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CO_2 Absorption in Aqueous Solutions of Alkanolamines: Mechanistic Insight from Quantum Chemical Calculations

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DFT and high-level ab initio calculations (among them B3LYP and G3MP2B3) have been used to describe molecular reactions relevant for CO_2 absorption in aqueous (alkanol)amine solutions. Reaction mechanisms for various reactions of CO_2 with ammonia, monoethanolamine (MEA), and diethanolamine (DEA) to carbamic acid and ion pair products have been investigated and interpreted in light of experimental observations. Additional water, ammonia, MEA, and DEA molecules have also been added to the molecular complexes to simulate microsolvation effects. These extra molecules may act as catalysts for the desired reactions, and in several cases they have a large impact on activation and reaction energies. Solvent effects were estimated by applying electrostatic continuum models for selected systems. Our calculated transition state energies agree well with experimental activation energies.

Introduction

Removal of carbon dioxide (or other acidic gases like, e.g., H_2S) from gas mixtures by liquid absorbents is important for several industrial processes. Processing of natural gas, upgrading of town gases, and manufacture of CO_2 for several applications are some examples.[1,2] There is also an increasing interest in technology for CO_2 capture from the effluent stream from power plants, because of environmental concerns. Present technology for CO_2 separation involves sorption in aqueous solutions of alkanolamines. It is assumed that the reaction takes place between a nonbonding electron pair at the amino nitrogen atom and an antibonding empty orbital in CO_2 for a donor−acceptor interaction. Several reaction mechanisms for this process have been proposed in the literature.[2] One possibility is the following sequential reaction:

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NCOOH \qquad (1)$$

$$R_1R_2NCOOH + B \rightleftharpoons R_1R_2NCOO^- + BH^+ \qquad (2)$$

R_1 and R_2 represent substituents attached to the amino nitrogen. B represents a base molecule which may be OH^-, water, or an (alkanol)amine. The first step, in which a carbamic acid is formed, is bimolecular, of second order, and rate determining, while the second proton transfer step is assumed to be rapid.[2] The resulting anionic species is termed a carbamate, and in the following, that term will be used for such a species regardless of the nature of the R_1 and R_2 groups. In analogy, the term carbamic acid will be used for the corresponding acids independently of the nature of the R_1 and R_2 groups.

It has also been proposed that carbamate formation may take place via a mechanism involving a zwitterion intermediate in the following way:[1,2]

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NH^+CO_2^- \qquad (3)$$

$$R_1R_2NH^+CO_2-^- + B \rightleftharpoons R_1R_2NCO_2^- + BH^+ \qquad (4)$$

Again, the second step is an assumedly rapid deprotonation. This mechanism has been a favored interpretation of experimental kinetic measurements.[2]

Crooks and Donnellan[3] proposed an alternative termolecular mechanism that starts with a loosely bound encounter complex. A schematic drawing of this single step, concerted reaction mechanism is shown in Figure 1. Bond formation between the alkanolamine's nitrogen atom with the carbon atom in CO_2 takes place with a simultaneous proton transfer from the amino nitrogen atom to a nearby base molecule. It is somewhat similar to the zwitterion mechanism described above, but it does not include any intermediate species.

In industrial CO_2 absorption processes, monoethanolamine (MEA) and diethanolamine (DEA) have been and still are the chosen adsorbents, and CO_2 sorption in aqueous solutions of these alkanolamines has been the subject of extensive experimental study. Versteeg et al.[2] have compiled kinetic data for CO_2 sorption in aqueous solutions of MEA, DEA, and similar systems. For MEA, there is consensus that the overall reaction order is 2, and that the partial order of MEA is 1. For DEA, the total reaction order is found to be between 2 and 3 for both aqueous and nonaqueous solutions. Additionally, only 0.5 mol CO_2 is absorbed per mole amine, regardless of whether MEA or DEA is used.[4]

We are only aware of a few reported quantum chemical studies on the formation of carbamic acids/carbamates from CO_2 and alkanolamines relevant for CO_2 sorption processes. Very recently, da Silva and Svendsen[5] investigated the formation of carbamates from CO_2 and alkanolamines with ab initio methods. An electrostatic model was employed to describe the longer-distance solute/solvent interaction. The same authors have also carried out quantum chemical studies on carbamate stabilities and basicities of alkanolamines.[6−8]

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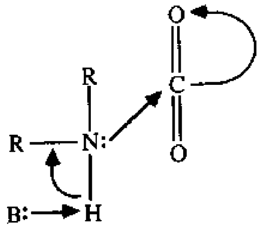

Figure 1. Schematic drawing of the single step, termolecular reaction mechanism for the formation of carbamates according to Crooks and Donnellan.[3] B is a base acting as a proton acceptor/abstractor during the reaction and may be either water or another alkanolamine.

Jamroz et al.[9] have undertaken quantum chemical studies of the reaction between CO_2 and two dimethylamine molecules to form a dimethylcarbamic acid complex with dimethylamine. They found an activation barrier of some 40 kJ/mol, which was about four times smaller than their result for only one dimethylamine molecule.

In the present work we have investigated reactions of CO_2 with either NH_3, MEA, or DEA. The reactions take place either directly or catalyzed by water, ammonia or another alkanolamine molecule. Some of the reactions are also studied in the presence of a second water molecule. Electrostatic solvent effects on the activation energies are estimated by including a continuum field for selected reactions.

Computational Details

The Gaussian03 program package was used for all calculations.[10] All structures were optimized at the B3LYP/6-31G** level of theory. Further, the compound method G3MP2B3,[11] as implemented in Gaussian03, has been used for all species but a few which were too large for the computationally demanding QCISD(T)/6-31G* single point energy step in the G3MP2B3 method.

IRC calculations (as implemented in Gaussian03) were performed to ensure that the transition states connected the desired minima. In some cases, the IRC calculations failed after a few steps. In these cases, the Hessian matrix was calculated for a structure found after the first/a few IRC steps and regular optimizations were then carried out down to the minima which were then assumed to be connected via the transition state in question.

For some reactions, we used a continuum model of water to observe solvent effects beyond the first coordination shell. We optimized some structures using the PCM method.[12] Further, single point energy calculations were performed for selected species using the IPCM and SCIPCM methods.[13]

Method Evaluation

CO_2 reacting with NH_3 catalyzed by one water molecule to form carbamic acid was chosen as the benchmark reaction for testing different methods. For this particular reaction, the geometries for start, transition state, and end complexes were calculated using B3LYP and MP2 methods combined with various basis sets and with the G3B3 and G3MP2B3 compound methods. Since experimental enthalpies of formation for many of the investigated species are unavailable, the G3B3 and G3MP2B3 results serve as calibration data, as they can be expected to give energies within 10 kJ/mol of experiment.[11] Single point energies for the test reaction were also calculated with the B3LYP, MP2, and MP4 methods using large basis sets (cc-pVTZ, aug-cc-pVTZ, and aug-cc-pVQZ). Table 1 shows binding strength of the complex, activation, and reaction energies for the test reaction with various computational schemes. The geometries found from the MP2 and B3LYP calculations with various basis sets are very similar. However, the activation and reaction energies did depend more strongly on the level of theory. The activation barrier calculated at the MP4/cc-pVTZ//MP2/6-311G** + ZPE level and with the G3B3 (at 0 K including ZPE) method were equal (120 kJ/mol) and should thus represent our best estimate. The corresponding B3LYP/6-31G**//B3LYP/6-31G** + ZPE barrier is only 84 kJ/mol and underestimates the barrier significantly. In conclusion, B3LYP gives good results for the geometries of the species presently studied, but the energies need to be calculated at a high ab initio level, presumably with a large basis set. The G3B3 and G3MP2B3 methods actually fit this picture very well since they find geometries using the B3LYP/6-31G* method and the energy with the QCISD(T) method and a large basis set. We note that the MP2/6-31G** energies also appear to be quite good, and similar to the MP4 values. Further, the B3LYP/6-31G** energies become more similar to the G3MP2B3 values as the size of the system under study increases, vide infra. In the following, all reported energies are calculated with G3MP2B3, including corrections for zero point energy (ZPE) unless explicitly stated otherwise. The corresponding zero point corrected B3LYP/6-31G** energies are included in the tables.

TABLE 1: Activation and Reaction Energies for the Reaction between NH_3 and CO_2 with a Water Molecule Acting as Catalyst Calculated at Various Levels of Theory

method	binding energy[a]	activation energy[b]	reaction energy[b]
B3LYP/6-31G**//B3LYP/6-31G**	34	84	26
B3LYP/cc-pVTZ//MP2/6-31G**	22	107	38
B3LYP/cc-pVTZ//B3LYP/6-31G**	20	107	40
B3LYP/aug-cc-pVTZ//B3LYP/6-31G**	7	107	39
B3LYP/aug-cc-pVQZ//B3LYP/6-31G**	7	108	39
MP2/6-31G**//MP2/6-31G**	34	118	49
MP2/cc-pVTZ//B3LYP/6-31G**	25	111	44
MP2/cc-pVTZ//MP2/6-31G**	27	112	44
MP2/cc-pVTZ//MP2/6-311G**	28	113	44
MP4/cc-pVTZ//MP2/6-311G**	28	120	49
G3MP2B3	19	126	41
G3B3	18	120	39
Solvent Field Single Point Energy			
IPCM model			
B3LYP/6-31G**//B3LYP/6-31G**	11	52	2
B3LYP/cc-pVTZ//B3LYP/6-31G**	2	76	16
SCIPCM Model			
MP2/6-31G**//B3LYP/6-31G**	10	87	23

[a] Binding energy of the complex at the G3MP2B3 level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [b] Energies relative to the complexes in kJ/mol at 0 K with ZPE corrections. The ZPE corrections are taken from the method used for the geometry optimizations.

Continuum models were employed to extend solvent effects beyond the microsolvation level. Our efforts were hampered by convergence problems, and this limits the amount of results available. Selected structures were optimized using the PCM method, and additional single point calculations were done using the IPCM and SCIPCM approaches. For the PCM geometry optimizations, some of the converged minima showed one or two imaginary frequencies. These were, however, smaller than $20i$ cm^{-1}. Reactant and product geometries of the test reaction were successfully optimized with two different models (B3LYP and MP2 both with the 6-31G** basis set) using PCM, but the initial complexes showed each two imaginary frequencies. However, geometry changes upon application of the PCM field were rather small for the stationary points found. For the initial complex, the C−N distance between CO_2 and NH_3 changed from 2.754 Å at the B3LYP/6-31G** level to 2.786 Å for the optimization using PCM and B3LYP/6-31G**. The corresponding change when using MP2/6-31G** was from 2.820 to 2.835 Å using PCM. For the end complexes, the newly formed C−N bond changed from 1.413 to 1.360 Å at the B3LYP level and from 1.408 to 1.359 Å at the MP2 level. A transition state for the test reaction was not found when we employed the PCM model during the optimization. Other geometry parameters also changed slightly when the PCM model was employed but probably have less impact on the energies. These numbers indicate that application of solvent models through single point energy calculations is a reasonable approximation.

Reaction and activation energies from successful IPCM and SCIPCM single point energy calculations, using gas-phase geometries, are given in Tables 1 and 5. Upon including a solvent model, the activation energy for the test reaction becomes lower by some 30 kJ/mol. However, the SCIPCM result for a complex that includes two MEA, water, and CO_2 (shown in Figure 7) gives an activation energy lowering of 18 kJ/mol (Table 5). Note the apparent lesser effect imposed by the solvent field on the larger system. In contrast to above, optimization using PCM and B3LYP/6-31G** of the start complex in Figure 7 shortened the C−N distance from 1.68 to 1.58 Å. The structure has, however, two small imaginary frequencies.

Results

After an initial discussion of the conformational analysis, the results for the different reactions will be presented.

On Conformers. For all reactions, we have tried to keep a maximum number of intramolecular hydrogen bonds in the reactants, transition states, and products. Since we have followed reactions paths from the transition states down to the minima quite rigorously, we have achieved reactants and products that have similar intramolecular hydrogen bond arrangements as the transition state. Our choice of using complexes with the maximum intramolecular hydrogen bonds was made to increse the probability of using the most stable conformers. To evaluate this approach, the two reactions where MEA or DEA react with CO_2 together with a water molecule catalyst (vide infra) were chosen as test cases. For these complexes, we repeated the calculations at the B3LYP/6-31G** level starting from conformers that showed the least possible number of intra- and intermolecular hydrogen bonds. The absolute energies of these systems were higher compared to those with more hydrogen bonds, but the changes in the activation energies of these two cases were minimal, only 2 and 7 kJ/mol for MEA and DEA, respectively. In a recent work by da Silva et al., it was found that the carbamate conformer that had the most stable gas-phase conformer also would be most stable in solution (water modeled as a dielectric continuum)[8] which is a further indication that our models are realistic.

Carbamic Acid Formation from CO_2 and Either NH_3, MEA, or DEA. The Effects of Water, NH_3, or Methanol on the Activation and Reaction Energies. The simplest reaction, $NH_3 + CO_2$, is shown in Figure 2. Table 2 shows the binding energy of the complexes and activation and reaction energies for the three reactions without any catalyst or additional water. A negative complex energy indicates that the complexes are more stable than separated species. The barriers are quite high, 204 kJ/mol for the ammonia reaction and 170 kJ/mol for both the MEA and DEA reactions. All the reactions are slightly endothermic. The distance between the amine nitrogen atom and the CO_2 carbon atom in the reactant molecular complexes varies between 2.9 and 3 Å. During the reaction these two atoms approach each other (not exceeding 1.6 Å in the transition states), and simultaneously, a proton on the nitrogen atom transfers via a 1−3 shift to an oxygen atom on the former CO_2 molecule. The O−C−O angle of the latter changes from ∼178°, via ∼137° in the transition state down to ∼120° in the products. Note that the CO_2 molecule is slightly perturbed from linearity already in the initial complex. The products are carbamic acids in all cases.

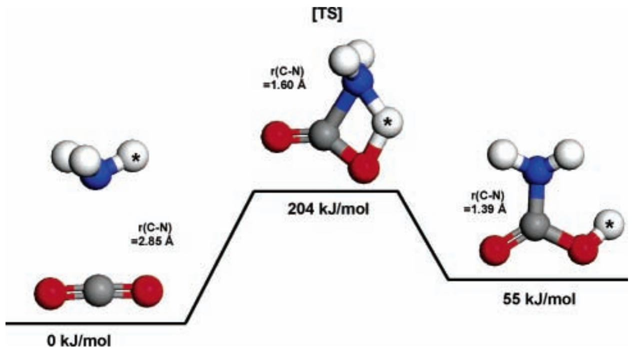

Figure 2. G3MP2B3 structures and relative energies to the start complex (in kJ/mol, 0 K + ZPE) of the reaction between CO_2 and ammonia. The star indicates the hydrogen atom that moves during the transition state. Carbon atoms are rendered in gray, hydrogen in white, nitrogen in blue, and oxygen in red. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

TABLE 2: Complex, Activation and Reaction Energies for Carbamate Acid Formation from CO_2 with Either NH_3, Monoethanolamine (MEA), or Diethanolamine (DEA)

reactants	binding energy[a]	activation energy[b]	reaction energy[b]
$NH_3 + CO_2$	8	204 (176)	55 (44)
$MEA + CO_2$	15	170 (149)	29 (22)
$DEA + CO_2$	30	170 (155)	22 (9)

[a] Binding energy of the complex at the G3MP2B3 level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [b] G3MP2B3(B3LYP/6-31G**) values in kJ/mol, 0 K + ZPE. Activation energies relative to the complexes.

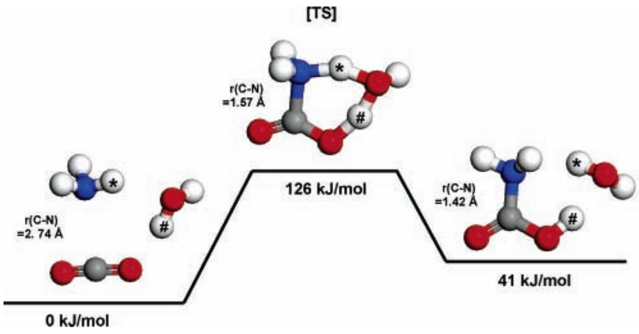

Figure 3. G3MP2B3 structures and relative energies to the start complex (in kJ/mol, 0 K + ZPE) of the reaction between CO_2 and ammonia catalyzed by water. The star and number symbols are used to identify the two hydrogen atoms that move during the reaction. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

Including water molecules in the three above-mentioned reactions causes them to proceed with smaller activation energies, indicating a catalytic action of water molecules. Figure 3 shows the reaction in which NH_3 adds to CO_2 to form carbamic acid catalyzed by one water molecule. The barrier in this case is 126 kJ/mol, and the reaction is endothermic by 41 kJ/mol. If a second water molecule is included, an even lower

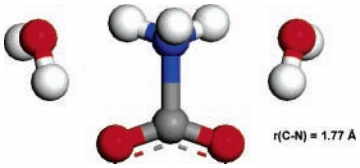

Figure 4. B3LYP/6-31G* structure of the reactant complex in the reaction between $\mathrm{CO_2}$ and ammonia catalyzed by two water molecules. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

TABLE 3: Activation and Reaction Energies for Carbamate Acid Formation from $\mathrm{CO_2}$ and $\mathrm{NH_3}$, MEA, or DEA with One or Two Water Molecules Acting as Catalysts

reactants[a]	binding energy[b]	activation energy[c]	reaction energy[c]
$\mathrm{NH_3} + \mathrm{CO_2} + \mathit{H_2O}$	18	126 (84)	41 (26)
$\mathrm{NH_3} + \mathrm{CO_2} + \mathit{H_2O} + \mathrm{H_2O}$	−17	60 (43)	−21 (−11)
MEA + $\mathrm{CO_2} + \mathit{H_2O}$	35	108 (70)	15 (5)
MEA + $\mathrm{CO_2} + \mathit{H_2O} + \mathrm{H_2O}$	29	57 (41)	3 (12)
DEA + $\mathrm{CO_2} + \mathit{H_2O}$	40	90 (69)	−5 (−14)
DEA + $\mathrm{CO_2} + \mathit{H_2O} + \mathrm{H_2O}$	9	56 (46)	−34 (−30)

[a] Direct catalysts, i.e., the species that exchange a proton during the reactions, are indicated in *italics*. [b] Binding energy of the complex at the G3MP2B3 level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [c] G3MP2B3(B3LYP/6-31G**) values in kJ/mol, 0 K + ZPE. Activation energies relative to the complexes.

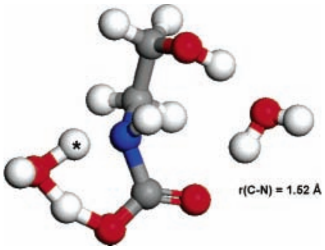

Figure 5. B3LYP/6-31G* structure of the transition state during the reaction between $\mathrm{CO_2}$ and monoethanolamine catalyzed by two water molecules. The hydrogen atom marked with a star was initially bonded to the nitrogen atom. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

barrier is found, 60 kJ/mol, and the reaction energy is −21 kJ/mol. The start complex for this reaction is shown in Figure 4, and it is quite similar to the one shown in Figure 3. Note also that the C−N distance in the start complex goes from 2.75 Å down to 1.78 Å by inclusion of the second water molecule. Table 3 shows the binding energy of the complexes and activation and reaction energies for the whole water catalyzed series of $\mathrm{NH_3}$, MEA, and DEA reactions. In contrast to the reactions described in the paragraph above, the proton bonded to the nitrogen atom is now transferred to the nearby water molecule and not directly to the $\mathrm{CO_2}$ molecule. At the same time, another proton on the water molecule is transferred to an oxygen atom in the $\mathrm{CO_2}$ moiety. At the transition state, the structure of the water moiety resembles that of a $\mathrm{H_3O^+}$ ion. The catalyst action of the water molecule is quite similar to what was observed by Loerting et al.[14] and Lewis et al.[15] for the water-catalyzed hydrolysis of $\mathrm{CO_2}$. In the following, the water molecule that actually exchanges a proton, as described above, will be termed the direct catalyst. Other protic molecules may also assume this role, vide infra.

TABLE 4: Activation and Reaction Energies for Carbamate Acid Formation from $\mathrm{CO_2}$ and $\mathrm{NH_3}$, MEA, or DEA with $\mathrm{NH_3}$, or Methanol in One Case, Acting as Direct Catalyst

reactants[a]	binding energy[b]	activation energy[c]	reaction energy[c]
$\mathrm{NH_3} + \mathrm{CO_2} + \mathit{NH_3}$	19	123 (87)	30 (16)
$\mathrm{NH_3} + \mathrm{CO_2} + \mathit{NH_3} + \mathrm{H_2O}$	-16	54 (45)	−34 (−24)
MEA + $\mathrm{CO_2} + \mathit{NH_3}$	33	83 (64)	7 (−6)
MEA + $\mathrm{CO_2} + \mathit{NH_3} + \mathrm{H_2O}$	31	58 (46)	−33 (−31)
DEA + $\mathrm{CO_2} + \mathit{NH_3}$	39	73 (57)	7 (−5)
DEA + $\mathrm{CO_2} + \mathit{NH_3} + \mathrm{H_2O}$	11	62 (56)	−33 (−30)
MEA + $\mathrm{CO_2}$ + *MeOH* + $\mathrm{H_2O}$	38	49 (−)	2 (−)

[a] Direct catalysts, i.e., the species that exchange a proton during the reactions, are indicated in *italics*. [b] Binding energy of the complex at the G3MP2B3 level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [c] G3MP2B3(B3LYP/6-31G**) values in kJ/mol, 0 K + ZPE. Activation energies relative to the complexes.

TABLE 5: Activation and Reaction Energies for Carbamate Acid Formation from $\mathrm{CO_2}$ and MEA, with MEA Acting as Direct Catalyst without and with a Spectator Water Molecule

reactants[a]	binding energy[b]	activation energy[c]	reaction energy[c]
MEA + $\mathrm{CO_2}$ + *MEA*	47	78 (63)	−15 (−28)
MEA + $\mathrm{CO_2}$ + *MEA* + $\mathrm{H_2O}$	53	39 (33)	−55 (−58)
MEA + $\mathrm{CO_2}$ + *MEA* + $\mathrm{H_2O}$	NA	(15)[d]	NA

[a] Direct catalysts, i.e., the species that exchange a proton during the reactions, are indicated in *italics*. [b] Binding energy of the complex at the G3MP2B3 level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [c] G3MP2B3(B3LYP/6-31G**) values in kJ/mol, 0 K + ZPE. Activation energies relative to the complexes. [d] B3LYP/6-31G** SCIPCM solvent field single point activation energy (0 K + ZPE) using B3LYP/6-31G** gas phase geometries and ZPE correction.

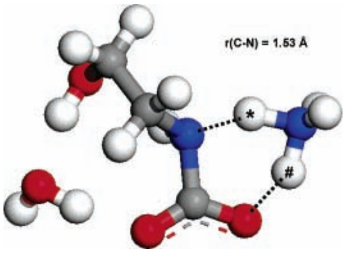

Figure 6. B3LYP/6-31G* structure of the transition state of the reaction between $\mathrm{CO_2}$ and monoethanolamine catalyzed by ammonia and water. Ammonia is a direct catalyst. The star and number symbols are used to identify the two hydrogen atoms that move during the transition state. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

The activation energies for the reactions of DEA and MEA with $\mathrm{CO_2}$ show the same trend as with ammonia when one or two water molecules are added. Figure 5 shows the transition state of the reaction between MEA and $\mathrm{CO_2}$ with two extra water molecules. For this reaction, the activation and reaction energies are 57 and 3 kJ/mol, respectively.

The reactions between $\mathrm{NH_3}$, MEA and DEA with $\mathrm{CO_2}$ to form carbamic acid may also be catalyzed by ammonia or methanol as direct catalysts. Binding energies for the complexes and activation and reaction energies for these reactions are given in Table 4. Figure 6 shows the transition state for the reaction between MEA and $\mathrm{CO_2}$ catalyzed by a $\mathrm{NH_3}$ molecule and water; we note the tetrahedral geometry around the ammonia nitrogen.

Carbamic Acid Formation from MEA with $\mathrm{CO_2}$ Assisted by MEA and a Water Molecule. We have seen that water, ammonia, and methanol may catalyze carbamic acid formation by acting as proton transfer agents. MEA may also act as a catalyst, and Figure 7 shows the reaction between MEA and $\mathrm{CO_2}$ catalyzed by another MEA molecule. The activation energy for this reaction was quite low, 39 kJ/mol, and the reaction was

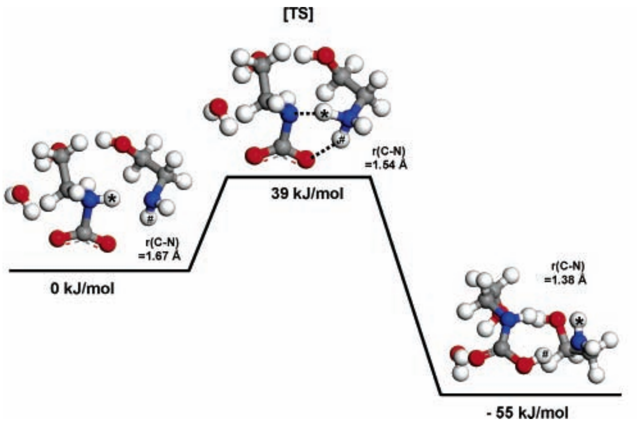

Figure 7. G3MP2B3 structures and relative energies to the start complex (in kJ/mol, 0 K + ZPE) of the reaction between CO_2, monoethanolamine (MEA) catalyzed by another MEA, and water. MEA is the direct catalyst. The star and number symbols are used to identify the two hydrogen atoms that move during the reaction. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

exothermic at −55 kJ/mol. The nitrogen atom in the MEA molecule in the product is coordinated toward the acidic proton and may therefore rapidly abstract the latter, thus forming an ion pair. The rate of this proton transfer should be high since the two molecules are already in favorable positions. Without the extra water, the activation energy is 78 kJ/mol, hence illustrating the importance of the first coordination sphere of solute molecules. Table 5 gives energies for these reactions. Adding SCICPM solvent corrections through single point energy calculations at the B3LYP/6-31G** level as described above for the water assisted reaction lowers the activation energy by 18 kJ/mol.

A search for a similar reaction involving DEA as a direct catalyst instead of MEA failed. Even if we explored a large conformational space we could not locate any transition state where a DEA molecule acted as a direct catalyst similar to ammonia, water, or MEA as described above. There are apparently no steric reasons that could explain why DEA could not be found as a direct catalyst, but we observed that the whole molecular complex had a strong tendency to twist away from any geometry that could lead to such a transition state. Note, however, that this negative result does *not* rule out that any such transition state may exist.

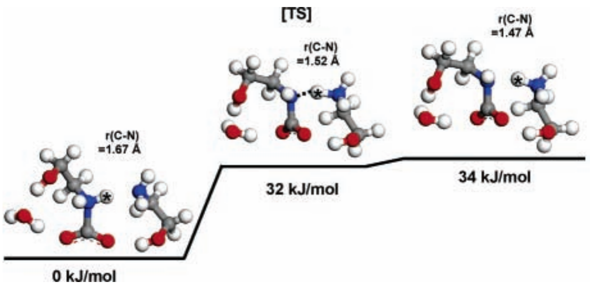

Figure 8. G3MP2B3 structures and relative energies to the start complex (in kJ/mol, 0 K + ZPE) of the reaction between CO_2, two monoethanolamine molecules (MEA), and water. The proton is transferred directly from one MEA to another during the reaction. The star indicates the proton that is transferred between the two amines. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

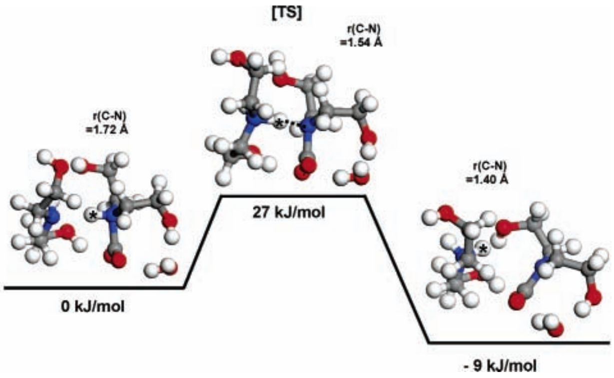

Figure 9. B3LYP/6-31G** structures and relative energies to the start complex (in kJ/mol, including ZPE corrections) of the reaction between CO_2, two diethanolamine molecules (DEA), and water. The proton is transferred directly from one DEA to another during the reaction. The star indicates the proton that is transferred between the two amines. The distance between the C−N atoms that connect during the reaction is indicated in the figure.

TABLE 6: Activation and Reaction Energies for Carbamate Formation from CO_2 and MEA with MEA as a Proton Acceptor

reactants	binding energy[a]	activation energy[b]	reaction energy[b]
MEA+ CO_2 + MEA	12	40 (27)	27 (33)
MEA+ CO_2 + MEA+ H_2O	49	32 (35)	34 (40)

[a] Binding energy of the complex at the G3MP2B3 level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [b] G3MP2B3(B3LYP/6-31G**) values in kJ/mol, 0 K + ZPE. Activation energies relative to the complexes.

TABLE 7: Activation and Reaction Energies for Carbamate Formation from CO_2 and DEA with DEA as a Proton Acceptor

reactants	binding energy[a]	activation energy[b]	reaction energy[b]
DEA + CO_2 + DEA	NA (64)	NA (34)	NA (40)
DEA + CO_2 + DEA + H_2O	NA (102)	NA (27)	NA (−9)

[a] Binding energy of the complex at the B3LYP/6-31G** level, 0 K + ZPE, relative to separated molecules. A positive value indicates a stable complex relative to separated species. [b] B3LYP/6-31G** values in kJ/mol, 0 K + ZPE. Activation energies relative to the complexes.

Carbamate Formation from Alkanolamines and CO_2 Using Another Alkanolamine as a Proton Acceptor. Instead of forming a carbamic acid directly, as described above, the corresponding base may instead be formed in one step, in analogy with the reaction mechanism proposed by Donnellan and Crook[3] and shown in Figure 1. In these cases, the resulting product species are ionic. The reaction where an MEA molecule binds to CO_2 as another MEA abstracts a proton is shown in Figure 8. Note that an additional water molecule is present to model microsolvation. The corresponding DEA reaction is given in Figure 9, and Tables 6 and 7 show the energies for the MEA and DEA reactions, both without and with additional water, respectively. The initial complex in Figure 8 has similarities with the initial complex in Figure 7. Both show the nitrogen atom of the proton accepting MEA molecule directed toward a hydrogen atom of the other MEA molecule. The largest apparent difference is the orientation of the terminating −OH group. At the transition state, a proton is transferred between the two nitrogen atoms, but in contrast to the reaction shown in Figure 7, there is no transfer of another proton to the CO_2 moiety. The resulting minimum in Figure 8 is an ion pair with an energy slightly above the transition state. The activation energies of the MEA reactions without and with water were found to be 40 and 32 kJ/mol, respectively, at the G3MP2B3 level. At the

TABLE 8: Some Experimentally Found Activation Energies, in kJ/mol, for Reactions of CO_2 with Alkanolamines in Aqueous and Nonaqueous Environment[a]

alkanolamine	activation energy[b]	ref
MEA	40	20
	41	21
	46	23
DEA	44	20
	53	21
	54	22
	56	23

[a] See text and references for more details. [b] kJ/mol.

B3LYP/6-31G** level, the corresponding energies are 27 and 35 kJ/mol. For reasons of computational feasibility, the DEA reactions are not calculated with the G3MP2B3 method, and we resort to the B3LYP results. The activation energies for the DEA reactions without and with water were found to be 34 and 27 kJ/mol, respectively. Note the similar barriers at the B3LYP level for both the MEA and DEA reactions. Some of the resulting ion pair products for these four reactions actually had a slightly higher energy than the transition states. This is undoubtedly a computational artifact resulting from the absence of solvent models to stabilize the ions. Note that the DEA reaction that has one extra water added is exothermic even when an ion pair is a product in the gas-phase.

Discussion

The results presented above clearly show the important catalytic role of protic molecules in reactions of CO_2 with aqueous solutions of alkanolamines. Further, the presence of an additional water molecule invariably lowers the barriers dramatically even if it does not participate directly in the reaction. Such microsolvation effects have also been observed for other aqueous reactions studied with quantum chemical methods.[15−19]

All but two of the reactant complexes presented here are stable compared to their gas-phase constituents; all the complexes that include MEA or DEA are stable. This finding strongly indicates that in aqueous alkanolamine solutions, which have surplus amounts of both water and alkanolamines, formation of complexes that may eventually react with CO_2 as described above is favorable. In addition, complex formation of MEA with CO_2, two MEAs, DEA and CO_2 and two MEAs have been evaluated both at the G3MP2B3 level and at the B3LYP/6-31G** level including IPCM(solvent = water) single point energy corrections. These four complexes are also found to be stable compared to the separated constituents. Details on these energies are reported in the Supporting Information. Stable complexes of water, CO_2, MEA, and DEA are also stable due to the many intramolecular hydrogen bindings. These findings indicate that the pre-exponential factors (in an Arrhenius picture) for the reactions under study are reasonably large.

To the authors' knowledge, most experimental reports on activation barriers for the reaction between CO_2 and alkanolamines are from the 1970s and early 1980s. Activation energies of relevance for the present work are compiled in Table 8. Leder[20] studied CO_2 absorption in a potassium carbonate−bicarbonate buffer solution promoted with various alkanolamines or morpholine (∼2.5 wt % amines in the reactions) and reported Arrhenius plots that gave activation energies of 40 and 44 kJ/mol for MEA and DEA reactions with CO_2, respectively. Another interesting work on activation energies was carried out by Hikita et al.[21] They estimated activation barriers for the reaction of CO_2 with aqueous solutions of MEA or DEA of 41 and 53 kJ/mol, respectively. Nunge et al.[22] found an activation energy of 54 kJ/mol for CO_2 absorption in pure DEA. In 1983, Blauwhoff et al.[23] published several works reporting activation energies for a number of reactions including some of those mentioned above.

Crooks and Donnellan[3] suggested some activation energies for reactions of MEA and DEA for different proton abstracting agents (B in Figure 1) based on adapted kinetic equations to observed rates. For the case of proton abstraction by MEA or DEA, they estimated activation enthalpies to be slightly below 20 kJ/mol, while substituting water for the alkanolamine led to a significantly higher activation enthalpy of about 50 kJ/mol. The corresponding free energies were found to be 46 and 56 kJ/mol, respectively, which are close to values given by other workers.

When comparing our calculated reaction barriers with experimental findings, we assume that the solvent corrected barrier reduction of 18 kJ/mol found in one of the studied MEA reactions is also reasonable for other MEA and DEA reaction systems. If our computed proton abstraction barriers (given in Table 6 and 7) are reduced by roughly 18 kJ/mol, they become close to the enthalpies of the activation barriers estimated by Crooks and Donnellan.[3]

A possible reaction between CO_2, water, and two MEA molecules involves one MEA molecule as a proton transfer catalyst. In another reaction, an MEA molecule abstracts a proton from the other, forming an ion pair. Since these two reactions include the same species, the absolute energies for the various steps are directly comparable. The ion pair end product is, however, not included in this analysis because it has an artificially high energy compared to the start structures due to lack of solvent stabilization. The lowest lying initial complex in these two series is the one where MEA acts as a direct catalyst, and it will be used as the zero level. The initial complex in the proton abstraction reaction path is only 3 kJ/mol above this zero level. The transition state with the lowest absolute energy is the proton abstraction transition state, which is 35 kJ/mol above the defined zero level. The transition state where MEA is a direct catalyst is 39 kJ/mol above zero level. The difference is too small to allow any firm conclusions to be drawn regarding the preferred mechanism.

Experiments indicate strongly that the order of MEA in reactions with CO_2 in aqueous environment is 1. Since this points to the fact that only one MEA molecule apparently participates per sorption step, the mechanism where MEA functions as a proton abstractor is not plausible. Therefore, only purely water catalyzed paths or the path where another MEA is a direct catalyst is in accord with the observed kinetic order. However, only the MEA catalyzed reaction has an activation barrier in accord with experiments. On this basis, it appears that the reaction where MEA acts as a direct catalyst for another MEA's reaction is the most plausible.

There is no consensus about the reaction order of DEA, but it has been reported to be somewhere between 1 and 2. On the basis of our calculations, a mix of the pure water catalyzed reaction and the reaction that involves two DEA molecules (where one of them is a proton abstractor) would give a reaction order somewhere in that range. The difference in activation barriers for these two reactions implies that the order of DEA should be 2 or at least closer to 2 than 1.

A zwitterion mechanism has been put forth in the literature to yield kinetic equations describing observed rates. We will try to evaluate this mechanism on the basis of the present computational results. In their theoretical work, Hall et al.[24] studied zwitterion intermediates in the reaction between methylamine and formaldehyde. They were unable to find a stable zwitterion species in the gas phase, but by adding two water molecules to the molecular complex, they were able to locate a minimum that could be characterized as a zwitterion. Inclusion of only a solvent field (no waters) also afforded an energy minimum that was a zwitterion. By including both a solvent field and two water molecules, the zwitterion was further stabilized. In the zwitterions, they found a C−N bond length of 1.60 Å, which is not too far from our atomic distance of 1.68 Å in the initial complex in the MEA reaction with two water molecules. We inspected the Mulliken partial charges on the amine nitrogen atom in the reaction where a MEA reacts with CO_2, assisted by two water molecules, and they did not change significantly from the isolated molecules to the reactant complex, giving us no basis for assuming that the latter should be regarded as a zwitterion, at least in the gas phase. However, we did carry out some calculations using solvent fields that may shed some light on this topic. As noted above, our test reaction was optimized using the PCM approach at the B3LYP/6-31G** and MP2/6-31G** levels, but the C−N distance in the initial complex in fact became longer by inclusion of the solvent field. The initial complex in the MEA reaction where another MEA acted as a direct catalyst was also optimized using the PCM method at the B3LYP/6-31G** level. In this complex, the C−N distance did become shorter relative to the gas phase value, down from 1.68 to 1.58 Å. The structure has two small imaginary frequencies. However, to some extent our calculations support a zwitterion description of the start complexes.

Even if methanol has a certain catalytic effect, it is not efficient enough to produce activation energies in accord with experiment. However, this reaction shows that other protic molecules may also function as catalysts for CO_2 sorption reactions with amines.

Conclusion

We have carried out a quantum chemical study, mainly using G3MP2B3 and B3LYP, of various reaction paths where CO_2 reacts with ammonia, monoethanolamine (MEA), and diethanolamine (DEA) to form carbamic acids or the corresponding bases (thus, in the latter case, forming ion pair products). The results obtained are in quite good agreement with observations and lend strong support to direct involvement of both solute (alkanolamines) and solvent (water) molecules during CO_2 absorption processes in aqueous alkanolamine solutions. The reactions may be catalyzed by water, ammonia, or alkanolamines, or there may be a direct proton transfer from the reaction alkanolamine to another alkanolamine molecule. This last reaction type is similar to the mechanism proposed by Crooks and Donnellan.[3]

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Supporting Information Available: XYZ coordinates for all stationary states and imaginary frequencies for the transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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