Chemical and Molecular Descriptors for the Reactivity of Amines with CO_2

*Anita S. Lee[1,2], John R. Kitchin[1,2]**

1. US-DOE National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15236, United States

2. Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh Pennsylvania 15213, United States

*jkitchin@andrew.cmu.edu

Abstract

Amine-based solvents are likely to play an important role in CO_2 capture applications in the future, and the identification of amines with superior performance will facilitate their use in CO_2 capture. While some improvements in performance will be achieved through process modifications, modifying the CO_2 capture performance of an amine also implies in part an ability to modify the reactions between the amine and CO_2 through development of new functionalized amines. We present a computational study of trends in the reactions between CO_2 and functionalized amines with a focus on identifying molecular descriptors that determine

trends in reactivity. We examine the formation of bicarbonate and carbamate species on three classes of functionalized amines: alkylamines, alkanolamines, and fluorinated alkylamines including primary, secondary and tertiary amines in each class. These functional groups span electron-withdrawing to donating behavior, hydrogen-bonding, extent of functionalization, and proximity effects of the functional groups. Electron withdrawing groups tend to destabilize CO_2 reaction products, whereas electron-donating groups tend to stabilize CO_2 reaction products. Hydrogen bonding stabilizes CO_2 reaction products. Electronic structure descriptors based on electronegativity were found to describe trends in the bicarbonate formation energy. A chemical correlation was observed between the carbamate formation energy and the carbamic acid formation energy. The local softness on the reacting N in the amine was found to partially explain trends carbamic acid formation energy.

Keywords: Carbon dioxide, CO_2 capture, conceptual density functional theory, amine solvents

Introduction

Growing concerns about the long term environmental impacts of anthropogenic CO_2 emissions have fueled the development of carbon capture technologies, specifically technologies to address emissions from the power generation industry. Currently, the most mature technology to address emissions from coal-fired power plants is a post combustion continuous flue gas scrubbing process using amine solvents, typically 30wt.% monoethanolamine (MEA). The National Energy Technology Laboratory has estimated that implementing an MEA CO_2 capture process at a 550 MW power plant to capture 90% of the CO_2 from the plant flue gas stream will lead to an 80% increase to the cost of electricity and a 30%

loss in overall plant efficiency.[1] The poor economics and energy intensity of this process are the largest hurdles to commercialization and large scale implementation.[2]

The MEA post combustion CO_2 capture process is a cyclic two-tower process shown in Figure 1. Though some of the heat supplied to the stripper is recovered in the cross heat exchanger, the largest parasitic energy demand of the process is the energy associated with thermal regeneration of the amine in the stripper. Models of the MEA process show that about 40% of the plant's low pressure steam needs to be fed to the stripper reboiler to meet the heat duty necessary to regenerate the amine, leading to reduced power output and lowered overall plant efficiency.[3,4]

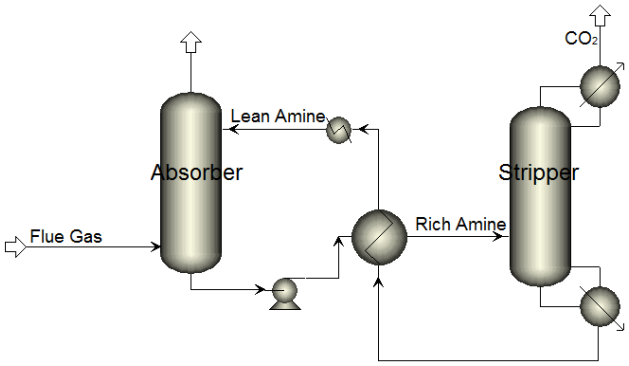


Figure 1: Schematic of MEA CO_2 post combustion capture process. Plant flue gas enters the absorber and the MEA solvent chemically absorbs CO_2. The processed flue gas, low in CO_2, leaves the absorber overhead and a CO_2 rich solvent stream leaves the bottoms and is passed to a stripper. In the stripper, CO_2 is thermally driven out from the solvent, yielding a concentrated CO_2 stream in the stripper overhead and regenerated amine solvent in the bottoms.

Four main heating demands contribute to the overall stripper heat duty: the heat of desorption of CO_2, the heat of vaporization of water to generate stripping steam, the sensible

heating of the process streams, and the equipment heating requirement. The heat of desorption is equivalently the negative of the amine-CO_2 reaction enthalpy (ΔH_{rxn}). Though a direct contributor to the stripper heat duty, the relationship between the amine-CO_2 reaction enthalpy and the overall energy requirements of the capture process is not direct. The reaction enthalpy also affects other process parameters that also impact the energy requirements.[5,6] Amines with a lower CO_2 reaction enthalpy would have decreased heat of desorption requirements, but they would tend to suffer from lower capture capacity, which leads to increased circulation rates and the sensible heating requirement.[7]

The delicate balance between the effects of the amine CO_2 reaction enthalpy on the heat of desorption and sensible heat requirements suggests that there may not be an optimal amine CO_2 reaction enthalpy suitable for all operating conditions and emphasizes the significance of the reaction enthalpy as a design parameter of the process. As illustrated by Onekyken and Rochelle, using a range of theoretical reaction enthalpies, a range in stripper heat duty for the traditional stripping process is achievable.[8] Additionally, for some reaction enthalpies, alternate stripper designs, e.g. vacuum desorption, may lead lower overall energy demands.[8] Thus, gaining insight in to how to control the amine-CO_2 reaction enthalpy through molecular design will aid in the development of new amine-based solvents with the purpose of addressing the economic and energy intensity challenges associated with solvent based CO_2 capture. Of course, other properties are important as well, such as corrosiveness, viscosity and stability, but the reaction enthalpy is a significant property that determines whether these other properties even need to be considered.

The chemical absorption of CO_2 in amine solvent systems typically occurs through the formation of two products, a carbamate and/or bicarbonate species.[9] The overall carbamate reaction is shown in equation 1, where the protonated base, B, is usually another amine, giving an upper limit of 2:1 amine to CO_2 ratio. This pathway is favored for primary and unhindered secondary amines.[10] The overall mechanism is still debated; the two leading theories are that reaction occurs through the formation of a zwitterion intermediate or carbamic acid formation.[11-14]

$$CO_2 + RNH_2 + B \rightleftharpoons BH^+ \cdots RNHCO_2^- \quad (1)$$

Bicarbonate formation occurs from the reaction of the amine with carbonic acid (equation 2). CO_2 and water naturally equilibrate to form carbonic acid, bicarbonate, and carbonate species, but the equilibrium is not product (i.e. captured CO_2) favored in neutral water.[15] Bicarbonate formation is enhanced in amine solvent solutions, which have a much higher pH than neutral water. The amine acts as a more favorable Brønsted base than water to enhance product formation.[16] The bicarbonate pathway is commonly associated with hindered secondary and tertiary amines, where the barrier for carbamic acid formation is high due to steric hindrance around the interacting amine site or prohibited due to the lack of an N-H bond in the tertiary amine. As these two reactions are each equilibrium reactions, there will be speciation between them that is determined by the relative reaction energies.

$$CO_2 + H_2O + RNH_2 \rightleftharpoons RNH_3^+ \cdots HCO_3^- \quad (2)$$

Previous work studying reactions of amine with CO_2 focused predominantly on evaluating the CO_2 capture capacity of a range of amines with different functional groups, but an understanding of the relationship between amine properties and reaction enthalpy with CO_2 is

still limited. Steric hindrance and amine basicity have long been the standard descriptors used to describe amine-CO_2 reactivity.[10,17] The work of Puxty et al challenges the completeness of this point of view. They measured the equilibrium CO_2 capacity of 76 amine solvents spanning primary, secondary, tertiary, and poly amines, and observed a wide range in capacity for the solvent systems.[18] In some cases, solvents showed capacities exceeding the maximum theoretical performance predicted by either an amine pK_a based capacity model for the bicarbonate pathway or a 2:1 amine to CO_2 interaction ratio along the carbamate pathway. Their work suggests that that relationship between reaction energy for the bicarbonate and carbamate pathway is more complicated than the simple framework of amine base strength, local geometry, and interaction ratios previously used to characterize amine- CO_2 reactions. Equally significant is that work did not directly provide any molecular insight to the observed variations in performance.

More systematic studies of amine functionalization have shown evidence that the size and type of functional group play a role in amine-CO_2 reactivity. Singh et al experimentally studied the effects of functional group chain length with alkylamines and alkanolamines and showed that the amine-CO_2 reaction was stabilized as the functional chain length increased.[19] Mindrup and Schneider conducted a computational study on five groups of substituted amines using density functional theory (DFT) to measure the trends in reaction energies relevant to CO_2 capture in the gas phase.[20] Their work showed that carbamic acid formation is more stable for the group of amines substituted with electron-donating substituent and destabilized for amines with electron-withdrawing substituents. Additionally, they showed that the changes in reaction energy to form carbamic acid do not correlate with changes in amine protonation

energy, suggesting that different properties of the amine control the reaction energy for carbamic acid formation and amine protonation energy.

The work of Chakraborty et al provided some foundational insight into how the functional group alters the amine reaction site to control the energetics of the amine-CO_2 reaction.[21] As the first to document the effects of functionalizing the alpha carbon of alkanolamines on the amine-CO_2 reaction energy, they suggested that there was a molecular orbital interaction between the alpha carbon functional group and the local environment of the electron density around the nitrogen that led to destabilization of the amine-CO_2 interaction. However, how the local electron density changes was not addressed nor did the study consider the longer chain functional groups, which are now known to also impact amine-CO_2 reactivity. Xie et al presented a closer look at substituent effects on carbamate and carbamic acid reaction energies by studying the reaction energy of alpha and beta carbon substituted monoethanolamine with CO_2.[22] Their work showed that the destabilization of the substituent effects on carbamate and carbamic acid formation was decreased as the number of carbons between the amine and the substituent increased, showing tunability of substituent effects. However, there remains a gap in understanding what molecular features control the amine-CO_2 reaction energies and how those features can be controlled through amine substitution, which has limited the design of new solvents with targeted properties.

The present work focuses exclusively on the relationship between molecular properties of amines and their influence on the reactions between the amine and CO_2. Molecular modeling within the framework of density functional theory (DFT) was used to evaluate the reaction energy associated with the formation of product species within the amine-CO_2 system.

Conceptual density functional theory was used to relate electronic structure properties of the amines to trends in their reactivity, with the purpose of providing the foundational understanding necessary for the design of amine solvents for CO_2 capture with target reactivities towards CO_2.[23-25] The objectives of this work are (1) to assess the impact of functionalizing amines on their reactivity, and (2) to identify descriptors based on electronic structure and reactivity properties that would enable the prediction of the reactivity of a new candidate amine towards CO_2. In this work three classes of amines were studied: alkylamines, alkanolamines, and trifluoroalkylamines. These functional groups span a range of electron-donating and electron-withdrawing behavior. Within each class of amine, primary, secondary, and tertiary amines were considered with three different functional group lengths to determine the effects of type and proximity of the functional group and degree of functionalization on the amine CO_2 reactivity.

Computational Methods

The energy and electronic structure of molecular systems were computed with density functional theory (DFT) calculations using Gaussian 09 with the B3LYP functional and 6-31+G(d,p) basis set.[26] The B3LYP functional has been shown to be sufficient to establish trends in molecular reactions of systems of the size considered in this study. [12,20,27,28] Energy and electronic descriptor calculations were performed for a subset of the amines studied with a larger basis set, with no change in energy correlations, indicating that this level of theory was sufficient for the trends we observed. The solvent environment was simulated in the calculations using a polarizable continuum solvation model, using the integrated equation formalism model (IEFPCM) with the united atom cavity model and the dielectric constant of

water, which has been shown to be reasonably accurate for solvent phase calculations compared to more complex representations of the solvent phase.[29-32]

The reaction enthalpy (ΔH_{rxn}) for a generalized CO_2 capture reaction is expressed in equation 3. From the thermodynamic pathway shown in Figure 2, the overall enthalpy of reaction can be expressed as the sum of two enthalpies, the enthalpy of CO_2 solvation and the liquid phase amine-CO_2 reaction enthalpy (equations 4-5).

$$\Delta H_{rxn} = H_{Am-CO_2\,(\ell)} - H_{Am(\ell)} - H_{CO_2(g)} \qquad (3)$$

$H_{Am-CO_2\,(\ell)}$: H of amine-CO_2 product in liquid phase
$H_{Am(\ell)}$: H of amine in liquid phase
$H_{CO_2(g)}$: H of CO_2 in gas phase

$$\Delta H_{rxn} = \Delta H_{solv\,CO_2\,(\ell)} + \Delta H_{rxn}{}^{\ell} \qquad (4)$$

$$\Delta H_{rxn}{}^{\ell} = H_{Am-CO_2\,(\ell)} - H_{Am(\ell)} - H_{CO_2(\ell)} \qquad (5)$$

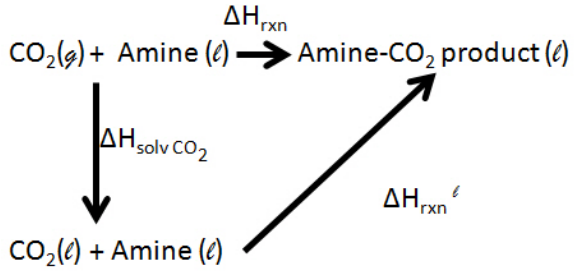


Figure 2: Thermodynamic pathway of amine CO_2 reaction showing relationship between overall reaction and solvent phase reaction.

Given the largely aqueous environment of amine solvents, the CO_2 solvation enthalpy is assumed to be constant for all amines. Thus, any variation in overall reaction enthalpy will be captured in $\Delta H_{rxn}{}^{\ell}$. The reaction enthalpy ($\Delta H_{rxn}{}^{\ell}$) of the liquid phase reaction can be approximated by the change in internal energy (ΔE), assuming the liquid system is

incompressible, i.e. for the reaction $\Delta PV \approx 0$ (equation 6). Thus, the reaction enthalpy analysis in this work focuses on $\Delta E_{rxn,}$ expressed in equation 7, where the internal energy ($E_{298,i}$) of each species is DFT computed energy in the simulated solvent environment of the IEFPCM model with zero point energy and temperature corrections.[33]

$$\Delta H_{rxn}^{\ell} = \Delta E_{rxn} + \Delta(PV)_{rxn} \approx \Delta E_{rxn} \qquad (6)$$

$$\Delta H_{rxn}^{\ell} \approx \Delta E_{rxn}^{\ell} = \sum_{i}^{products} E_{298,i} - \sum_{j}^{reactants} E_{298,j} \qquad (7)$$

For each reaction, the most thermodynamically relevant systems were considered by using the lowest energy conformation of each species to compute ΔH_{rxn}^{ℓ}. The lowest energy conformation was determined from a stochastic conformer search, detailed in the supplemental material. The same conformation was used to perform the electronic structure property analysis using the mathematical relationships of conceptual density functional theory described in the following section.

Theory of DFT Based Chemical Reactivity Descriptors

The context of the electronic structure property analysis is based in conceptual density functional theory connects mathematical relationships that naturally arise from density functional theory (DFT) to common empirical chemical concepts of chemical reactivity.[23-25] The fundamental relationship between DFT and chemical reactivity was defined by Parr, Donnelly, Levy and Palke linking the electronic chemical potential, μ, to the first derivative of energy, E, with respect to the number of electrons, N, at a fixed external potential, $v_o(\vec{r})$.[34] The chemical potential can be related to electronegativity using equation 8.[35] This relationship is consistent with the qualitative understanding of these concepts; the chemical potential is the escaping

tendency of electrons from the system, while electronegativity measures the tendency of the system to attract electrons.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v_o(\vec{r})} = -\chi \qquad (8)$$

Sanderson's electronegativity equalization principle uses electronegativity as a descriptor for the reaction between two states to form an overall product state.[36] This principle states that two bodies of different electronegativity values interact in a manner such that the electronegativity of the product species is equalized to a value intermediate of the electronegativity of the reactants. The necessary electronegativity equalization between two reacting bodies could be conceptualized as the driving force for interaction.

Through a perturbation analysis, the derivative of energy with respect to the external potential at a constant number of electrons can be shown to be equal to the electron density, $\left(\frac{\partial E}{\partial v_o(\vec{r})}\right)_N = \rho(\vec{r})$. Collectively, this definition of density and equation 8 are referred to as the first order energy response functions. Second order response functions, shown in equation 9 and equation 10, are related to the concepts of absolute hardness and the fukui function respectively, which can be used to derive the local softness of a reacting site.[37,38] The fukui function (equation 10) quantifies the concepts in the frontier electron theory of Fukui et al.[41,42] This theory describes the site selectivity of a reaction for a given molecule. Sites with a larger fukui function are favored as the reaction site. This theory has correctly predicted well known trends in intermolecular reactivity of many molecular systems, such as aromatics and carbonyl compounds.[37,43-47]

$$\left(\frac{\partial^2 E}{\partial N^2}\right)_{v_o(\vec{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v_o(\vec{r})} = \eta \qquad (9)$$

$$\left(\frac{\partial^2 E}{\partial v_o(\vec{r})\partial N}\right) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right) = f(\vec{r}) \qquad (10)$$

The concepts of hardness and softness stemmed from Pearson's work in understanding trends in the reactivity of Lewis acid base systems. Known as the principle of Hard and Soft Acids and Bases (HSAB), this work states that hard acids react more strongly with hard bases and soft acids react more strongly to soft bases.[39,40] Hard-hard interactions are more electrostatic in nature, while soft-soft interactions are more covalent in nature. Qualitatively, hardness describes systems of low polarizability, high electronegativity, and that are difficult to oxidize. Its conceptual counterpart, softness (*S*), refers to systems of the exact opposite characteristics: high polarizability, low electronegativity, and easily oxidizable. Mathematically, the definition of hardness, equation 9, measures the electron chemical potential's resistance to change with a change in the number of electrons. Parr and Pearson showed that is conceptually equivalent to the qualitative chemical concept of hardness that Pearson first introduced. The softness is defined as the inverse of hardness (equation 11).

$$S = \frac{1}{\eta} \qquad (11)$$

A localized version of the HSAB principle, connecting concepts of frontier electron theory and HSAB principles, was used to describe trends in intermolecular reactivity based on local properties of the reacting site.[44] This principle states that the soft-soft interaction of an acid (A) with a base (B) is favored when the reacting sites of the A and B have similar local softness values, s_i. The local softness of a reacting site is determined by integrating the spatial representation of the global softness, $S(\vec{r})$, over the volume of the reacting atom, Ω_i, where the local softness is spatially resolved by projecting the global softness onto the fukui function

(equation 12). We will use the localized softness as an electronic structure descriptor for reactivity in this work. Local softness was determined using equation 12, with the fukui function computed as defined above and the volume of integration defined by the nitrogen (N) volume determined from Bader population analysis of the neutral molecule.[49,50]

$$s_i = \int_{\Omega_i} s(\vec{r})dV = \int_{\Omega_i} Sf(\vec{r})\,dV \qquad (12)$$

A finite difference approximation was used evaluate the derivatives in equations 8-10. In the case of electronegativity, a centered finite difference approach was used, shown in equation 13.

$$\chi = -\left(\frac{(E_{N-1} - E_N) + (E_N - E_{N+1})}{2}\right)_{v_o(\vec{r})} \qquad (13)$$

This is equivalent to Mulliken's definition of electronegativity, $\chi = \left(\frac{I+A}{2}\right)$, where *I* is the vertical ionization energy and *A* is the electron affinity.[48] For the density derivative associated with the fukui function, finite difference approaches to evaluation of the derivative have been established for different types of reactions.[42] These are shown in equation 14 and equation 15, where ρ_N is the density of an *N*-electron system, with both densities calculated at a fixed external potential. The local densities of the N, N+1, and N-1 systems were computed using Bader population analysis.[49]

$$f^+(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho(\vec{r}) \text{ (nucleophilic attack)} \qquad (14)$$

$$f^-(\vec{r}) = \rho(\vec{r}) - \rho_{N-1}(\vec{r}) \quad \text{(electrophilic attack)} \qquad (15)$$

Relationships between electronic property descriptors and reaction energies in this work were made using reaction energies computed using DFT electronic energies. Temperature and vibrational corrections to the energies were neglected in building the electronic property

relationships to reactivity because these corrections are more a function of the molecular mechanics and not the molecular electronic state descriptors examined.

Results and Discussion

Reaction Energy Analysis

Three groups of structurally similar amines were studied; alkylamines, alkanolamines, and trifluoroalkylamines. Each amine group consists of primary, secondary, and tertiary amines, with substituent chains of one to three carbons in length. The alkylamine group is illustrated in Table 1. The product systems considered for the bicarbonate and carbamate pathway are shown in Table 2 and Table 3.

Table 1: Primary, secondary, and tertiary amines studied in alkylamine group (R=CH_3)

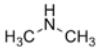
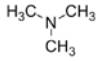
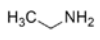
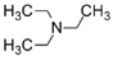
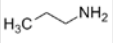
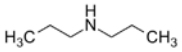
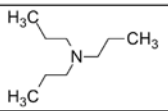
R= CH_3	Primary	Secondary	Tertiary
-R			
-(CH_2)R			
-(CH_2)$_2$-R			

Table 2: Reactions considered in this work along the bicarbonate pathway. In Reaction 1, the energies of the protonated amine and bicarbonate ion are computed in separate calculations. In Reaction 2, the energy of the protonated amine and bicarbonate is calculated for the interacting pair in a single calculation.

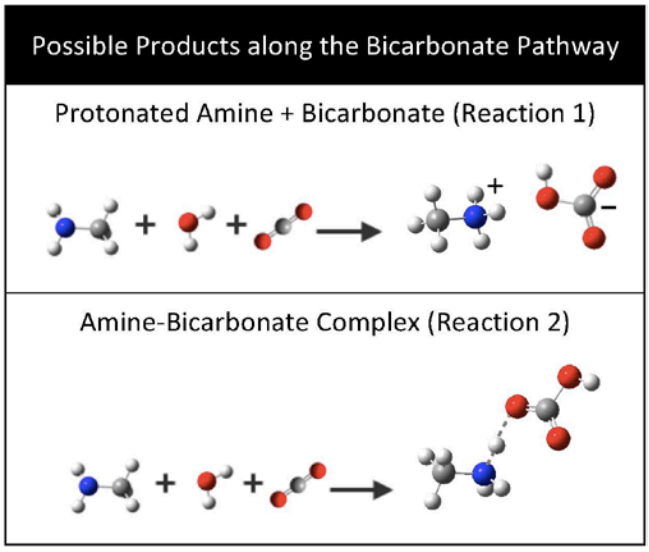
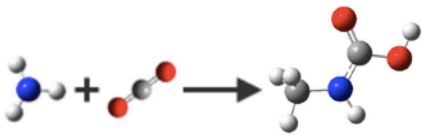
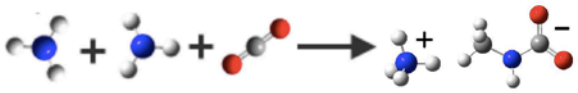
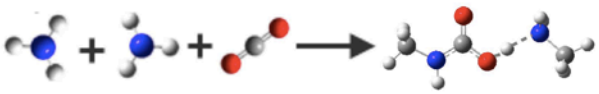


Table 3: Reaction along the carbamate pathway considered in this study. In Reaction 5, the Carbamate ion and protonated amine energies are computed in separate calculations. In Reaction 6, the energy is calculated for the carbamate/protonated amine pair in a single calculation.

Possible Products along the Carbamate Pathway
Zwitterion (Reaction 3) 
Carbamic Acid (Reaction 4) 
Carbamate + Protonated Amine (Reaction 5) 
Carbamate + Protonated Amine (Reaction 6) 

Previous work studying the reaction energy of forming an amine-CO_2 product concentrated on the reaction energy associated with forming a carbamate species or a protonated amine.[12,13,20,51] This approach views the product state as two non-interacting ions and does not consider the possibility of ion-pair formation through the interaction of these charged products with another charged species present in the system. Recently, transition state studies and ab initio molecular dynamics of amine-CO_2 systems showed in the case of the carbamate pathway, the stable product is a protonated amine-carbamate ion-pair, not the non-interacting two ion

state. [11,22,52] In this work, we performed reaction calculations for both a non-interacting ions and interacting ion-complex product systems for the bicarbonate and bicarbonate pathways (Shown in Table 2-Table 3, Bicarbonate non-interacting ions: Reaction 1, Bicarbonate ion-complex: Reaction 2, Carbamate non-interacting ion: Reaction 5, Carbamate ion-complex: Reaction 6). For all amines, the reaction energy calculations showed that the ion-complex formation along both the bicarbonate and carbamate pathway was more favorable compared to the non-interacting ion product system. The reaction pathway diagrams shown in Figure 3 illustrate this point for NH_3 and MEA.

The amine-bicarbonate ion complex (Reaction 2) is characterized by an N-H-O interaction between the amine and bicarbonate, with the proton shared between them and a characteristic N-O distance of 2.66±0.19 Å. In the cases of the secondary and tertiary trifluoromethyl substituted amines ($NH(CF_3)_2$ and $N(CF_3)_3$) the characteristic ion-complex product was not found. In these cases, the N-O distance is 3.12 Å and 4.5 Å respectively, with the H closely bound on carbonic acid, indicating that these amines are not very basic. The interacting system for both of these amines was lower in energy than the corresponding non-interacting state, indicating that possibly a long range weak electrostatic interaction existed between the amine and carbonic acid leading to a more stable product-like state, though not the amine-bicarbonate complex.

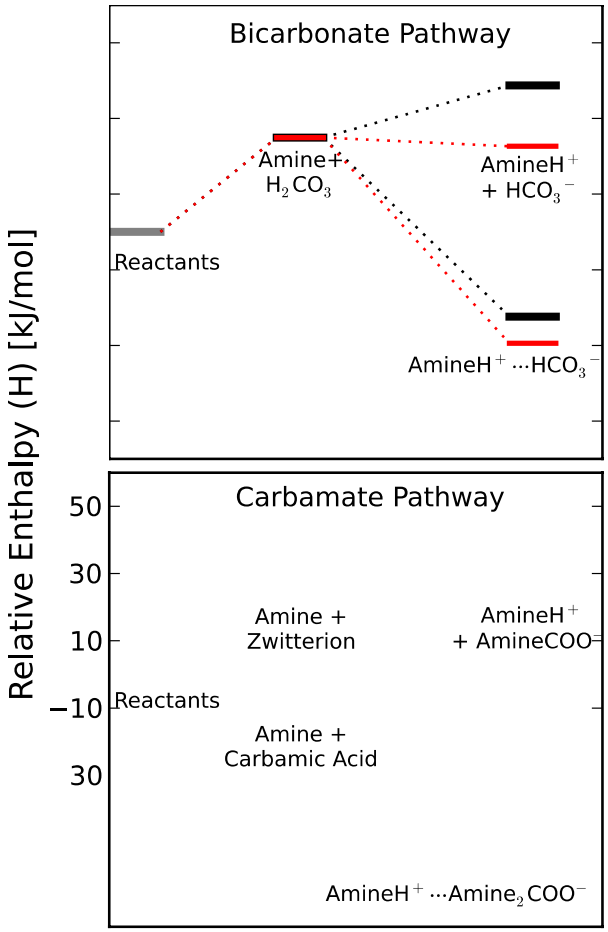


Figure 3: Reaction pathway diagrams showing the relative enthalpy (compared to enthalpy of reactants) of product states considered for the bicarbonate (a) and carbamate (b) pathway. Results for NH_3 are shown in black (▬) and results for MEA are shown in red (▬).

The carbamate pathway analysis was only performed for primary and secondary amines. Stable zwitterion species were found for all alkylamines and alkanolamines, and for primary and secondary trifluoropropylamines ($(CH_2)_2CF_3$ NH_2 and 2-($(CH_2)_2CF_3$)NH). With the other trifluoroalkylamines, the presence of the CF_3 group close to the reacting site of the amine has a destabilizing effect that prevents the close interaction with CO_2 necessary for zwitterion formation. Across all of the amines, the zwitterion system was higher in energy than the

carbamic acid product. This is consistent with the view that the zwitterion, if present, would be a short lived intermediate in the amine-CO_2-water system, given the energetic favorability of the proton transfer from amine nitrogen to either another base or to one of the oxygen atoms of the reacted CO_2.[11,53]

Figure 4 and Figure 5 show the reaction enthalpy of the bicarbonate ion-complex (Reaction 2) and carbamate ion-complex (Reaction 6) formation for the three groups of amines showing that the degree of substitution and type of substituent groups impact the stability of both product systems. Functionalizing NH_3 with an alkyl chain to form a primary alkylamine stabilized the formation of both product complexes as compared to the product complexes formed with NH_3 (Figure 4-a). Further functionalizing the amine with additional alkyl chains to form secondary and tertiary alkylamines increased the stability of the amine-bicarbonate complex, while decreasing the stability of the amine-carbamate complex. Both of these effects were independent of the length of the substituent chain, indicating that the minor increase in the inductive electron donating ability of the alkyl chain due to an increase in the chain length on the reactivity of the amine is outweighed by the effect of replacing a hydrogen atom with a carbon chain. Similar enhancement due to the presence of an alkyl functional group is seen with ionic liquids and gas phase amines.[20,27]

Functionalizing NH_3 with a trifluoroalkyl groups, destabilized the formation of both the amine-bicarbonate and amine-carbamate complex (Figure 4-b). The destabilization was strongest when CF_3, a strong inductive electron withdrawing group, was closest to the reacting site of the amine. As the carbon chain length separating the CF_3 group from the amine increased, the destabilizing effect was lowered. This is consistent with observations made by

Xie et al showing that destabilization effects of substituents on MEA were reduced as the substituent moved from the alpha to the beta carbon.[22] Because the effect persists in cases where the functional group is beyond the alpha carbon of the amine, something beyond interactions between the molecular orbitals of the alpha carbon and the reacting amine site alters the local electronic environment and causes destabilization of the product species.

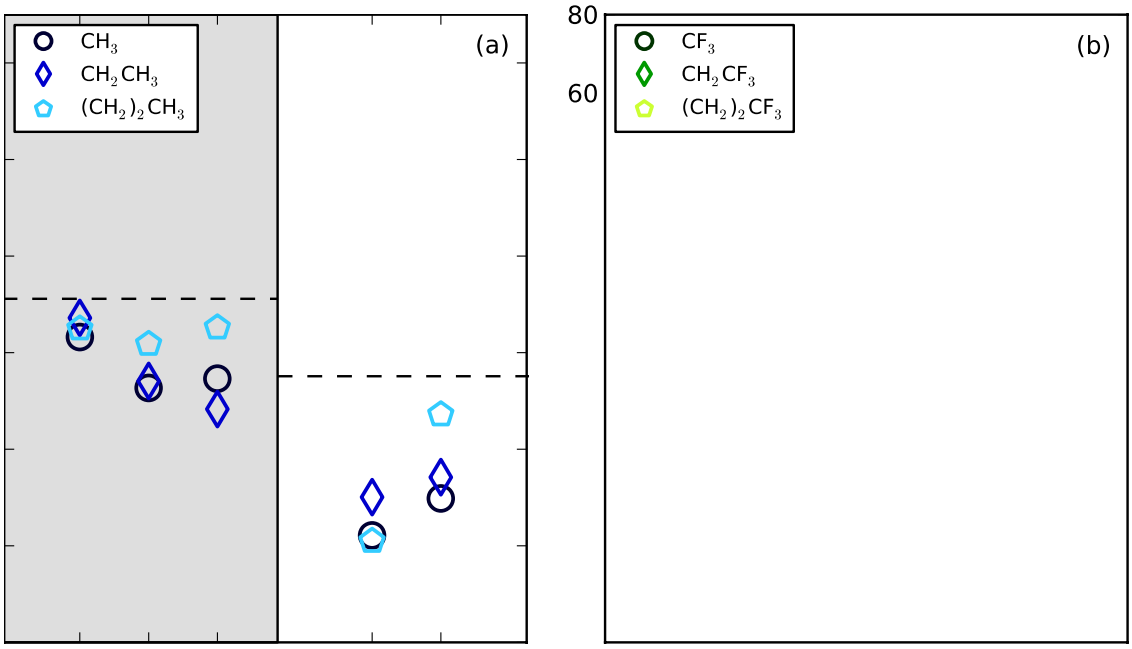


Figure 4: Reaction energy of amine-bicarbonate complex, Reaction 2, (shaded in gray) and amine-carbamate complex, Reaction 6, formation for primary (1°), secondary (2°), and tertiary (3°) alkylamines (a) and trifluoroalkylamines (b). The reaction energy associated with respective product formation from NH_3 is denoted by a dashed line.

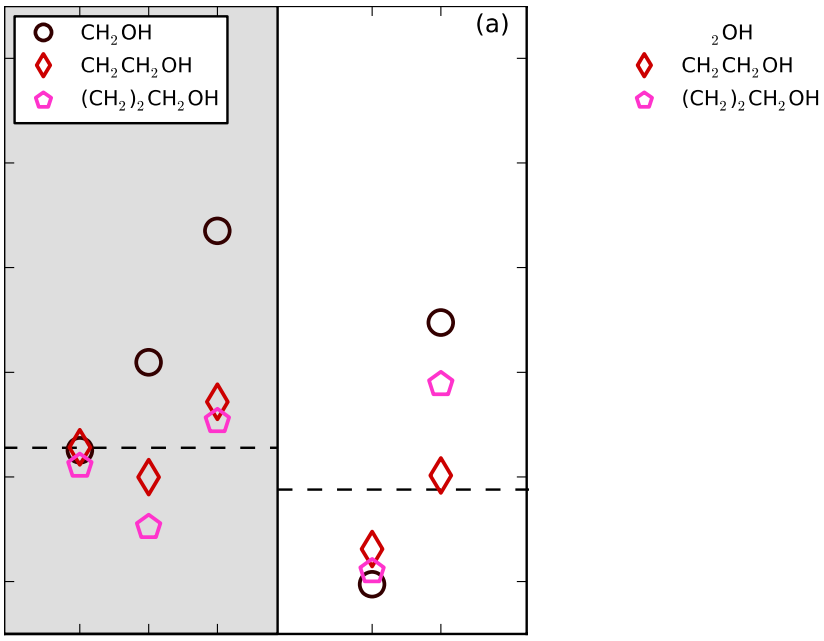


Figure 5: Reaction energy of amine-bicarbonate, Reaction 2, (shaded in gray) and amine-carbamate, Reaction 6, complex formation for primary (1°), secondary (2°), and tertiary (3°) akanolamines without effects of intermolecular hydrogen bonding(a) and alkanolamines including intermolecular hydrogen bonding (b). The reaction energy associated with respective product formation from NH_3 is denoted by a dashed line.

Alkanolamines showed behavior in between the other two groups of amines, which was expected given the moderate inductive electron-withdrawing nature of the OH group and its ability to participate in product stabilizing hydrogen bonding (Figure 5-a).[54] First considering the product species without hydrogen bonding, with the primary methanolamine, the moderate electron-withdrawing effect OH has a slight destabilizing effect, but is enhanced as the amine is further functionalized with methanol groups. As the functional chain length increases, the destabilizing effect of the OH group is reduced as observed with the trifluoroalkylamines.

Figure 5-b shows the reaction energy analysis including the additional stabilization due to hydrogen bonding was observed with both product complexes. Hydrogen bonding was observed in alcohol amine systems large enough to form five to six member rings through intramolecular hydrogen bonds. The trends in reactivity attributed to amine functionalization are clearer within the non-hydrogen bonding data set, thus the non-hydrogen bonded systems will be used in the further analysis.

The molecular and electronic structure analysis of bicarbonate formation

We now discuss the identification of chemical descriptors that may describe trends in reactivity. Sanderson's concept of two body interactions is applicable to the interaction between carbonic acid and amines to form the amine-bicarbonate complex. The electronegativity difference of the amine and carbonic acid drives the charge transfer between the bodies necessary to equalize their electronegativity, resulting in an acquired partial charge and electrostatic interaction in the product species. Based on this principle, one expects that the electronegativity difference of two reactants may be a descriptor of reactivity for the bicarbonate formation reaction. The reaction energy for amine-bicarbonate complex formation is plotted against the electronegativity difference between the two reactants, amine and carbonic acid in Figure 6. As the electronegativity difference between the two reactants, the amine and carbonic acid, gets larger, the reaction energy to form the amine-bicarbonate complex is larger leading to a more stable amine-bicarbonate complex. Figure 7 shows that this relationship between amine-bicarbonate reaction energy and electronegativity is not sensitive to molecular conformation. When performing the same analysis on reactant conformations within 0.1 eV of the lowest energy conformation, the relationship persists.

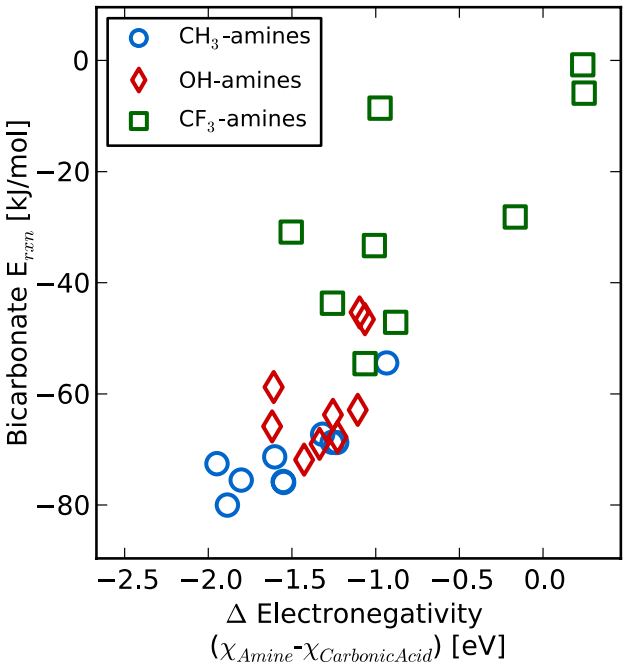


Figure 6: The Amine-bicarbonate complex reaction energy as a function of the difference in the electronegativity of the amine reactant and carbonic acid.

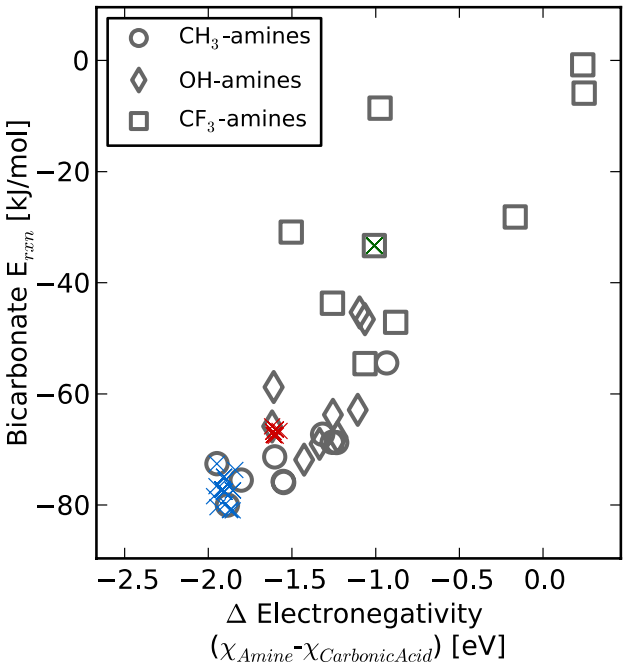


Figure 7: The Amine-bicarbonate complex reaction energy as a function of the difference in the electronegativity of the amine reactant and carbonic acid for the lowest energy amine reactant conformation (gray) and conformations with 0.1 eV of the lowest energy conformation for triproplyamine (blue), tripropanolamine (red), and di-trifluoroethylamines (green).

There is a broad range of reactivity for the formation of an amine-bicarbonate complex, spanning approximately 0 to -80 kJ/mol, suggesting a broad range of tunability based on the molecular structure of the amine. Utilizing this correlation to guide the development of new amines, since the electronegativity of carbonic acid is a constant, any tuning of the reaction energy along the bicarbonate pathway can solely be achieved by changes in the amine electronegativity through modifications to the molecular structure. Figure 8 shows the relationship between amine electronegativity and substituent groups on the amine. Electron withdrawing functional groups like CF_3 and OH increase the electronegativity of the amine. This effect is the strongest when the electronegative group is directly substituted on the amine

and is dampened when the carbon length of the substituent chain increases. With a longer chain substituent, the variations in electronegativity approach that seen with alkyl amines. The electronegativity of the amine can be systematically varied through the addition of substituent groups. However, there is a finite range over which the electronegativity of the amine can rationally be varied, of which a large portion has been sampled in this study, given the range in electron donating and electron withdrawing groups studied. This implies a limit to the range in achievable reactivity with amine-based solvents.

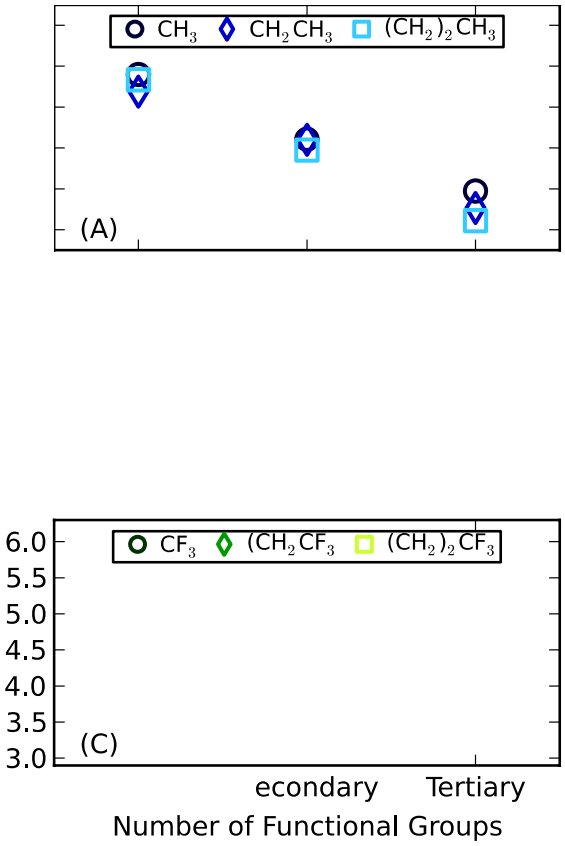


Figure 8: Electronegativity of primary, secondary, and tertiary amines for the (A) alkylamines, (B) alkanolamines, and (C) trifluoroalkylamines groups calculated using equation 13.

The molecular and electronic structure analysis of carbamate formation

The defining characteristic of the carbamate pathway reaction is the formation of the N-C bond of the carbamic acid intermediate. We found that the carbamate reaction energy was reasonably correlated with the carbamic acid formation reaction energy (Figure 9). Thus, for the electronic structure analysis of carbamate formation, we will focus on the reaction energy for the formation of the carbamic acid intermediate.

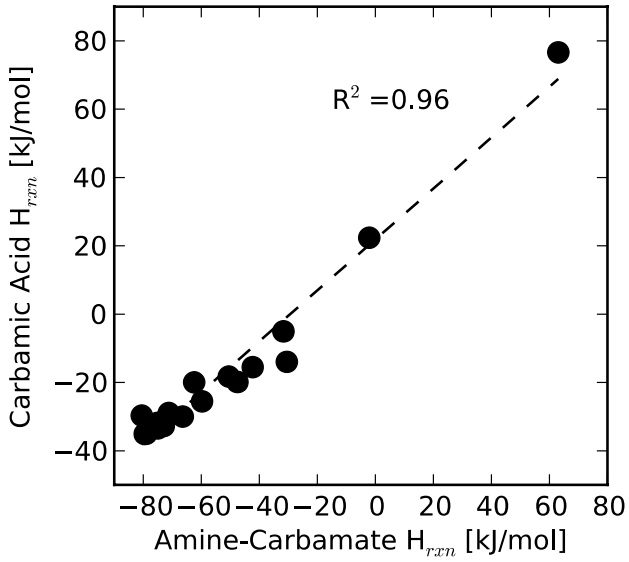


Figure 9: Correlation between amine-carbamate reaction energy and carbamic acid reaction energy.

The formation of carbamic acid is a Lewis acid base interaction between the amine and CO_2, where the amine undergoes electrophilic attack by CO_2. The local Hard Soft Acids and Bases principle (HSAB) suggests that the energy associated with the covalent bond formation in carbamic acid should be correlated with the relative softness of the amine site to that of CO_2. Figure 10 shows the relationship between the carbamic acid formation reaction energy and the localized softness of the amine nitrogen (s_N). The relationship is qualitatively consistent with the concepts of the HSAB; the closer in value the localized amine softness of the nitrogen site is

to the localized softness of the reacting site on CO_2, the more exothermic the formation of carbamic acid. However, a single correlation for all of the amine families was not observed. Two correlations can be seen with the carbamic acid reaction energy and nitrogen site softness: one for trifluoroalkylamines and the other for alkanolamines and alkylamines. The response of the trifluoroalkylamine carbamic acid reaction energy to changes in s_N is strong, whereas the carbamic acid reaction energy dependence on s_N is much weaker for the alkyl and alkanolamines. This suggests that nitrogen softness is a good descriptor of the carbamic acid reaction energy for some amines, but not simultaneously for all of them. It may be possible that inclusion of mechanical effects like steric hindrance need to be included to capture the remaining variations in reactivity.[55]

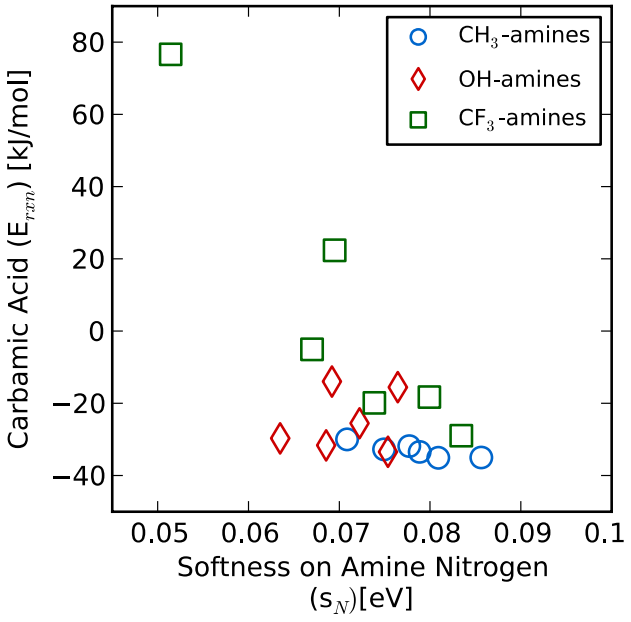


Figure 10: The reaction energy for carbamic acid formation as a function of the localized softness of the amine nitrogen (s_N). The softness of the reacting carbon (s_O) on CO_2 is 0.09 eV

The localized nitrogen softness of the amine can be tuned with amine functionalization as seen in Figure 11. Functionalizing the amine with strong electron withdrawing groups like with the trifluoroalkylamiens gives a large range in s_N. The presence of the electron-withdrawing group decreases s_N, with the effect being strongest when CF_3 is closest to the nitrogen site and diminishing as the chain length increases. The s_N can be further reduced with the addition of more electron-withdrawing groups through amine functionalization (primary to a tertiary amine). The range in s_N observed with the alkanolamines is much smaller, though the trend from the presences of the moderate electron-withdrawing –OH group has similar qualitative effects as in the trifluoroalkylamines.

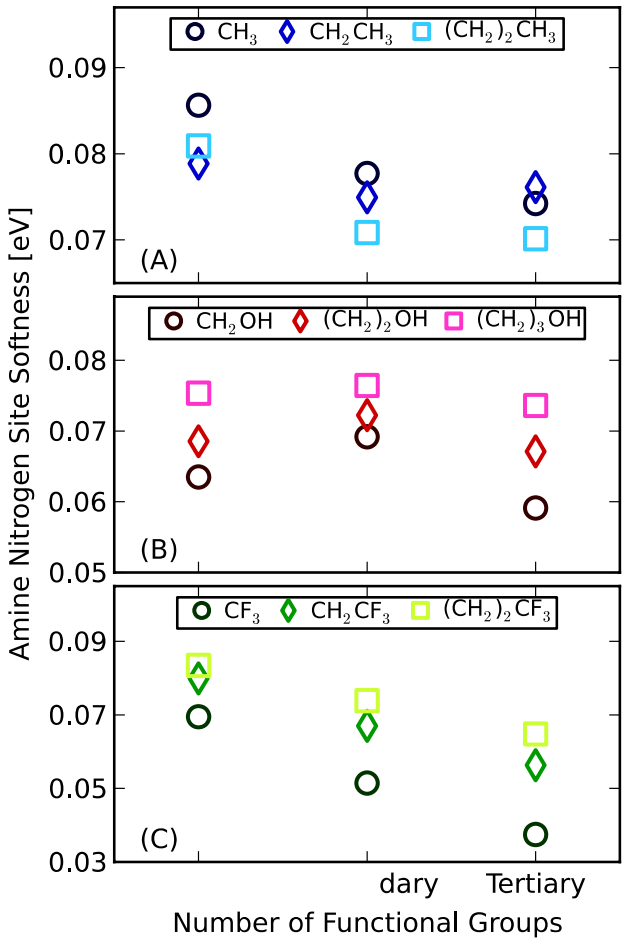


Figure 11: Trends in the localized softness on the amine nitrogen primary, secondary, and tertiary amines for (A) alkylamines, (B) alkanolamines, and (C) trifluoroalkylamines groups.

The multiple correlations can be rationalized through a subtle point within HSAB theory, which states that the relationship between the relative reactivity and reaction site softness holds only for Lewis acid base groups that are similar in nature, e.g. structurally or chemically similar.[44] The three groups of amines in this study were selected to maximize structural similarity between the groups. However, Figure 10 suggests that there are some underlying differences between the trifluoroalkylamines and the alkanolamines and alkylamines. This point is further substantiated when examining the geometric characteristics of the carbamic

acid product of each group of amines. Figure 12 shows the N-C bond length between the amine and CO_2 and the O-C-O bond angle each carbamic acid intermediate. The bond distance and O-C-O bond angle between CO_2 and the trifluoroalkylamines is characteristically larger compared to the other two groups of amines. These differences could suggest that a different type of interaction occurs with the trifluoroalkylamine group, which may be possibly attributed to long-range effects of the molecule's electrostatic potential that does not allow a more intimate interaction between CO_2 and these amines.

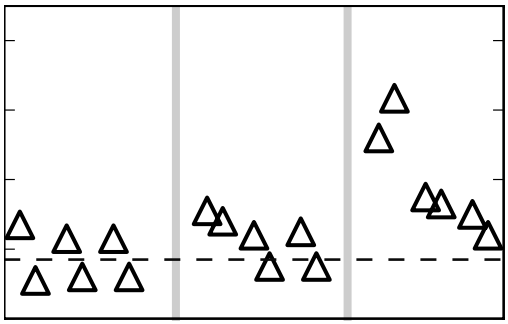


Figure 12: Molecular geometry descriptors of carbamic acid, O-C-O bond angle [°] (top) and N-C bond length [Å] (bottom) for (A) alkylamines, (B) alkanolamines, and (C) trifluoroalkylamines.

Conclusions

This work evaluated the reactivity of three groups of functionalized amines: alkylamines, alkanolamines, and trifluoroalkylamines, along the two main CO_2 capture pathways using density functional theory. Reaction energies including solvation effects were computed for several possible product species along each pathway. For both the bicarbonate and carbamate pathway it was determined that the respective product ion-pair complex, amine-bicarbonate (Reaction 2) and amine-carbamate (Reaction 6), was more stable than the disassociated counterpart product. Additionally, with respect to the carbamate pathway, it was determined that the carbamic acid is a likely intermediate state.

Trends in reaction energies were correlated to electronic structure properties through conceptual understanding of molecular interactions. In this work we selected two electronic property descriptors, electronegativity and local softness, for their connection to qualitative principles of reactivity. Leading from Sanderson's electronegativity equalization principle, the electronegativity difference between the amine and carbonic acid was identified as a good descriptor of the reaction energy to form the amine-bicarbonate complex. Additionally, it was found that through amine functionalization the electronegativity of the amine could be tuned. Following from the Hard Soft Acids and Bases principle, the local softness of the amine site was identified as a partial descriptor of the reaction energy along the carbamate pathway. The correlation between local amine softness and carbamate reaction energy was found to be weak for alkylamine and alkanolamine groups, and moderate for the trifluoromethyl functionalized amines. This indicates that a single descriptor may not be adequate in describing the reaction energy along the carbamate pathway.

Disclaimer

This project was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government through a support contract with URS Energy & Construction Inc.

Supporting Information Available:

A description of the stochastic approach to molecular conformation search used to determine the lowest energy conformation of each molecular systems considered in this work is presented in the supplemental material. Additionally, cartesian coordinates and energies of the amine and amine product systems are available, along with computed electronegativity, hardness, and condensed fukui function for each amine. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ciferno, J.; Litynski, J.; Plasynski, S.; Murphy, J.; Vaux, G.; Munson, R.; Marano, J. DOE/NETL Carbon Dioxide Capture and Storage RD&D Roadmap. *US DOE National Energy Technology Laboratory, Pittsburgh* **2010**.

(2) Rubin, E. S.; Chen, C.; Rao, A. B. Cost and Performance of Fossil Fuel Power Plants with CO_2 Capture and Storage. *Energy Policy* **2007**, *35*, 4444.

(3) NETL *Cost and Performance Comparison Baseline for Fossil Energy Power Plants*; 2nd ed. 2010; pp. 1–626.

(4) Rochelle, G. T. Amine Scrubbing for CO_2 Capture. *Science* **2009**, *325*, 1652.

(5) Oexmann, J.; Kather, A. Minimising the Regeneration Heat Duty of Post-Combustion CO_2 Capture by Wet Chemical Absorption: the Misguided Focus on Low Heat of Absorption Solvents. *International Journal of Greenhouse Gas Control* **2010**, *4*, 36.

(6) Oyenekan, B. A.; Rochelle, G. T. Energy Performance of Stripper Configurations for CO_2 Capture by Aqueous Amines. *Ind. Eng. Chem. Res.* **2006**, *45*, 2457.

(7) Brennecke, J. F.; Gurkan, B. E. Ionic Liquids for CO_2 Capture and Emission Reduction. *J. Phys. Chem. Lett.* **2010**, *1*, 3459.

(8) Oyenekan, B. A.; Rochelle, G. T. Alternative Stripper Configurations for CO_2 Capture by Aqueous Amines. *AIChE J.* **2007**, *53*, 3144.

(9) Versteeg, G.; Van Dijck, L.; Van Swaaij, W. On the Kinetics Between CO_2 And Alkanolamines Both in Aqueous and Non-Aqueous Solutions. An Overview. *Chem. Eng. Commun.* **1996**, *144*, 113.

(10) Sartori, G.; Savage, D. W. Sterically Hindered Amines for Carbon Dioxide Removal From Gases. *Ind. Eng. Chem. Fundamen.* **1983**, *22*, 239.

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

(12) da Silva, E. F.; Svendsen, H. F. Computational Chemistry Study of Reactions, Equilibrium and Kinetics of Chemical CO_2 Absorption. *International Journal of Greenhouse Gas Control* **2007**, *1*, 151.

(13) 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*, 3413.

(14) 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*, 1222.

(15) Danckwerts, P. V. The Reaction of CO_2 With Ethanolamines. *Chem. Eng. Sci.* **1979**, *34*, 443.

(16) Donaldson, T. L.; Nguyen, Y. N. Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes. *Ind. Eng. Chem. Fundamen.* **1980**, *19*, 260.

(17) Hook, R. J. An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds. *Ind. Eng. Chem. Res.* **1997**, *36*, 1779.

(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*, 6427.

(19) Singh, P.; Niederer, J. P. M.; Versteeg, G. F. Structure and Activity Relationships for Amine Based CO_2 Absorbents—I. *International Journal of Greenhouse Gas Control* **2007**, *1*, 5.
(20) Mindrup, E. M.; Schneider, W. F. Computational Comparison of the Reactions of Substituted Amines with CO_2. *ChemSusChem* **2010**, *3*, 931.
(21) Chakraborty, A.; Bischoff, K.; Astarita, G.; Damewood, J. Molecular Orbital Approach to Substituent Effects in Amine-CO_2 Interactions. *J. Am. Chem. Soc.* **1988**, *110*, 6947.
(22) 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 CO_2. *J. Phys. Chem. A* **2011**, *115*, 342.
(23) Parr, R. G.; Weitao, Y. *Density-Functional Theory of Atoms and Molecules (International Series of Monographs on Chemistry)*; Oxford University Press, USA, 1994.
(24) Gázquez, J. L. Perspectives on the Density Functional Theory of Chemical Reactivity. *Journal of the Mexican Chemical Society* **2008**, *52*, 3.
(25) Geerlings, P.; De Proft, F.; Langenaeker, W. Conceptual Density Functional Theory. *Chem. Rev.* **2003**, *103*, 1793.
(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A. 02, Gaussian **2009**.
(27) Yu, G.; Zhang, S.; Yao, X.; Zhang, J.; Dong, K.; Dai, W.; Mori, R. Design of Task-Specific Ionic Liquids for Capturing CO_2: A Molecular Orbital Study. *Ind. Eng. Chem. Res.* **2006**, *45*, 2875.
(28) De Proft, F.; Geerlings, P. Calculation of Ionization Energies, Electron Affinities, Electronegativities, and Hardnesses Using Density Functional Methods. *J. Chem. Phys.* **1997**, *106*, 3270.
(29) Scalmani, G.; Frisch, M. J. Continuous Surface Charge Polarizable Continuum Models of Solvation. I. General Formalism. *J. Chem. Phys.* **2010**, *132*, 114110.
(30) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. New Developments in the Polarizable Continuum Model for Quantum Mechanical and Classical Calculations on Molecules in Solution. *J. Chem. Phys.* **2002**, *117*, 43.
(31) Iida, K.; Yokogawa, D.; Ikeda, A.; Sato, H.; Sakaki, S. Carbon Dioxide Capture at the Molecular Level. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8556.
(32) Sato, H.; Sakaki, S. Comparison of Electronic Structure Theories for Solvated Molecules: RISM-SCF versus PCM. *J. Phys. Chem. A* **2004**, *108*, 1629.

(33) Ochterski, J. W. Thermochemistry in Gaussian. *Gaussian Inc, Pittsburgh, PA* **2000**.
(34) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. Electronegativity: The Density Functional Viewpoint. *J. Chem. Phys.* **1978**, *68*, 3801.
(35) Iczkowski, R. P.; Margrave, J. L. Electronegativity. *J. Am. Chem. Soc.* **1961**, *83*, 3547.
(36) Sanderson, R. T. Electronegativity and Bond Energy. *J. Am. Chem. Soc.* **1983**, *105*, 2259.
(37) Li, Y.; Evans, J. N. S. The Fukui Function: a Key Concept Linking Frontier Molecular Orbital Theory and the Hard-Soft-Acid-Base Principle. *J. Am. Chem. Soc.* **1995**, *117*, 7756.
(38) Parr, R. G.; Pearson, R. G. Absolute Hardness: Companion Parameter to Absolute Electronegativity. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
(39) Pearson, R. G. Hard and Soft Acids and Bases, HSAB, Part 1: Fundamental Principles. *J. Chem. Educ.* **1968**, *45*, 581.
(40) Ayers, P. W. The Physical Basis of the Hard/Soft Acid/Base Principle. *Faraday Discuss.* **2006**, *135*, 161.
(41) Fukui, K.; Yonezawa, T.; Shingu, H. A Molecular Orbital Theory of Reactivity in Aromatic Hydrocarbons. *J. Chem. Phys.* **1952**, *20*, 722.
(42) Parr, R. G.; Yang, W. Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
(43) Thanikaivelan, P.; Padmanabhan, J.; Subramanian, V.; Ramasami, T. Chemical Reactivity and Selectivity Using Fukui Functions: Basis Set and Population Scheme Dependence in the Framework of B3LYP Theory. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)* **2002**, *107*, 326.
(44) Torrent-Sucarrat, M.; De Proft, F.; Ayers, P. W.; Geerlings, P. On the Applicability of Local Softness and Hardness. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1072.
(45) Mendez, F.; Gázquez, J. L. Chemical Reactivity of Enolate Ions: the Local Hard and Soft Acids and Bases Principle Viewpoint. *J. Am. Chem. Soc.* **1994**, *116*, 9298.
(46) Mondal, P.; Hazarika, K. K.; Deka, R. C. Reactivity of A,B-Unsaturated Carbonyl Compounds Towards Nucleophilic Addition Reaction: a Local Hard–Soft Acid–Base Approach. *PhysChemComm* **2003**, *6*, 24.
(47) Pérez, P.; Simón-Manso, Y.; Aizman, A.; Fuentealba, P.; Contreras, R. Empirical Energy−Density Relationships for the Analysis of Substituent Effects in Chemical Reactivity. *J. Am. Chem. Soc.* **2012**, *122*, 4756.
(48) Mulliken, R. S. A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities. *J. Chem. Phys.* **1934**, *2*, 782.
(49) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Computational Materials Science* **2006**, *36*, 354–360.
(50) De Proft, F.; Martin, J. M. L.; Geerlings, P. Calculation of Molecular Electrostatic Potentials and Fukui Functions Using Density Functional Methods. *Chem. Phys. Lett.* **1996**, *256*, 400.
(51) Nguyen, M. T.; Raspoet, G.; Vanquickenborne, L. G.; Van Duijnen, P. T. How Many Water Molecules Are Actively Involved in the Neutral Hydration of Carbon Dioxide? *J. Phys. Chem. A* **1997**, *101*, 7379.
(52) Han, B.; Zhou, C.; Wu, J.; Tempel, D. J.; Cheng, H. Understanding CO_2 Capture Mechanisms in Aqueous Monoethanolamine via First Principles Simulations. *J. Phys.*

Chem. Lett. **2011**, *2*, 522.
(53) Faurholt, C. Etudes sur les solutions aqueuses de carbamates et de carbonates. *J. Chim. Phys.* **1925**, 1.
(54) da Silva, E. F.; Svendsen, H. F. Study of the Carbamate Stability of Amines Using ab Initio Methods and Free-Energy Perturbations. *Ind. Eng. Chem. Res.* **2006**, *45*, 2497.
(55) Jhon, Y. H.; Shim, J.-G.; Kim, J.-H.; Lee, J. H.; Jang, K.-R.; Kim, J. Nucleophilicity and Accessibility Calculations of Alkanolamines: Applications to Carbon Dioxide Absorption Reactions. *J. Phys. Chem. A* **2010**, *114*, 12907.