Degradation Pathways in Aminonaphthols
Kacie Nelson, Class of 2019

Introduction

Proton coupled electron transfer (PCET) plays an important role in fields that vary from energy harvesting to determination of protein function[1]. Within biological systems, quinone and quinoid compounds are essential for a variety of metabolic pathways, including photosynthesis and respiration, because of their properties as PCET partners. Due to the variety of quinone and quinoid compounds and the complexity of biological systems, model compounds in controlled environments are useful for elucidation of PCET mechanisms.

Figure 1. Oxidation of hydroquinone (phenol) to 1,4-benzoquinone via a PCET mechanism

Phenols are a popular model compounds because of their structural simplicity, easy functionalization, and the relative stability of their quinone oxidation products (Figure 1). As such, a variety of phenol-benzoquinone systems have been extensively studied in a variety of environmental conditions[2]. Naphthols are similar to phenols in structure, but with an additional aromatic ring (Figure 2). Naphthol-naphthoquinone systems are an interesting extension of PCET studies because of the distribution of electrons around the additional ring, as well potential distal effects not possible with the one-ring phenol system. Additionally, the fluorescent properties of naphthols and naphthol derivatives allows us to probe the excited state behavior of these compounds. The Takematsu lab is interested in testing the potential of aminonaphthols as probes for PCET. In particular, we wish to determine if the species 8-amino-2-naphthol (8N2OH) and 5-amino-2-naphthol (5N2OH) can be used to probe PCET dynamics when functional groups are placed on separate rings. When excited with light in basic conditions, preliminary data suggests that these species may be forming quinone intermediates.

Summer Goals and Accomplishments

Because this has been my second summer with the Takematsu lab I was able to gain greater fluency with a variety of skills. Included among these are spectroscopic techniques, particularly UV / Vis spectroscopy and Steady-State fluorescence spectroscopy, as well as proficiency in MATLAB coding and skills in literature review. New to me this summer was work with High-Performance Liquid Chromatography (HPLC) and Mass Spectrometry (LCMS). Along with training on the machinery, I also learned how to work with data on MATLAB and MassHunter software.

Using UV / Vis spectroscopy to determine the extent of product formation, we were able to refine our protocol and demonstrate reproducibility under constant conditions. Using HPLC and LCMS, we have been able to begin to elucidate the structure of the light reaction products. The preliminary data from LCMS analysis suggests that the 8N2OH may be forming a quinone product, but more analysis will be required. The 5N2OH appears to be undergoing a more complicated mechanism, perhaps undergoing cycloaddition or dimerization.

Future Directions

In the short term, we hope to continue to analyze the photolysis products with LCMS and HPLC, as well as with techniques such as Nuclear Magnetic Resonance (NMR) and Infrared Spectroscopy. Additionally, we would like to determine the reactivity of these species in different pH regimes outside of the highly basic. In the longer term, we hope that we can use steady-state and time-resolved fluorescence spectroscopy to probe the mechanism of PCET in aminonaphthols.

Faculty Mentor: Kana Takematsu
Funded by the James Stacy Coles Fellowship

References:

1) Chang. *BBA- Bioenergetics.* **2004,** *1655*, 13-28.
2) Rinehard, K. L., *Oxidation and Reduction of organic Compounds*. Prentice-Hall: Englewood Cliffs, N.J., 1973.