Theoretical Investigation on the Reaction of CO_2 with Amines

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INTRODUCTION

The high amounts of greenhouse gases, particularly CO_2, as a product of the fossil fuels combustion has been claimed as one of the main reasons for the fast global climate change.[1] This has motivated the search for methods able to capture and separate CO_2, among them, aqueous solutions of primary, secondary or tertiary alkanolamines, e.g., methylamine (MAM), monoethanolamine (MEA), and diethanolamine (DEA), have been widely used as chemical absorbents of CO_2.[2] It is known that the rate-determining step and favored reaction channel between alkanolamines and CO_2 to form carbamate involves a zwitterion as intermediate specie.[3] In a recent communication, we have used MP2 and DFT methods to investigate the first step of the reaction between CO_2 and primary pure amines to form a zwitterion specie.[4] Now, the second step of this reaction is under study, i.e., the proton abstraction of the zwitterion amino group by a second alkanolamine (1) to form a carbamate and its possible devolution to the carboxylic acid group to form a carbamic acid (2).

$$RNH_2^+CO_2^- + RNH_2 \rightarrow RNHCO_2^- + RNH_3^+ \qquad (1)$$

$$RNHCO_2^- + RNH_3^+ \rightleftharpoons RNHCOOH + RNH_2 \qquad (2)$$

METHODS

Three alkanolamines were considered in this study, MAM, MEA, and DEA. After a previous conformational analysis using PM3 semi-empirical method was performed for MEA and DEA the geometry of all species were fully optimized with the 6-311++G(2d,2p) basis set and CAM-B3LYP density functional followed by the frequency calculation to confirm that the optimized structure is a true minimum on the potential energy surface or a transition state. All calculations included the solvent effects through the IEFPCM approach and counterpoise correction for the basis set superposition error. The calculations were performed with Spartan and G09 packages.

RESULTS AND DISCUSSION

The conformational analysis revealed two energetically most stable geometries for MEA, chair (MEA-r) and chain (MEA-n), and three for DEA, one with zero, one, and two hydrogen bonding (HB) involving the hydroxyls (DEA-hb0, DEA-hb1, DEA-hb2).

The reaction mechanism study shows that the energy barrier for the reaction (1) increases from MAM to MEA and from MEA to DEA. Particularly, the energy barrier for reaction (1) is higher than for MEA-n than for MEA-r, and is higher for DEA-hb2 than for DEA-hb1 and DEA-hb0. On the other hand, the energy barrier for the reaction (2) is lower than that for the reaction (1) in all cases with no significantly differences among different conformations of the alkanolamines. Besides, the proton turned back in the reaction (2) always involve a different proton than that withdrawal in the reaction (1) characterizing a rotation of the amino group of the second amine.

CONCLUSIONS

Besides MAM, two different conformations for MEA e three for DEA were obtained and analyzed. The energy barrier for reaction (1) increases with the number of intramolecular HBs and is lower than that for reaction (2). The reaction (2) always involves a different proton than that involved in the reaction (1).

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