

Abstract

The aim of the present thesis is to study proton transfer reactions inside single walled carbon nanotubes functionalized with amino acid sidechains and hydroxyl groups. The system under investigation provides us with a simple model to study the effect of hydrophobic confinement on such reactions. The model may also serve as a starting point for constructing mimics of protein structural pores and membrane channels. The effect of confinement is investigated in this thesis by anchoring chosen functional groups both on inner and outer surfaces of single walled carbon nanotube. The variation of propensities of different amino acid sidechains participating in a proton transfer reaction is described in terms of (i) proton affinity in the gas phase and (ii) free energies of reaction and activation in solution phase. While proton affinity explores reactivity changes in confinement under non-equilibrium conditions, the free energies reveal thermodynamic and kinetic feasibilities of proton transfer reactions under confinement. The role of hydrogen bonding with polar neighboring groups is also investigated in each case.

A wide range of theoretical methods such as gas phase electronic structure calculations, classical molecular dynamics simulations, free energy estimates using hybrid quantum mechanical-molecular mechanical simulations based on empirical valence bond theory have been used in this thesis. Our results show that reactivity and free energies of proton transfer reaction inside such confined systems crucially depend on the identity and protonation state of amino acid sidechain and also on the water structure formed around the reactant groups. The findings of this thesis provide the first benchmarking study on the effect of hydrophobic confinement on proton transfer reactions largely decoupled from inherent complexities of the reaction medium.

Key words: Proton transfer, carbon nanotube, protein, hydrophobic cavity, confinement, amino acid sidechain, hydroxyl group.