Chemoselectivity of acetylene hydratase towards afew amines and alchols

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Abstract: Acetylene hydratase is a metaloenzyme which converts acetylene to acetaldehyde. It was demonstrates that the enzyme is inactive ethylene, acetonitryl and propyn [1]. The catalytic mechanism of the enzyme is fully investigated and it was demonstrated the the central tangestan ion and Asp-13 are the main groups of the active site articipating in the reaction mechanism [1,2]. In this work we are looking for chemical species that can be converted by the enzyme. Then we studied the energetics of of conversion of methyl vinil, propagylalcohl, propagylamine and 3-butyn-2-ol by the enzyme.

We have applied the quantum mechanical cluster (QM-cluster) approach to study the chemical selectivity of the enzyme. Then a model of the enzyme was construted from the crystal structure (pdb ID: 2E7Z) [3]. All QM-cluster calculations of were performed using the density functional B3LYP. The structures of reactants, transition states, intermediates, and products were optimized using the 6-31G* basis set for the H, C, N, O and S atoms and the LANL2TZ pseudo potential for the W ion. To consider the surroundings, solvation effects were evaluated at the B3LYP/6-31G*/LANL2TZ level of theory by performing single-point calculations using the CPCM solvation model. Frequencies of the stationary states on the potential energy surface were calculated to obtain zero-point energies. The frequency calculations were performed at the same level of theory as the geometry optimizations. The final energy of each stationary point discussed in this work was obtained by including the electrostatic part of the solvation energy, zero point energy and thermal correction energy as a correction to the electronic energy.

The results show that methyl vinil has a high barrier in the first step of the reaction and then it can not be converted by the enzyme. However, the propagylamine and 3-butyl-2-ol can cross the first two barries of the reaction and can be converted by the enzyme. Our results show that propagylalchol is a good substrate for the enzyme with a similar energy profile to the native enzyme of the substrate (acetylene). The obtained energy barrier of the propagylamine is 13.0 kcal/mol. This barrier is the lowest one among the barriers of other studied substrates. However, it is higher than the barrier of the natural substrate which is 7.0 kcal/mol.

Keywords: Chemoselectivity; Acetylen hydratase; Metalloenzyme; Mechanism.

References

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