Excited-State Intermolecular Proton Transfer in Aminonaphthols

Malcolm Groves, 2017

Proton transfer is a fundamental chemical reaction involved in a wide range of organic reactions. It plays an integral role in the survival of all living organisms via pathways such as oxidative phosphorylation. Despite its ubiquity, proton transfer kinetics are poorly understood at a molecular level and there are no well-defined predictive models for proton transfer in large biomolecules. The Takematsu lab studies proton transfer kinetics in small molecules called aminonaphthols with the goal of understanding the general factors that influence proton transfer. We hypothesize that proton transfer kinetics can be predicted from molecular structure and solvation environment.

Aminonaphthols bind protons at a hydroxyl site and an amine site. The proton affinity of each site is quantified by the pK$a$ with large values indicating a stronger bond. The proton binding sites can be distributed at different points around the naphthalene backbone, making it possible to study different structural isomers. Depending on the pH, the aminonaphthol exists as either a cation, neutral, anion, or zwitterion (Figure 1). These protonation states equilibrate by proton transfer to or from the water solvent.

Aminonaphthols have different electronic energy levels. The lowest energy level is the ground state and the subsequent higher energy levels are the excited states. Studying proton transfer in the ground state is not feasible because the ammonium hydrogen had a pK$a$ of 3.9 for 5N2OH and 4.8 for 8N2OH. The hydroxyl hydrogen had a pK$a$ of 9.4 for 5N2OH and 8N2OH. There was no zwitterion presence in the ground state. The excited state species were investigated with steady-state fluorescence emission spectroscopy and TCSPC. The major change from the ground state was the formation of the zwitterion at pH 1 to 5 for both isomers. The excited-state pK$a$ for the 8N2OH hydroxyl hydrogen was calculated as 9.64 using the steady-state fluorescence and TCSPC data.

In the future, the excited state kinetics of the other equilibria will be calculated for both isomers. Computational chemistry will be used to support the experimental conclusions and provide structural justification for the observed trends. Finally, I will compare my results with those of my lab mates who are studying proton transfer in other aminonaphthol isomers and other solvent environments and we will draw conclusions about the effect of structure and solvation on proton transfer kinetics.

Figure 1. The four protonation species of the 8-amino-2-naphthol isomer (left to right): cation, zwitterion, neutral, and anion.

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