GENERAL RESEARCH

Ab Initio Study of the Reaction of Carbamate Formation from CO_2 and Alkanolamines

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Ab initio calculations and a continuum model have been used to study the mechanism for formation of carbamate from CO_2 and alkanolamines. The molecules studied are ethanolamine and diethanolamine. A brief review is also made of published experimental observations relevant to the reaction mechanism. The ab inito results suggest that a single-step, third-order reaction is the most likely. It would seem unlikely that a zwitterion intermediate with a significant lifetime is present in the system. A single-step mechanism also seems to be in good agreement with the experimental data.

Introduction

The absorption of CO_2 by alkanolamines in aqueous solutions is a well-established technology, and both the equilibrium and kinetics of the reactions involved have been studied extensively.[1] It is also well-known that CO_2 reacts to form carbamate and/or bicarbonate, with the relative ratio of these depending on the nature of the alkanolamine and process conditions such as temperature and CO_2 loading (mol of CO_2 absorbed/mol of amine). The mechanism of the carbamate formation has, however, been the subject of some controversy, and the origin of the reaction barrier in carbamate formation has not been satisfactorily explained in the literature.

Versteeg et al.[1] cite the following two-step reaction for the formation of carbamate from CO_2 and alkanol-amines:

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2N^+HCOO^- \qquad (1)$$

$$R_1R_2N^+HCOO^- + B \rightleftharpoons R_1R_2NCOO^- + BH^+ \quad (2)$$

where B is a base, usually a second amine molecule. The first step of the reaction is bimolecular, and the product of the first reaction step is a zwitterion. The mechanism is usually referred to as the zwitterion mechanism. In cases where an overall second-order reaction is observed, one would assume the first step to be rate-determining. Versteeg cites Caplow[2] as the one who proposed this mechanism and also notes that it was later reintroduced by Danckwerts.[3] The notation used by Versteeg is, however, somewhat different from the

original one used by Caplow:[2]

$$(3)$$

A key feature of eq 3 that is lost in eqs 1 and 2 is that Caplow assumed that a hydrogen bond is formed between the amine and a water molecule before the amine reacts with the CO_2 molecule. It would also seem that such a hydrogen bond could be formed between the amine and any basic species.

An alternative mechanism was suggested by Crooks and Donnellan:[4]

$$(4)$$

Again B is used to represent a base molecule. In this mechanism, the bond formation and proton transfer to the base take place simultaneously, giving a single-step,

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Figure 1. Approach of CO_2 to MEA. Hydrogens on carbon are not shown.

third-order reaction. While this mechanism appears to be quite different from mechanisms 1 and 2, it is seen to be quite similar to eq 3 (with water as the base in eq 3).

In this work, simple ab initio calculations were done to investigate which mechanism is the more probable one. Experimental results relevant to the determination of the reaction mechanism are also reviewed.

It would be instructive to do calculations for alkanolamines that display different kinetics and attempt to account for the differences between them. We have here chosen ethanolamine (MEA) and diethanolamine (DEA). MEA is known to have overall second-order kinetics in an aqueos solution, while DEA shows overall third-order kinetics.[1] These molecules show markedly different behavior, at the same time they both are among the more common alkanolamines used for absorption purposes.

Methods

In this work, we have used HF/3-21G* calculations on the alkanolamines. The solvent effects were studied by the use of a continuum (implicit) solvation model and the inclusion of a small number of water molecules. A continuum model represents the effects of the solvent as a dielectric continuum. It captures the overall solvation effects and some of the effects of hydrogen bonding. Such a model cannot be used to model interactions with the solvent such as proton transfer, and it only captures the average effect of the solvent rather than explicit interactions between a single solvent molecule and the solute. To study such explicit interactions, water molecules have been added.

The carbon (CO_2)−nitrogen (in amine) bond length was identified as the key reaction coordinate. The reactions were, therefore, modeled by doing a series of calculations where this bond length was kept constant while the rest of the geometry was optimized. This is shown in Figure 1. For the stable configurations identified, calculations were done without any restraints on the geometry.

All calculations were initially done as calculations on the explicit molecules at the HF/3-21G* level in a vacuum. Single-point calculations with the SM 5.4A[5] solvation model were done on the optimized gas-phase configurations. The total energy calculated in these cases, referred to as SM in the figures, is then the sum of the HF/3-21G* gas-phase energy and SM 5.4A energy (SM 5.4A//HF/3-21G*), with the total energy shown then being the free energy in the solution. All calculations were done using PC Spartan Pro, version 1.0.7.[6]

Calculations were done with one and three water molecules and with a second alkanolamine molecule acting as a base. The water molecules were placed in positions where they would constitute a representative model of the solvent interactions with the amine func-
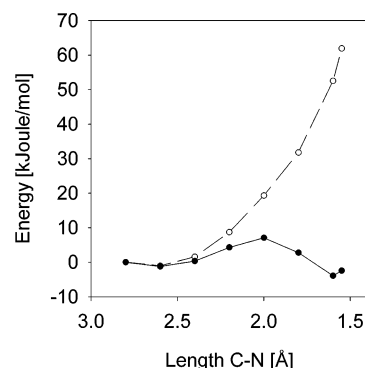
Figure 2. Approach of CO_2 to MEA in a vacuum (open circles) and in a solvent field (SM, black circles).

tionality. In the case of a single water molecule, it was placed such that it would interact as a base with the amine functionality (water oxygen facing the amine hydrogen). In the case of three water molecules, two molecules were placed to interact as bases with the amine nitrogen and one water molecule was placed so that one hydrogen atom forms a hydrogen bond with the free-electron pair of the nitrogen. The hydrogen atoms on the alcohol groups can form hydrogen bonds both with the CO_2 oxygens and with the water molecule oxygen. In the present work, we have chosen, somewhat arbitrarily, to use conformers of MEA and DEA with no alcohol group−CO_2 interaction.

In the Results and Discussion section, one set of calculations is shown for the full transfer of the proton to the base, giving the final products. The calculations are for two MEA molecules. Modeling of the proton-transfer step is somewhat difficult when using clusters of molecules in a vacuum because the molecules tend not to separate. The final configuration often shows protonated molecules and carbamate bonded to each other (particularly when water is used as a base). It is, however, known from the equilibrium states of the system that the final carbamate product is more stable than any intermediate state, and it is this observation that will be used in the discussion.

It should be emphasized that the purpose of this work is to achieve a qualitative understanding of the reaction mechanism. The uncertainty in choice of conformers, level of ab initio calculation, and representation of the solvent all contribute to making it difficult to draw any quantitative conclusions from this work. The need to have a consistent and accurate representation of both intermolecular and intramolecular hydrogen bonds for these molecules represents a particularly difficult issue.[7] We do, however, believe that the present level of modeling is adequate to identify stable intermediates and reaction barriers between the unreacted amine, CO_2, and the final reaction product.
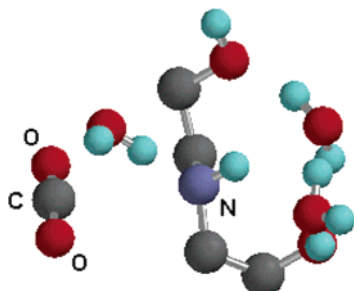
Results and Discussion

Optimizations were initially done for the unreacted molecules placed next to each other. The energies obtained for these starting configurations were defined to be zero for all calculations, and all other energies are given relative to these. The plots in Figures 2−4, 6, and 7 all show the energy as a function of the carbon−nitrogen bond length. The energy is plotted from the starting configuration to the energy minimum (or slightly longer) along the reaction coordinate. In Figure 8, the energy is plotted as a function of the distance
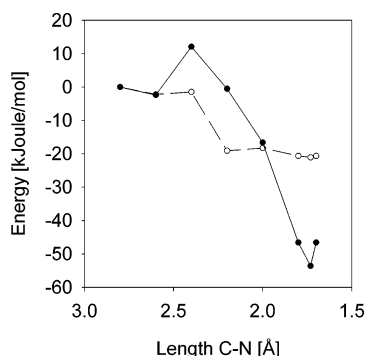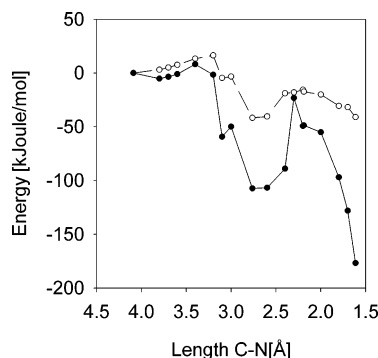
Figure 3. Approach of CO_2 to MEA and one water molecule in a vacuum (open circles) and in a solvent field (SM, black circles).

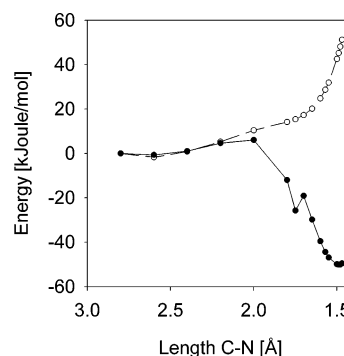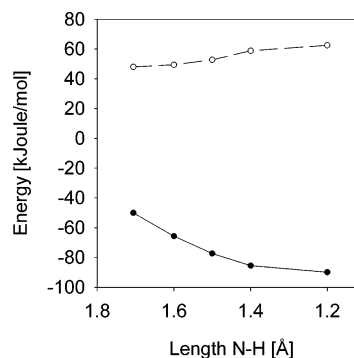**Figure 7.** Approach of CO_2 to two MEA molecules in a vacuum (open circles) and in a solvent field (SM, black circles).
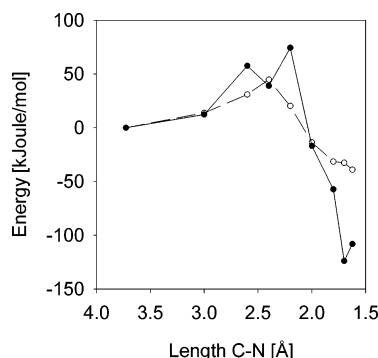
Figure 4. Approach of CO_2 to MEA and three water molecules in a vacuum (open circles) and in a solvent field (SM, black circles).

Figure 8. Transfer of proton between two MEA molecules to form carbamate and protonated MEA. Open circles are results in a vacuum, and black circles are results in a solvent field (SM).

Figure 5. Approach of CO_2 to DEA in the presence of three water molecules. Hydrogens on carbon are not shown.

Figure 6. Approach of CO_2 to DEA and three water molecules in a vacuum (open circles) and in a solvent field (SM, black circles).

between a hydrogen atom on the nitrogen and the base atom it is being transferred to.

Figure 2 shows the results for the approach of CO_2 to a single MEA molecule in a vacuum and in the continuum solvation model (SM). In a vacuum, no stable product is formed, while in the solvent field, a stable configuration is produced. In Figure 3, the results of CO_2 approaching MEA in the presence of one water molecule

are shown, and Figure 4 shows the results with MEA in the presence of three water molecules. As in Figure 2, energies both in a vacuum and in the solvent field are shown. It can be seen that in the presence of one water molecule in a vacuum the reaction proceeds without a barrier. This suggests that the reaction has no intrinsic barrier. In the case of three water molecules, one of them is hydrogen bonded to the free electron pair on the nitrogen. For the CO_2 to bond, this hydrogen bond must first be displaced, and this gives rise to a reaction barrier. The same kind of barrier can be seen with the solvent field calculations (Figures 2 and 3), suggesting that with both presentations of the solvent the reaction barrier is caused by the CO_2 molecule having to displace the solvation shell of the amine functionality.

When the energies of the products in Figures 2−4 are compared, it can be seen that, in the cases where base (water) molecules are included explicitly in the calculations, the formed product is much more stable. This strongly suggests that the presence of the base is necessary for the reaction to proceed. In all cases it was also found that the bond lengths of the amine hydrogen(s) changed during the reaction. In the case of the MEA reaction with CO_2 in the presence of a single water molecule, the amine hydrogen had an initial H−N bond length of 1.008 Å and was at a distance of 2.006 Å from the oxygen in the water molecule. Once the CO_2 had bonded to the amine, the H−N bond length increased to 1.026 Å, while the hydrogen's distance from the oxygen decreased to 1.765 Å. These changes in bond lengths suggest a gradual proton transfer as the CO_2 reacts with the amine molecule.

In Figure 6, the results for CO_2 approaching DEA in the presence of three water molecules are shown (the configuration of this approach at a C−N distance of 3.2 Å is shown in Figure 5). In this case there are appar-

ently two reaction barriers. The first one (at around 3.2 Å) is caused by the displacement of the water molecules around the amine functionality and is of the same nature as the barrier identified for MEA. When the CO_2 molecule approaches the amine functionality, the water molecules reorganize. In this set of DEA calculations, the water molecule hydrogen bonded as a base to the DEA is displaced while the water molecules reorganize, and it this displacement that results in the second barrier seen. However, in these calculations we were only looking at single set of configurations of the DEA molecule and the water molecules. The second barrier is probably a result of the particular set of configurations that we have chosen and is probably not representative of the DEA formation reaction barrier. It does however (again) show that the presence of a base molecule is necessary for a stable product to be formed.

While not shown, calculations with CO_2 approaching DEA without the presence of water molecules and CO_2 approaching DEA in the presence of one water molecule have been performed. These calculations show a qualitative agreement with the results shown for MEA. While the present calculations are not accurate enough to make any quantitative comparison between MEA and DEA, the results do suggest that their reaction with CO_2 proceeds along the same reaction path.

In Figure 7 is shown the approach of CO_2 to MEA, with a second MEA molecule working as the base. The two MEA molecules were oriented toward each other so they only interact through the amine functionality. Because of sterical repulsion, the amine functionalities maintain an N−N distance of around 3 Å. This limits the degree of hydrogen bonding between them, which results in no stable intermediate being formed in the gas phase. In Figure 8, the transfer of the proton from the carbamate to the base is shown. In this figure, the x axis shows the distance between the proton being transferred and the amine group (nitrogen atom) it is being transferred to; the starting configuration is identical with the final products in Figure 7. From this figure, it is seen that such a proton transfer can take place without any reaction barrier.

These results strongly suggest that, for the CO_2 to react with an amine center, basic solvent molecules must be present. On the basis of this observation, we can see two possible reaction mechanisms.

One possibility is the mechanism proposed by Crooks and Donnellan (eq 4), i.e., amine bonding to CO_2 and proton transfer taking place simultaneously. In a general way, this can be written as

$$CO_2 + R_1R_2NH\cdots B \rightleftharpoons R_1R_2NCOO^-\cdots BH^+ \quad (5)$$

A second alternative is that the CO_2 bonds to the amine, with the solvent molecules stabilizing the zwitterion-like intermediate with hydrogen bonds. Such an intermediate is, however, likely to have a very short lifetime. If a strong base molecule (usually an amine molecule) appears in the vicinity, the proton would be transferred to the base and carbamate is formed; if the reaction to carbamate is not completed, the zwitterion-like intermediate is likely to revert back to free CO_2 and amine.

While this second alternative is a form of the zwitterion mechanism, it must be emphasized that any zwitterion-like intermediate would have a very short lifetime and we would argue that the single-step mech-

anism is in any case the most suited to conveying the nature of the reaction taking place.

Review of the Experimental Data

As shown in the Introduction to this paper, there has been considerable discussion in the literature regarding the reaction of carbamate formation. Most of the discussion has been based on the analysis of experimental kinetic data. For the zwitterion mechanism, Versteeg et al.[1] have presented the following expression for the reaction rate:

$$R_{CO_2} = -k_2[CO_2][R_1R_2NH]/(1 + k_{-1}/\sum k_B[B]) \quad (6)$$

If the zwitterion formation is rate-determining, the expression reduces to

$$R_{CO_2} = -k_2[CO_2][R_1R_2NH] \quad (7)$$

This expression can explain the first-order kinetics with respect to amine observed for aqueous MEA. For second-order kinetics, as for cases with DEA, one needs to assume that the deprotonation is rate-determining, leading to the following expression:

$$R_{CO_2} = \frac{-k_2\sum k_B[B]}{k_{-1}}[CO_2][R_1R_2NH] \quad (8)$$

Here B is any base in the system. With amine, water, and other bases B, eq 8 can be written as

$$R_{CO_2} = \frac{-k_2}{k_{-1}}(k_{am}[R_1R_2NH] + k_{H_2O}[H_2O] + \sum k_B[B])[CO_2][R_1R_2NH] \quad (9)$$

If the amine deprotonation term dominates in eq 9, this equation becomes

$$R_{CO_2} = \frac{-k_2}{k_{-1}}k_{am}[CO_2][R_1R_2NH]^2 \quad (10)$$

This gives a reaction order of 2 with regard to the amine. Reaction orders between 1 and 2 are explained by a mix between the two cases. Arrhenius expressions based on this are in the literature[1,8] presented not only for k_2 but also for k_2k_{am}/k_{-1} and $k_2k_{H_2O}/k_{-1}$. The deprotonation constants k_{am} and k_w, however, cannot be obtained alone but only in the groups given.

The consequence of the direct third-order formulation is that water, amine, and other bases can influence the reaction in parallel. With water and amine as the dominating bases, we get

$$R_{CO_2} = -(k_3^{am}[R_1R_2NH] + k_3^{H_2O}[H_2O])[CO_2][R_1R_2NH] \quad (11)$$

Here k_3^{am} and $k_3^{H_2O}$ are real third-order rate constants. However, for practical purposes, eq 11 is the analogue to eq 9 with k_2k_{am}/k_{-1} and $k_2k_{H_2O}/k_{-1}$ equal to k_3^{am} and $k_3^{H_2O}$, respectively.

From eq 11, two extreme cases can be defined. If $k_3^{H_2O}c_{H_2O} \gg k_3^{am}c_{am}$, then water is the dominating base. Because water is the solvent, this will be observed as a

first-order reaction in amine:

$$R_{CO_2} = -k_3^{H_2O}[H_2O][CO_2][R_1R_2NH] =$$
$$-2k_2[CO_2][R_1R_2NH] \quad (12)$$

If $k_3^{am}c_{am} \gg k_3^{H_2O}c_{H_2O}$, then the amine itself is the dominating base and the reaction is second-order with respect to the amine, as observed for DEA.

$$R_{CO_2} = -k_3[CO_2][R_1R_2NH]^2 \quad (13)$$

This is identical with the third-order reaction rate expression for the zwitterion mechanism, eq 10. As already seen, eq 12 is the same reaction rate equation as that for the second-order zwitterion mechanism, eq 7. The two reaction mechanisms can, therefore, be seen to give identical rate functions, and any set of experimental kinetic data can be fitted to either mechanism. The same observation has also been made by Kumar et al.[9] This clearly means that it is very difficult to deduce the reaction mechanism from kinetic studies.

Some arguments have however been made in the literature on the nature of the reaction based on the kinetics, and these will be discussed presently.

Kumar et al.[9] observed that in some systems, such as DEA in water, the reaction rate can change with the amine concentration in the system.[10] In the case of DEA, the reaction order apparently falls at low concentration. They claimed that this change in reaction order could only be accounted for with the zwitterion mechanism. We propose an alternative explanation for this observation. Starting with eq 11, an expression for the apparent reaction order with respect to amine can be derived by differentiating the equation

$$n = \frac{\partial \ln r_{CO_2}}{\partial \ln c_{am}} = 1 + \frac{k_3^{am}c_{am}}{k_3^{am}c_{am} + k_3^{H_2O}c_{H_2O}} \quad (14)$$

At high DEA concentrations, the effect of the amine as the base will be strong, and $k_3^{am}c_{am} \gg k_3^{H_2O}c_{H_2O}$ in eq 14. This is seen to lead to a reaction order of $n = 2$ in eq 12. When the DEA concentration is lowered, the two terms in the denominator become more equal. At very low concentrations, then $k_3^{am}c_{am} \ll k_3^{H_2O}c_{H_2O}$ and an order of $n = 1$ is predicted.

It would also seem that all amines can contribute to base catalysis of bicarbonate formation. This reaction is first-order in amine concentration, and while it is slower than carbamate formation, the reaction might be significant at low amine concentrations. If significant, the bicarbonate formation would contribute to a lowering of the observed overall reaction order.

It has previously been argued that a single-step, third-order mechanism cannot explain the broken-order kinetics observed for some systems. When eq 11 is looked at, it is, however, clear that this is not the case. The extent to which water, or another solvent, works as a base will vary (as explained above), and this can directly account for the broken-order kinetics observed.

Equation 11 also suggests that when the solvent is changed to a weaker base, the reaction order in the amine will increase. This depends on the autoprotolytic constant of the solvent. For water, pK_w is 14, whereas for ethanol, pK_{EtOH} is 19, and this effect is indeed observed for MEA (and other alkanolamines) when solvents such as methanol and ethanol are changed.[1]

We are not aware of any physical explanation having been offered in the framework of the zwitterion mechanism to account for the different alkanolamines displaying different reaction order.

For the single-step, third-order reaction, an explanation will presently be suggested. Sartori and Savage[11] reported in an NMR study that MEA forms a more stable carbamate than DEA, a conclusion that can also be inferred from kinetic data. Because MEA has a more stable carbamate form, even a weak base, such as water, might be enough to drive the reaction forward. For DEA, a stronger base might be required, giving an overall third-order reaction. This would suggest that amines that form stable carbamates, in general, will have lower reaction order than amines with less stable carbamate forms. Only limited data have been published for carbamate stability, but it would seem reasonable to use the reaction rate as a proxy parameter for carbamate stablity; i.e., a high reaction rate indicates strong carbamate formation. In their review, Versteeg et al.[1] report a high reaction rate and an overall second-order reaction for diglycolamine, 1-amino-2-propanol, 2-(methylamino)ethanol, and 3-amino-1-propanol. For di-2-propanolamine, the same authors report a low reaction rate and an overall third-order reaction. These observations are all consistent with the present explanation.

While a solvent such as water might be a strong enough base to (locally) allow the formation of carbamate for amines such as MEA, it is also clear that the presence of stronger bases in the system (usually other amine molecules) is required to shift the equilibrium toward the formation of carbamate. Water, or other solvents, might be thought of as transporting protons to bases not placed immediately next to the reacting amine group.

In a recent paper, Aboudheir et al.[12] argued that a single-step, third-order mechanism is best suited to explain all observed kinetic phenomena. They argued that when data are fitted to the expression for the zwitterion mechanism, some parameters take on unphysical values.

Spectroscopic techniques and NMR would seem to offer the most direct experimental insight into what species are present in a given system. Ohno et al.[13] have reported a detailed spectroscopic study of 2-(N-methylamino)ethanol and its reaction with CO_2 in an aqueous solution. Looking specifically at the issue of the zwitterion formation, they found no evidence of its existence and suggested that only the carbamate and base forms of the alkonolamine were formed. This observation is consistent with a single-step mechanism.

On the basis of the present conclusions, we can attempt to identify the origin of the reaction barriers. In the case of MEA and other molecules showing second-order kinetics in water, it would seem that the only barrier comes from the CO_2 molecule having to dislodge the solvent molecules in the solvation shell of the amine groups. For the systems where stronger bases are required, the need for a base molecule to approach the amine functionality clearly represents a barrier to the reaction taking place. We believe this effect to be dominant for molecules displaying an overall third-order reaction.

Conclusion

In studying the formation of carbamate from CO_2 and alkanolamines in solution, we find a single-step, third-order reaction mechanism to be the most likely. Such a mechanism is consistent with both ab initio calculations and experimental observations on these systems.

The apparent second-order mechanism for MEA in water can be explained by water acting as a base. The varying extent as to which the solvent can act as a base would also seem to account for the broken-order kinetics observed for this reaction. Overall third-order kinetics is most likely to be displayed by amines having less stable carbamate forms.

The barriers for this reaction could either originate from the CO_2 molecule having to displace the solvation shell around the amine group before reacting with the amine functionality and/or from the need for a base molecule to approach the amine functionality before reaction can take place.

Further studies are needed before any quantitative estimates of the various aspects of the reaction can be made. More advanced modeling of solvent effects for this reaction will then be needed.

Acknowledgment

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