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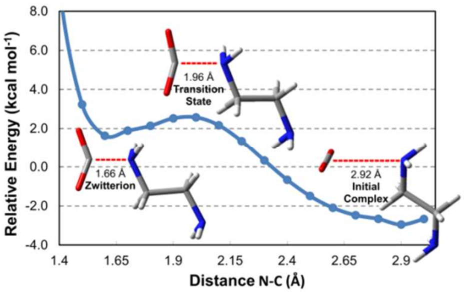

The interactions between CO_2 and aliphatic (primary, secondary, tertiary) and aromatic amines were computed using pure and hybrid density functionals.

Physical Chemistry Chemical Physics Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

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FULL ARTICLE

Insights into the interactions of CO_2 with amines: a DFT benchmark study

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

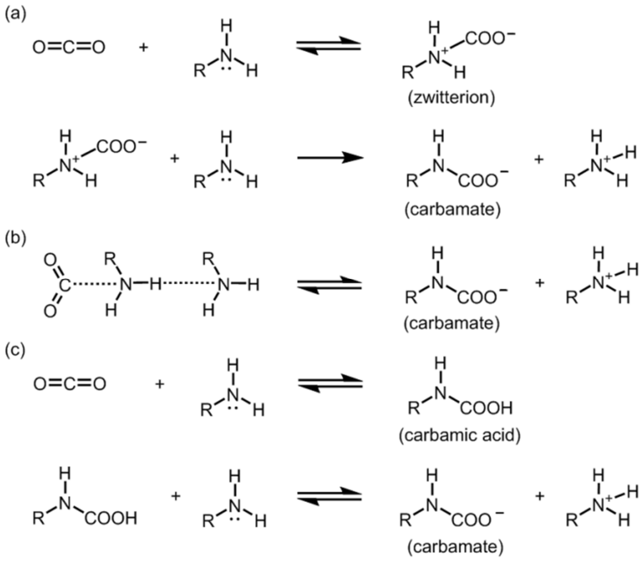
The interaction between CO_2 and 1,2-diaminoethane was computed using pure and hybrid density functionals. The CAM-B3LYP and wB97XD functionals using a triple-ζ basis set that includes diffuse and polarization functions are the best functionals for calculating the relative energies of the zwitterion intermediate compared to a Coupled Cluster with Single Double and Non-iterative Triple Excitation (CCSD(T)) approach extrapolated to a complete basis set limit. With the two functionals and the triple-ζ basis set, the zwitterion is 1.70 kcal mol^{-1} less stable than the reactants, close to the 1.63 kcal mol^{-1} computed using the CCSD(T) approach. The inclusion of vibrational and thermal corrections and of entropic effects increases the relative energy of the zwitterion to 14.7 kcal mol^{-1}. Bending of the CO_2 geometry increases its acidity due a 1.09 eV reduction in the LUMO energy. Calculation of the CO_2 interaction energy with a set of amines revealed that the interaction energies show a high correlation with their basicities, with the stronger bases stabilizing the zwitterion. For the most basic amine computed (3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidine), the Gibbs free energy of the zwitterion is 15.8 kcal mol^{-1} lower than the reactants. Therefore, for this highly basic amine, the zwitterion may have a longer life time, in contrast to the 2-aminoethanol (MEA), where it is only a transient species.

Introduction

The use of fossil fuels has been highlighted as the main source of climate change.[1] Their combustion emits high amounts of greenhouse gases, particularly CO_2. This emission has motivated the search for methods that can capture and separate CO_2 from postcombustion, precombustion and oxy-fuel combustion.[2] Among several methods used for CO_2 separation and capture, amine aqueous solutions using primary or secondary alkanolamines, e.g., 2-aminoethanol (MEA), 2,2-iminodiethanol (DEA), 2,2-methyliminodiethanol (MDEA), 1-(2-hydroxypropylamino)propan-2-ol (DIPA), and 2-amino-2-methylpropan-1-ol (AMP), have been widely used as chemical absorbents for CO_2 removal.[3] However, there are several drawbacks to this technology, such as equipment corrosion, amine degradation and high energy consumption to regenerate the solutions. Anchoring amines or polyamines onto solid supports has also been proposed as an alternative to aqueous solutions.[4-6] Although amine-functionalized solid materials are an interesting postcombustion approach to capturing and separating CO_2, the CO_2 molar adsorption capacity of these materials needs to be improved. There has therefore been a significant effort to identify other amines that can be either anchored onto solid supports or used as solvents to capture and separate CO_2 effectively.[7] In addition, understanding the interaction between CO_2 and different amines can aid in the design of new amine solvents or amine-functionalized hybrid materials with the objective of addressing the challenge of CO_2 capture and separation technology.

The interaction between CO_2 and amines has been investigated experimentally and theoretically.[8-16] Overall, however, there is still some debate regarding the reaction mechanism. The following question remains: does the reaction involve a zwitterion intermediate or a concerted carbamate ion formation? The mechanisms proposed for the MEA/CO_2 reaction are shown in Scheme 1.[13] Experimental studies show that the attack of the amine on CO_2 involves first-order kinetics, implying a 1:1 ratio between the CO_2 and the amines and the formation of the zwitterion as the rate determining step of the reaction.[8,9] The abstraction of a hydrogen atom from the zwitterion can occur only through the participation of a catalytic species, which may be either one additional amine molecule or water. However, the zwitterion has never been detected experimentally.

Theoretical studies have not led to any consensus regarding the relevance of the zwitterion intermediate in the course of the reaction. Da Silva and Svendsen[10] studied the formation of carbamate from CO_2 and MEA by means of the HF/3-21G(d) level. They proposed that MEA attacks CO_2 to form a zwitterion intermediate, which is subsequently decomposed by a hydrogen transfer without any activation energy. This mechanism implies a concerted reaction leading directly to carbamate ion formation. If the zwitterion is not a stable species, the reaction mechanism must occur through a single-step process (Scheme 1b).



Scheme 1. Reaction mechanisms proposed for MEA/CO_2: (a) zwitterion mechanism; (b) single-step mechanism and (c) carbamic acid reaction mechanism.

Arstad *et al.* [11] found an activation barrier of 9.3 kcal mol^{-1} to the hydrogen abstraction process between the zwitterion and a second MEA molecule at the G3MP2B3 level of theory. They supported the carbamic acid reaction mechanism catalyzed by another MEA molecule (Scheme 1c). A zwitterion description of the initial complex was presumed to some extent.[11] Xie *et al.*[13] reported a detailed study combining B3LYP and CCSD(T) methods with several basis sets and including solvent effects (water) using the CPCM formalism. Their calculations showed a two-step reaction mechanism where the zwitterion is formed at the rate-determining step with an activation Gibbs free energy of 12.0 kcal mol^{-1}, which is very close to the experimentally estimated value (12.4 kcal mol^{-1}). Proton abstraction from the zwitterion by a second MEA molecule forms the carbamate ion in a barrierless process. Using a microkinetic model the equilibrium of the zwitterion was estimated to be 4.8 x 10^{-11} mol/L, indicating that it is extremely difficult to be experimentally detected.[13]

Previous computations of the interaction energy between CO_2 and amines have been performed almost exclusively using the B3LYP functional.[11-18] It is known, however, that for certain systems, B3LYP does not give the highest quality DFT results compared to higher-level calculation methods, such as the methods including dispersion correction.[19-24] Interestingly, even a previous benchmark study on the CO_2-NH_3 interaction focused on the B3LYP as the method of choice.[11]

Thus, we noticed that the following questions still need to be addressed in this field: i) What is the best DFT method to reproduce a reference benchmark high-level calculation? ii) What is the relative stability of the zwitterion intermediate compared to the reactants on the basis of the selected method? iii) What is the driving force for the attack of the amines on CO_2? iv) What is the effect of the basicity of the amines on the interaction strength with CO_2?

Computational Details

To address the first question, we calculated the relative energy of the zwitterion intermediate compared to the reactants using 1,2-diaminoethane as the attacking amine. To evaluate the quality of the DFT results, we computed the CO_2-1,2-diaminoethane interaction energy using a set of functionals and basis sets. The DFT results were then compared to the corresponding values computed using the coupled-cluster method, which was adopted as the reference model. The coupled-cluster method includes single, double, and perturbative triple excitations (CCSD(T)) extrapolated to a complete basis set limit in a composed calculation, as suggested by D. G. Truhlar.[25] The composed calculation is based on Hartree-Fock (HF) and CCSD(T) single-point energies computed for geometries optimized at the MP2/aug-cc-pVXZ (X = D,T) level to approach the complete basis set (CBS) limit. The total energies of the CO_2, the amine and the zwitterion were obtained as a sum of the extrapolated HF total energy (E_{CBS}^{HF}) and the extrapolated correlation energy (E_{CBS}^{corr}), which were calculated using CCSD(T) according to equations 1 and 2.[25]

$$E_{CBS}^{HF} = \frac{3^{3.4}}{3^{3.4} - 2^{3.4}} E_3^{HF} - \frac{3^{3.4}}{3^{3.4} - 2^{3.4}} E_2^{HF} \qquad \text{(eq. 1)}$$

$$E_{CBS}^{corr} = \frac{3^{2.4}}{3^{2.4} - 2^{2.4}} E_3^{corr} - \frac{3^{2.4}}{3^{2.4} - 2^{2.4}} E_2^{corr} \qquad \text{(eq. 2)}$$

In equation 1, E_3^{HF} and E_2^{HF} are the single-point HF energies calculated using the aug-cc-pVTZ and aug-cc-pVDZ basis sets, respectively. In equation 2, E_3^{corr} and E_2^{corr} are the correlation energies obtained from a single-point CCSD(T) calculation using the aug-cc-pVTZ and aug-cc-pVDZ basis sets, respectively. The exponents 3.4 and 2.4 were optimized to achieve the CBS extrapolation[25] to which no basis set superposition error (BSSE) was included. The interaction energy (ΔE_{int}) was taken as the difference between the energy of the zwitterion and the sum of the energies of the reactants. Additionally, we applied the same CBS extrapolation scheme to obtain the total energy of the initial complex and a point on the first stage of the reaction as well as the energy of the transition structure connecting the first complex to the zwitterion. This approach has been proven to give excellent thermodynamic agreement for the calculation of the binding energies of noncovalent interactions.[26]

The set of functionals employed in this study includes pure (PW91, PBE and TPSS) as well as hybrid (B3LYP, CAM-B3LYP and WB97XD) functionals. The following double and triple zeta basis sets including polarization and diffuse functions were used: 6-31+G(d), 6-31++G(d,p), 6-31+G(2d,2p), 6-31++G(2d,2p), aug-cc-pVDZ, 6-311+G(d), 6-311++(d,p), 6-311+(2d,2p), 6-311++(2d,2p), and aug-cc-pVTZ.

The geometries of all species were fully optimized using all possible combinations of functionals and basis sets, with each optimization followed by the calculation of the Hessian matrix to confirm that the optimized structure is a true minimum on the potential energy surface (no negative eigenvalue in the second-order Hessian matrix) or a transition state (one negative eigenvalue in the second-order Hessian matrix). All calculations included the effect of water as an implicit solvent, according to the IEFPCM[27] approach using the UFF model to define the radii. A counterpoise correction for the basis set superposition error following the Boys-Bernardi procedure[28] was added to the energies of all complexes. All calculations were performed using the G09 package.[29]

Results and Discussions

Relative Energy of the Zwitterion

The CCSD(T) relative energy of the zwitterion intermediate extrapolated to the complete basis set (CCSD(T)/CBS) is 1.63 kcal mol^{-1}. This value is the benchmark to which we compare the DFT results. Figure 1 shows the relative energy (ΔE_{int}) calculated with several combinations of functionals and basis sets, including BSSE and the effect of solvent (water). The horizontal bar represents the CCSD(T)/CBS extrapolation benchmark. The vertical bars, which give the corresponding values obtained using the DFT calculations, clearly show a large variety of values. The results obtained using the full set of functionals and the smaller basis sets (6-31+G(d) and 6-31++G(d,p)) give negative relative energies for the zwitterion, in contrast to the positive value obtained with CCSD(T)/CBS. The exception is the B3LYP results obtained using these two basis sets, which agree nicely with the reference benchmark. Increasing the size of the basis sets leads to higher relative energies, approaching the CCSD(T)/CBS value. The exception again is the B3LYP functional, whose relative energies now become more than twice as large as the CCSD(T)/CBS values. Convergence is found only for the triple-ζ basis sets, including at least two sets of p and d polarization functions. For the 6-311+G(2d,2p), 6-311++G(2d,2p) and aug-cc-pVTZ basis sets, the relative energies become essentially constant. With these three basis sets, the best agreement with the CCSD(T)/CBS results is found using the CAM-B3LYP and WB97XD functionals[30,31] which are the two functionals that include corrections for long-range interactions and dispersion, respectively, an issue of fundamental importance in the present case. Therefore, our results show that the CAM-B3LYP and WB97XD functionals, using a triple-ζ basis set including diffuse and polarization functions, are the best choices for the calculation of the relative energies of the zwitterion intermediate. The commonly used B3LYP functional gives a relative energy that is at least twice as high as the reference CCSD(T)/CBS value.

A significant effect was found due to the inclusion of vibrational and thermal corrections in the relative energy. The formation of the zwitterion transforms three translational and two rotational degrees of freedom into five vibrational degrees of freedom, increasing the vibrational energy. The correction due to the zero-point vibrational energy (ZPVE, calculated from MP2(full)/aug-cc-pVDZ frequencies) increases the CCSD(T)/CBS relative energy of the zwitterion intermediate to 3.9 kcal mol^{-1} (Figure S1). Once again, the best DFT results are obtained using the CAM-B3LYP/aug-cc-pVTZ (4.2 kcal mol^{-1}) and WB97XD/aug-cc-pVTZ (4.8 kcal mol^{-1}) functionals, with the B3LYP/aug-cc-pVTZ combination giving a considerably higher relative energy (6.4 kcal mol^{-1}) (Figure S1). Thermal correction to 298 K and the inclusion of entropic effects lead to a relative Gibbs free energy for the zwitterion intermediate of 14.7 kcal mol^{-1} for both CAM-B3LYP/aug-cc-pVTZ and WB97XD/aug-cc-pVTZ (Figure 2). This high relative Gibbs free energy found for the zwitterion is predominantly due to the reduction in the number of translational degrees of freedom and the corresponding reduction in the translational entropy of the system (ΔS_{trans} = −32.8 cal mol^{-1} K^{-1} at MP2/aug-cc-pVTZ).

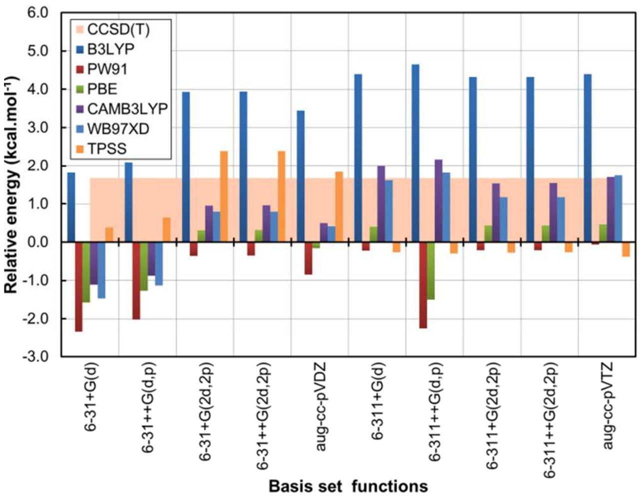


Figure 1. Relative energy (kcal mol^{-1}) of the zwitterion formed by 1,2-diaminoethane and CO_2 as a function of the basis set for various DFT functionals. The horizontal bar (1.63 kcal mol^{-1}) represents the benchmark CCSD(T)/CBS results computed according to the method proposed by Truhlar *et al.*[25]

In a recent study, Xie *et al.*[13] used the B3LYP/6-311++G(d,p) combination of functional and basis set, including the solvent effect (CPCM, water and UAHF as radii model), to obtain a relative Gibbs free energy of 2.4 kcal mol^{-1} for the zwitterion formed by the interaction between MEA and CO_2. Single-point CCSD(T)/6-311++G(2df,2p) calculations using a geometry optimized at the B3LYP/6-311++G(d,p) level and the UFF model yield a relative Gibbs free energy of 6.1 kcal mol^{-1}. However, in their calculations, the reference state used for the relative Gibbs free energy was a geometry with a distance between the MEA and the CO_2 molecule of 10 Å, therefore excluding the relevant contribution of the translational entropy. A similar calculation for 1,2-diaminoethane and the CO_2 molecule separated by 10 Å gives a relative Gibbs free energy for the zwitterion of 8.0 kcal mol^{-1} (CAM-B3LYP/aug-cc-pVTZ). Therefore, the relative Gibbs free energy of the zwitterion calculated in this study is 1.9 kcal mol^{-1} higher than the value obtained in the study of Xie *et al.* In addition, it must be considered that the B3LYP/aug-cc-pVTZ method gives relative energies that are 2.7 kcal mol^{-1} higher than the CAM-B3LYP/aug-cc-pVTZ method (Figure 1). Therefore, the difference between the values computed in the present work and the previous study increases to approximately 4.6 kcal mol^{-1}. This difference may be attributed to the fact that the hydroxyl group of the MEA molecule strongly interacts with the incoming CO_2 molecules stabilizing the zwitterion[32] (see discussion regarding the effect of the basicity of the different amines on the interaction energy with CO_2), in contrast to the 1,2-diaminoethane in the zig-zag orientation that we computed in this study, which does not show the same hydrogen bond pattern.

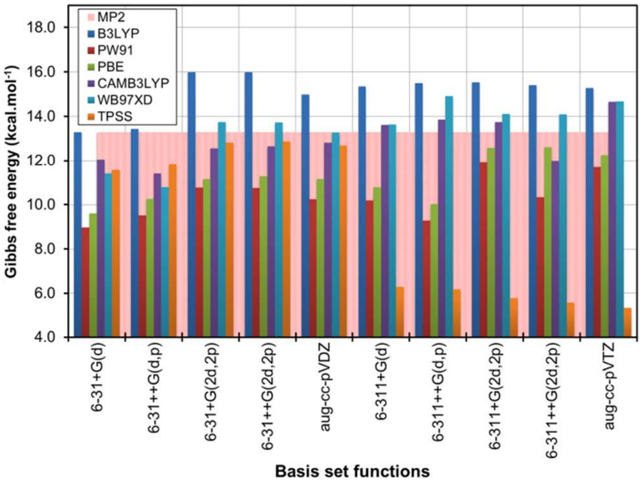


Figure 2. Relative Gibbs free energy (kcal mol^{-1}) of the zwitterion formed by 1,2-diaminoethane and CO_2 as a function of the basis set for various DFT functionals. The horizontal bar (13.3 kcal mol^{-1}) represents the MP2/aug-cc-pVTZ calculation.

The potential energy surface

The potential energy profile for the addition of 1,2-diaminoethane to the CO_2 molecule is shown in Figure 3.

Three stationary points are found when approaching 1,2-diaminoethane to CO_2 (Figure 3). Starting from an infinite separation between the two reactants, the first minimum energy complex is found when the distance between the CO_2 and the amine is 2.922 Å, with a relative energy of –3.0 kcal mol^{-1}. In this initial complex, the CO_2 molecule is still linear and approaches the amine with the OCO axis almost perpendicular to the N-C bond of the amine. From the initial complex, the system evolves through the transition structure, where the relative energy is 2.6 kcal mol^{-1} and the C…N distance is 1.963 Å. It must be observed that the arrangement of the CO_2 molecule with respect to the amine changes compared to the arrangement found in the initial complex. In the transition structure, the OCO angle is 150.8°, and the OCO group and the C…N bond are nearly in the same plane. After this point, the relative energy falls to the value found in the zwitterion (1.63 kcal mol^{-1}), a minimum on the potential energy surface with an equilibrium C-N distance of 1.663 Å. This is in line with a recent study carried out by Davran-Candan that showed that the formation of the carbamate follows a two-step mechanism with the zwitterion as intermediate in 2-aminoethanol and 1,2-diaminoethane aqueous solution.[18]

What are the driving forces for the CO_2-amine interaction? When the amine approaches the CO_2 molecule, there are at least two main types of forces that may contribute to the total interaction (or activation) energy. One force is due to the net interaction between the two reactants, ΔE_{int}, and the other force is due to the increasing deformation or bond reorganization, ΔE_{reorg}, of the reactants as they move along the reaction coordinate toward the transition structure and then the products.[33] As the molecules approach each other, there is an interaction component that can be repulsive or attractive and is given by the sum of the orbital and electrostatic interactions plus the Pauli repulsion and the dispersion terms.[34] All these terms, when summed together, give the interaction energy (ΔE_{int}) between the two reactants shown in Figure 4. For the present case, the interaction energy is strongly stabilizing up to the point corresponding to the structure of the zwitterion.

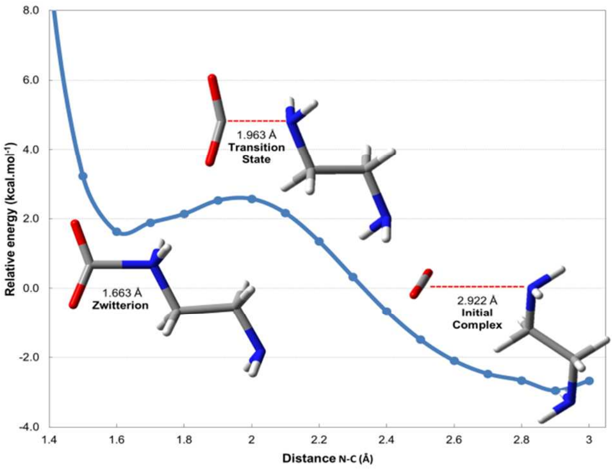


Figure 3. Potential energy (kcal mol^{-1}) profile for the interaction between 1,2-diaminoethane and CO_2 to form the zwitterion as a function of the distance between the nitrogen atom of 1,2-diaminoethane and the carbon atom of CO_2. Relative energies were obtained using the MP2/aug-cc-pVDZ level. The relative energies of the zwitterion (1.6 kcal mol^{-1}), the transition state (2.6 kcal mol^{-1}) and the initial complex (-3.0 kcal mol^{-1}) are MP2/aug-cc-pVDZ energies corrected according to the Truhlar approach.[25]

A second contribution to the relative energy is given by the preparation[35] or strain energy[33] (ΔE_{reorg}). This energy is associated with the reorganization of the structures of both reactants from their equilibrium geometry to the geometry they acquire in the transition state or the zwitterion. The reorganization energy (also shown in Figure 4) is a positive term that contributes to the destabilization of the system. From the initial complex up to a C…N distance of 2.4 Å, the ΔE_{int} remains essentially constant, whereas the ΔE_{reorg} term increases slightly and is solely responsible for the increase in the activation energy up to that point. For C…N distances below 2.4 Å, both the ΔE_{int} and ΔE_{reorg} terms start to change more strongly, although the ΔE_{reorg} increases more rapidly than the ΔE_{int} decreases. After the transition state, however, the gradient in ΔE_{int} dominates the relative energy, leading ultimately to the zwitterion minimum energy structure. The ΔE_{reorg} term comes mainly from the reorganization of the CO_2 structure. From the equilibrium linear arrangement of CO_2 up to the angular form it assumes in the zwitterion (OCO angle equal to 139.5°), the ΔE_{reorg} of CO_2 amounts to 29.0 kcal mol^{-1}, which is approximately 97% of the total ΔE_{reorg}. In the zwitterion, the reorganization in the structure of CO_2 is overcompensated by the interaction energy (ΔE_{int}) between the CO_2 and the amine. The interaction energy is predominantly due to the orbital interactions involving the sigma HOMO donor orbital of the amine and the sigma LUMO acceptor orbital of the deformed CO_2. The MP2/6-311++G(2d,2p) calculations of the energy changes in the CO_2 frontier orbitals (Figure S2) show that the energy of one of the two initially degenerated LUMO orbitals of CO_2 decreases by 1.02 eV, a value close to the value found for the interaction energy between the CO_2 and the amine.

Therefore, while the reorganization of the CO_2 structure to form the zwitterion increases the energy of the system, it simultaneously increases the acid-base interaction between the CO_2 and the amine. The latter energy more than compensates for the penalty energy necessary for CO_2 deformation.

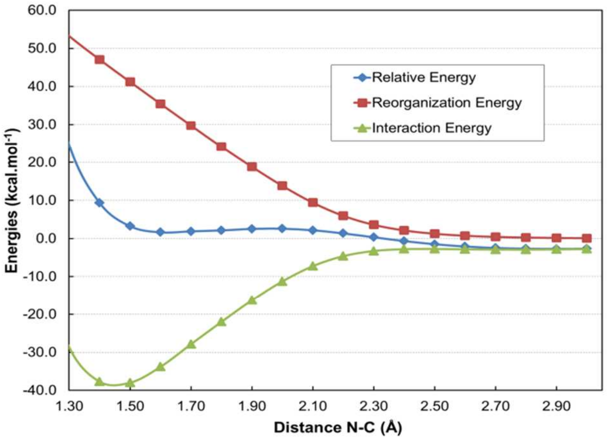


Figure 4. Decomposition of the relative energy (ΔE) of 1,2-diaminoethane and CO_2 into reorganization energy (ΔE_{reorg}) and interaction energy (ΔE_{int}) as a function of the distance between the nitrogen atom of 1,2-diaminoethane and the carbon atom of CO_2 (all energies are in kcal mol^{-1}).

To verify the effect of the basicity of different amines on the interaction energies, we calculated the interaction between CO_2 and the most basic nitrogen of a set of bases yielding a zwitterion (see Table S1 for the geometry of the zwitterion and selected geometrical parameters). In this set, there are primary (2-aminoethanol (MEA), methanamine, 1,2-diaminoethane), secondary (N-methylmethanamine, N-(2-aminoethyl)ethane-1,2-diamine), tertiary (N,N-dimethylmethanamine, 1-azabicyclo[2.2.2]octan-8-amine) and aromatic (pyridin-4-amine and N-methylpyridin-4-amine) amines and imino nitrogen (3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidine, TBD). Table 1 shows the interaction energies between the CO_2 and the amines as well as their basicities, calculated according to standard procedure.[36] There is a linear correlation between the interaction energy and the basicity (Figure S3). The strongest bases are the ones that interact more strongly with CO_2, whereas the weakest ones interact more weakly, as expected. As noted previously (Scheme 1), the proposed mechanism for carbamate formation requires a primary or secondary amine, which is not the case for the strongest base, guanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene), shown in Table 1. However, due to the possible resonance forms in the guanidine structure, the hydrogen atom bonded to the amino nitrogen may be transferred in a hydrogen atom transfer reaction. Indeed, all amines with a guanidine moiety are able to participate in the reaction with CO_2, followed by hydrogen transfer to form a carbamate. Figure 3 indicates that due to the high relative energy, the zwitterion is a transient species that may either decompose back to CO_2 and amine or transfer a hydrogen atom to form the carbamate. However, if the base is strong enough to reverse the stability order of the minimum energy point shown in Figure 3, it could be possible for the zwitterion to survive for a longer time and be detected. This case could hold for the guanidine base (TBD). Calculations of the relative energies of the stationary points for addition of CO_2 to TBD reveal that the zwitterion is the lowest point on the potential energy surface for the interaction between the two CO_2 and TBD, 15.8 kcal mol^{-1} below the isolated reactants. When including vibrational, entropic and thermal corrections to compute the relative Gibbs free energy of the zwitterion of TBD, we found it to be 4.0 kcal mol^{-1} more stable than the reactants. The computation of the transition structure connecting the initial complex to the zwitterion in the reaction of CO_2 with TBD led to activation energy of only 0.33 kcal mol^{-1}. Therefore, for this highly basic amine, the reaction between CO_2 and the amine involves an essentially barrierless reaction to form the zwitterion, which is 4 kcal mol^{-1} more stable than the isolated reactants.

Table 1. CAM-B3LYP/6-311++G(2d,2p) absolute basicity (kcal mol^{-1}) and relative energy of the zwitterion (kcal mol^{-1}), including solvent effects (water) using the IEFPCM approach and correction for basis set superposition error (BSSE)

Compound[a]	Interaction energy (kcal mol^{-1})	Basicity (kcal mol^{-1})
2-Aminoethanol, MEA (gauche-conformation)	-2.50	-162.53
2-Aminoethanol, MEA (zig-zag conformation)	2.66	-159.53
Methanamine	-0.01	-162.83
N-Methylmethanamine	-2.03	-164.73
N,N-Dimethylmethanamine	-0.53	-165.00
1,2-Diaminoethane	1.54	-161.16
N-(2-Aminoethyl)ethane-1,2-diamine	0.64	-226.84
Pyridin-4-amine	-4.67	-235.09
N-Methylpyridin-4-amine	-5.54	-237.95
3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidine, TBD	-15.81	-253.28
1-Azabicyclo[2.2.2]octan-8-amine	-2.39	-234.43

[a] For details on the structures and conformations of the amines see Table S1.

The interaction energies in Table 1 also reveal some interesting points. As expected, for the aliphatic amines, the interaction order is primary < tertiary < secondary, in agreement with the basicity order. The more basic tertiary quinuclidine has the highest interaction energy among the aliphatic amines. The aromatic pyridines have interaction energies higher than the aliphatic amines but much lower than the imino type amines, such as the guanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD). Comparing the interaction energies of the two MEA conformations shows that the hydrogen bonding in the gauche conformation increases the interaction energy by approximately 5 kcal mol^{-1}, in agreement with the 4.6 kcal mol^{-1} energy difference between the value computed in this study and the previous one,[13] as commented above. Another point revealed by the data in Table 1 is the effect of the substituent. Both the hydroxyl group in MEA and the amino group in 1,2-diaminoethane decrease the interaction energy, with the hydroxyl group having a stronger effect than the amino group. Also as expected, the methylamino group in N-methylpyridin-4-amine increases the interaction with the CO_2 molecule.

Conclusions

In summary, taking the CCSD(T) method extrapolated to a complete basis set limit, the DFT methods that give the most consistent results are the CAM-B3LYP and WB97XD with either the 6-311++G(2d,2p) or the aug-cc-pVTZ basis set, in contrast to the B3LYP method, which gives significantly higher interaction energies than the CCSD(T) approach. In this case, we selected the CAM-B3LYP method because it gives slightly better results than the WB978XD method. It can also be seen that the potential energy for the addition of CO_2 to 1,2-diaminoethane shows that the relative energy for the zwitterion is higher than for the reactants, indicating that its life time is short. It would either decompose back to the reactants or transfer hydrogen in the case of a primary or secondary amine to form the carbamate. However, highly basic amines, such as guanidines may form zwitterions that are more stable than the reactants (on a ΔG basis) in a barrierless reaction. Besides, the activation energy for the addition of CO_2 to the amine is low and originates predominantly from the bond reorganization of the CO_2 molecule. The energy for bond reorganization in CO_2 is compensated by the instantaneous interaction energy. The latter energy is associated with the reduction in the LUMO energy of CO_2 as its geometry distorts from the linear arrangement to the angular form it assumes in the zwitterion. Finally, the strength of the interaction energy shows a nearly linear correlation with the basicity, at least for the basis we studied in this work. The strongest bases lead to the higher interaction energies. For the strongest bases, the zwitterion becomes more stable than the reactants, allowing it to survive for a longer period of time

Acknowledgements

The authors gratefully acknowledge FAPERJ (JCNE, CNE and Pensa Rio grants and E.O. fellowship) and CNPq (Universal grant number 478302/2012-6) for financial support. C.M.R. and J.W.d.M.C. are recipients of CNPq research fellowships.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Figures cited in the main text with the label "S" are included in the supplementary information]. See DOI: 10.1039/b000000x/

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Cite this: DOI: 10.1039/c0xx00000x

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