

Theoretical Study for the Mechanism of Carbamates Formation through the Absorption of CO₂ by Alkanolamines

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【Introduction】

The absorption of CO₂ by alkanolamines in aqueous solutions is a well-established technology, and both the equilibrium and kinetics of the reactions involved have been studied extensively¹. It is also well-known that CO₂ reacts with alkanolamine to form carbamate and/or bicarbonate. The relative ratio of these ions depending on the nature of the alkanolamine and process conditions such as temperature and CO₂ loading (mol of CO₂ absorbed/mol of amine). In this work, we applied theoretical calculations to study the carbamates formation and explore the probable mechanism for the reaction. Here we have studied monoethanolamine (MEA) because it is one of the common alkanolamines used for absorption purposes. MEA is known to have overall second-order kinetics in an aqueous solution.

【Method】

DMol³ code based on the density functional theory was used for studying the reaction of CO₂ and monoethanolamine (MEA) in gas phase and aqueous solution. All optimizations were done using LDA functional and the energies were refined by GGA single point calculation. The solvent effects were studied by applying the COSMO method which uses a continuum solvent model. The dielectric continuum model represents the effect of water molecules. Moreover molecular dynamics simulation was carried out using Reaction-Ryudo program developed in our laboratories.

【Results and discussion】

Optimizations were initially done for the monoethanolamine (MEA), CO₂ and water 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 calculated relative to them. Optimization of (MEA-CO₂) complex in a vacuum field shows no interaction between CO₂ and the amine nitrogen. By addition of one water molecule to the model; the distance between the CO₂ carbon and the amine nitrogen decreases from 2.50 Å to 1.67 Å. It means that the water influences the interaction between the amine molecule and CO₂, also it stabilizes the complex energy from (-1.86 kcal/mol) to (-1.99 kcal/mol). These results strongly suggest that, for the CO₂ to react with an amine center, basic solvent molecules must be present. Applying the solvation field effect on the same model stabilizes further the (H₂O-MEA-CO₂) complex much more, where the binding energy became (-4.67 kcal/mol). When the formation energies for the carbamic acids of different alkanolamines are compared, it can be seen that the order of stability is (primary amine > secondary amine) as shown in table 1. Moreover, the dynamic interaction for the carbamate formation was investigated where the proton abstraction as well as the carbon nitrogen bond formation was followed by our MD simulation program.

Table 1. Formation energies for the formation of carbamic acids.

Compound	ΔH_f (kcal/mol)	
	Gas phase	Aqueous
Monoethanolamine	-4.38	-7.70
Aminomethylpropanol	6.84	-3.62
Methylaminoethanol	-4.53	-6.97
Propylaminoethanol	-4.79	-7.01
Ethylaminoethanol	-4.46	-0.50

Reference

1) G. F. Versteeg, L. A. J. Van Dijk, W. P. M. Van Swaaij, Chem. Eng. Commun. 144. 1996. 113.