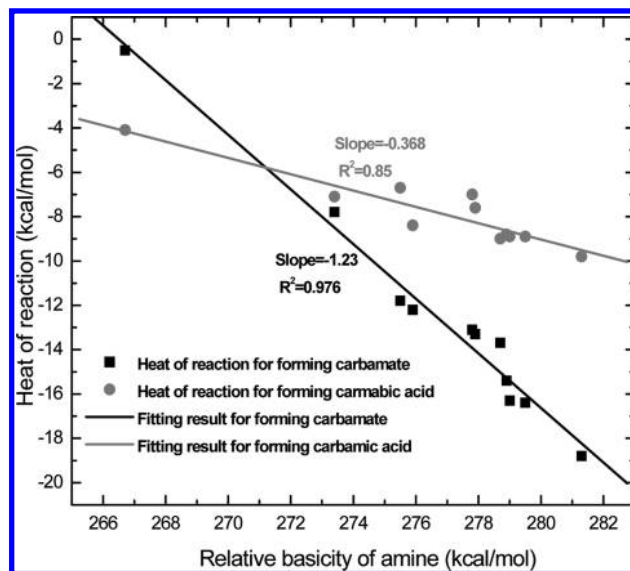

Figure 4. Heats of reaction for forming carbamate and carbamic acid as a function of the relative basicity of the substituted MEA.

Carbamate Heats of Reaction. We now consider the geometries and energetics of carbamates. The lowest-energy conformations of the ammonium cations formed from substituted MEA are presented in Figure 5. Hydrogen bonds are also identified for each cation in Figure 5. We note that for all cations except β-NH_2-MEA (Figure 5e), the lowest-energy conformers involve the formation of intramolecular HO$\cdots$$HNH_2$ hydrogen bonds. The ground state conformer for the β-NH_2-MEA-based cation has a $H_2N$$\cdots$$HNH_2$ hydrogen bond and is 1.7 kcal/mol lower in energy than the conformation with a HO$\cdots$$HNH_2$ hydrogen bond. The preference for the $H_2N$$\cdots$$HNH_2$ hydrogen bond can be rationalized by noting that in general, the H_2N lone pair of electrons is a stronger hydrogen bond acceptor (electron donor) than the O atom of the OH group. We also note from Figure 5 that several of the ammonium cations form double hydrogen bonds. This is the case for α-NH_2-MEA, α-OH-MEA, β-OH-MEA, and β-OCH_3-MEA, as seen in panels d, f, g, and i of Figure 5, respectively.
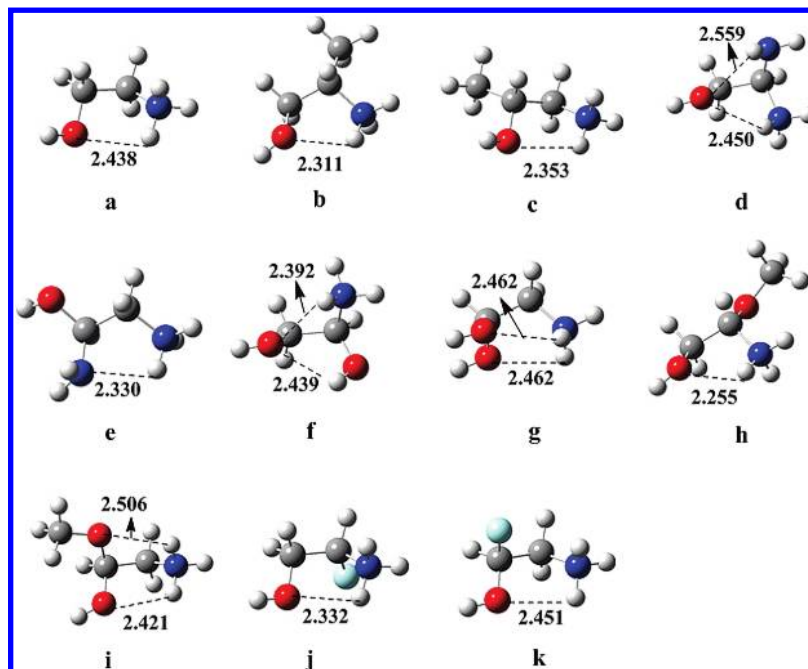
Figure 5. Lowest-energy conformers of ammonium cations formed from reactions of CO$_2$ with (a) MEA, (b) α-CH$_3$-MEA, (c) β-CH$_3$-MEA, (d) α-NH$_2$-MEA, (e) β-NH$_2$-MEA, (f) α-OH-MEA, (g) β-OH-MEA, (h) α-OCH$_3$-MEA, (i) β-OCH$_3$-MEA, (j) α-F-MEA, and (k) β-F-MEA. Hydrogen bonds are indicated by dashed lines, and bond lengths are given in angstroms. Atom definitions are as in Figure 2.
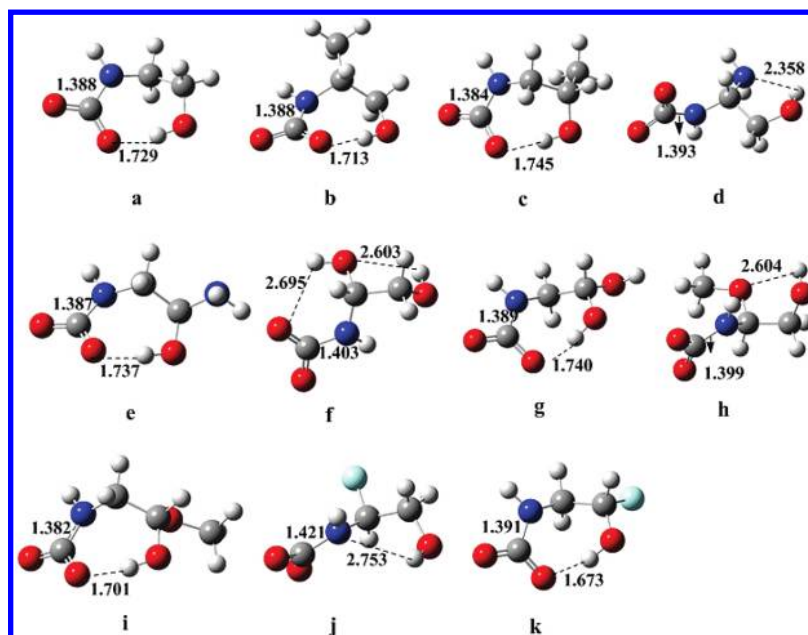

Figure 6. Lowest-energy conformers of carbamate anions formed from reaction of CO$_2$ with (a) MEA, (b) α-CH$_3$-MEA, (c) β-CH$_3$-MEA, (d) α-NH$_2$-MEA, (e) β-NH$_2$-MEA, (f) α-OH-MEA, (g) β-OH-MEA, (h) α-OCH$_3$-MEA, (i) β-OCH$_3$-MEA, (j) α-F-MEA, and (k) β-F-MEA. C−N and hydrogen bond (dashed lines) lengths are given in angstroms. Atom definitions are as in Figure 2.

The lowest-energy conformations of the carbamate anions, along with N−C bond lengths and hydrogen bond lengths, are shown in Figure 6. Similar to the cations, the anions also involve the formation of different types of intramolecular hydrogen bonds. The lowest-energy conformers for most of the carbamate anions involve hydrogen bonds between the O atom of the COO$^-$ group and the H atom of the OH group (see Figure 6a−c,e,g,i,k). However, the anions based on α-NH$_2$-MEA, β-OH-MEA, α-OCH$_3$-MEA, and α-F-MEA involve formation of other types of hydrogen bonds. Perhaps the most striking thing about the anions shown in Figure 6 is that the four atoms (COO and N) lie in the same plane for all of the conformers. This is also the case for the carbamic acid conformers shown

in Figure 2, as discussed previously. This indicates that the NCOO group of the anions also involves π conjugation. We here discuss the MEA-based carbamate anion as an example. The N−C bond length is 1.39 Å (Figure 6a), which lies between the N−C single and double bond lengths of 1.47 and 1.27 Å, respectively. The π conjugation character of the NCOO group can also be seen by plotting the molecular orbitals, as shown in Figure 3b.

The total and stepwise (eqs 3 and 4, respectively) heats of reaction for carbamate formation are listed in Table 5. We observe that the heats of reaction for the first step, ΔH_1 given by eq 3, are very sensitive to the substituent group, changing from 7.4 kcal/mol for α-F-MEA to −11.6 kcal/mol for β-OH-

TABLE 5: Heats of Reaction (kilocalories per mole) for the First Step, ΔH_1 from eq 3, the Second Step, ΔH_2 from eq 4, and the Total Reaction for Formation of Carbamate with Substituted MEA

species	ΔH_1	ΔH_2	ΔH
MEA	−9.7	−6.6	−16.3
α-CH$_3$-MEA	−7.1	−6.2	−13.3
β-CH$_3$-MEA	−8.9	−6.5	−15.4
α-NH$_2$-MEA	−7.9	−5.2	−13.1
β-NH$_2$-MEA	−10.7	−5.7	−16.4
α-OH-MEA	−6.1	−5.7	−11.8
β-OH-MEA	−11.6	−7.2	−18.8
α-OCH$_3$-MEA	−2.3	−5.5	−7.8
β-OCH$_3$-MEA	−7.8	−5.9	−13.6
α-F-MEA	7.4	−7.9	−0.5
β-F-MEA	−5.3	−6.9	−12.2

TABLE 6: Comparison of Calculated and Experimentally Determined Heats of Reaction (kilocalories per mole) for Carbamate Formation with Substituted MEA

species	calculated ΔH	experimental ΔH
MEA	−16.3	−17.3 ± 1.3
α-CH$_3$-MEA	−13.3	−12.9 ± 1.2
β-CH$_3$-MEA	−15.4	−15.6 ± 1.3

MEA. In contrast, heats of reaction in the second step, ΔH_2 from eq 4, range from −5.2 kcal/mol for α-NH$_2$-MEA to −7.9 kcal/mol for α-F-MEA. Total heats of reaction vary by more than 18 kcal/mol, from −0.5 kcal/mol for α-F-MEA to −18.8 kcal/mol for β-OH-MEA. We note that the implicit solvent model is known to be inaccurate for computing solvation free energies of ions. This affects the calculations in both eqs 3 and 4. However, the errors in these calculations, caused by inaccurate calculation of the solvation free energy for the ions, will largely cancel out because the isolated solvated ions are intermediate products in the thermodynamic path. Hence, we expect the total heats of reaction to be fairly accurate. We have plotted the carbamate heats of reaction as a function of the basicity of the amine in Figure 4. We see that the heats of reaction are a linear function of the amine basicity. The correlation coefficient (R^2) equals 0.976, indicating a good fit of the data. Hence, we can say with a good deal of confidence that the more basic the amine, the more exothermic the heat of reaction. This observation gives us both a design tool for modifying ΔH and a method for screening candidate amines.

We have experimentally determined the total heats of reaction for the parent MEA molecule as well as the two commercially available α- and β-methyl derivatives. The measured ΔH values are listed in Table 6. Our measured heat of reaction for MEA is −17.3 ± 1.1 kcal/mol. This value is in reasonably good agreement with the value reported by Kim and Svendsen[67] of −19.1 kcal/mol at 313 K. Our value is also in very good agreement with the value we calculated by fitting the equilibrium constants reported by Jou et al.[68] to an Arrhenius equation. The linear fit to their data gave an R^2 of 0.9935, and the slope yielded a heat of reaction of −16.5 kcal/mol. We also report the predicted values of ΔH for MEA, α-CH$_3$-MEA, and β-CH$_3$-MEA in Table 6 for comparison. The calculated and experimentally measured values are in remarkable agreement. Not only are the trends predicted by our calculations verified by the experimental data, but our predicted ΔH values agree with the experiments within the estimated experimental errors. This level of agreement is certainly fortuitous, given the approximations we have made. However, we have a high degree of confidence that the trends predicted from the calculations are correct. We

note that the experimental data were measured at 313 K while the calculations were performed at 298 K. We do not expect ΔH to vary significantly with temperature over this small temperature range. As a test, we have computed ΔH for MEA at 313 K, obtaining a value of −16.2 kcal/mol, in excellent agreement with the value of −16.3 kcal/mol at 298 K.

Tuning the Amine:CO$_2$ Stoichiometric Ratio. We note that the linear relationships between the heats of reaction and the basicity for carbamic acid and carbamate formation have very different slopes, as seen from Figure 4. The carbamic acid reaction displays a weak dependence on the basicity, having a slope of −0.368 (Figure 4). In contrast, the slope of the linear fit of the carbamate heats of reaction to the amine basicity is −1.23. Hence, there is a crossing point in the heats of reaction that is apparent from the plot shown in Figure 4. The heats of reaction should be equal, according to the linear fits, for an amine with a relative basicity of 271 kcal/mol, and the corresponding ΔH for both products should be −6 kcal/mol. This prediction is consistent with the observation that the heats of reaction for α-OCH$_3$-MEA, having a basicity of 273.4 kcal/mol, are −7.1 and −7.8 kcal/mol for the formation of carbamic acid and carbamate, respectively. Our simple model predicts that carbamic acid formation will be thermodynamically favored for amines having relative basicities of <271 kcal/mol. Indeed, the calculated heats of reaction for α-F-MEA are −4.1 and −0.5 kcal/mol for the formation of carbamic acid and carbamate, respectively. Assuming no kinetic limitations, our calculations predict that the relative amounts of carbamic acid and carbamate would be ~440:1 in solution at room temperature. This offers the possibility of tuning the stoichiometry of the reaction between the 2:1 carbamate and 1:1 carbamic acid amine:CO$_2$ ratios.

Conclusions

We have investigated the influence of various substituent groups on the heats of reaction of substituted MEA with CO$_2$ using ab initio calculations at the MP2/aug-cc-pVDZ level, coupled with geometries generated from B3LYP/6-311++G(d,p) density functional theory, in both cases using conductor-like polarizable continuum model formalism to account for solvent effects. Two reaction products were considered: carbamate, having a 2:1 amine:CO$_2$ reaction stoichiometry, and carbamic acid, having a 1:1 stoichiometry. We have considered five different substituent groups on both the α- and β-carbons of MEA, namely, CH$_3$, NH$_2$, OH, OCH$_3$, and F. We have taken experimental measurements of the heats of reaction for MEA and the α- and β-substituted MEA with CH$_3$ as the substituent. The predicted values of ΔH are in excellent agreement with the experimentally measured values, giving us confidence in our predictions for the other substituent groups. We have also computed the relative basicities of the various substituted amines. Our results indicate that heats of reaction for forming both carbamic acid and carbamate are linear functions of the relative basicities of substituted MEA: stronger basicity leads to more exothermic heats of reaction. Hence, a general strategy for reducing the heat of reaction for carbamate formation is to decrease the basicity of the amine. Importantly, the carbamate heats of reaction are much more sensitive to changes in the basicity than carbamic acid heats of reaction. Our linear models predict that carbamic acid formation will be thermodynamically favored over carbamate formation for amines with a relative basicity of <271 kcal/mol. Assuming no kinetic limitations, we predict that carbamic acid will be formed almost exclusively for α-F-MEA, which has a relative basicity of 266.7 kcal/mol.

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Supporting Information Available: Solvation free energies for univalent cations calculated by the cluster-continuum model and Gibbs free energies for unprotonated and protonated substituted MEA in aqueous solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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