QUANTUM-CHEMICAL MODELING OF PROTOLYTIC PROCESSES IN COMPLEXES OF OXYMETHYL RADICAL WITH WATER

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Oxymethyl $\cdot CH_2OH$ is the smallest organic OH-radical by size, that makes it unique. Due to this oxymethyl radical is an original particle for quantum-chemical modeling of protolytic processes in paramagnetic acid-base systems.

Quantum-chemical modeling of hydrogen-bonded complexes formed between oxymethyl radical and water have been carried out by using non-empirical approximation in connection with the UHF 3-21G basis set with the help of Gaussian03 program package [1]. We have found 2 stable types of complexes:

1) hydrogen-bonded linear complex (HBLC);
2) hydrogen-bonded cyclic complex (HBCC).

It was found through the analysis of HBLC and HBCC calculated geometric and energetic characteristics that linear complex was thermodynamically more stable than cyclic complex by 4.58 kcal/mol. The length of the hydrogen bridge R(O... N) was computed as 2.7 Å in both types of complexes. The shape of HBLC and HBCC frontier molecular orbitals was showed localization of unpaired electron on the oxymethyl radical. It is worth noting that the dipole moment of HBLC is larger compared with those of HBCC. These associated with higher polarity and lower symmetry of HBLC structure.

Profiles of the proton transfer reaction potential energy surface for linear-type complex were investigated. Calculations were performed with changes of hydrogen bridge length R(O...O) from 2.7 to 3.4 Å; with fixing of valence angle $\angle$(HOO) and with changes of the OH-bond length by 0.1 Å step. It was established that minimum of the total energy of oxymethyl radical-water system corresponds with the formation of molecular hydrogen-bonded complex. The profile of the potential energy surface with two wells was obtained for R(O...O) = 3.4 Å. The transition state of the system at R(O-H) = 2.1 Å and the final state of the system, corresponding with the formation of hydrogen bonding ionic complex (HBIC), were identified on the profile

References:

1. FRISCH, M. J., TRUCKS, G. W., SCHLEGEL H. B., et al. 2003. *Gaussian 03*. - Gaussian Inc., Wallingford CT.

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