Temperature dependence of merocyanine-based photoacids in different alcohols
Juyeon Lee, Class of 2026

The movement of protons, known as proton transfer (PT), is a ubiquitous phenomenon that dictates vital biological and chemical processes such as ATP synthesis and enzymatic catalysis. Photoacids provide an interesting system of PT as they release a proton upon irradiation. While the proton is typically short-lived, metastable photoacids are a special class of photoacids that have a longer lived deprotonated form. Merocyanine (MCH) is a metastable photoacid which under irradiation, isomerizes and ring-closes to form its deprotonated both protonated and deprotonated spiropyran (SP) forms can be observed using absorption spectroscopy (Figure 1). The differing spectral signatures of the MCH and SP allow for the measurement of kinetics, specifically the ring-opening reprotonation reaction. While this reaction was predicted to be second order, previous results demonstrated that the ring-opening reaction followed a pseudo first order reaction in both aqueous and non-aqueous solvents.

Although the kinetics of MCH in water occurs extremely quickly allowing for temporal control, the hydrolysis of the photoacid in aqueous solutions necessitates a better understanding of MCH in nonaqueous solvents. Alcohols, in particular, have similar properties with a hydroxyl (-OH) group and varying acidities. This study looks at MCH in various alcohols, ranging from pK_as of 9.3 to 18 to investigate the effects of acidity in nonaqueous environments. To examine the properties of alcohols in the MCH system, temperature-controlled experiments were performed to calculate the activation energies. The results demonstrated that lower pK_as were associated with shorter lifetimes, while activation energies were comparable among aqueous and alcohol solvents.

This trend of lower pK_as and shorter lifetimes is observed most likely due to the alcohols' ability to donate and receive protons. For example, an alcohol such as 2,2,2-trifluoroethanol with a low pK_a is able to deprotonate and reprotonate at faster rates than alcohols with high pK_as. This property allows 2,2,2-trifluoroethanol to quickly transfer protons, thus returning a proton to SP, reproducing the original MCH. Interestingly, MCH in 2,2,2-trifluoroethanol does not experience full conversion to SP as a result of the solvent's acidity.

For the temperature-controlled experiments, as the temperature increased, so did the rate of recovery of MCH in every solvent. All tested solvents showed similar trends and ultimately resulted in similar activation energies as well. This activation energy most likely corresponds to the ring-opening of SP after irradiation. Considering that the activation energies across solvents are similar, the difference in reaction rate can be attributed to other characteristics of the alcohols.

In conclusion, this study demonstrated that the ring-opening reaction of SP to MCH has dependence on both pK_a and temperature through differing mechanisms. While pK_a is responsible for the speed of PT within the solution, temperature provides energy to overcome the activation barrier. Both these factors drastically change the reaction rate and can be tuned to control the speed of the reaction. Eventually this system will be utilized in a carbon capture system, thus favoring the tuning of pK_a rather than temperature in order to consume less energy. Overall, the potential of photoacids, especially MCH, is vast and will continue to be studied.

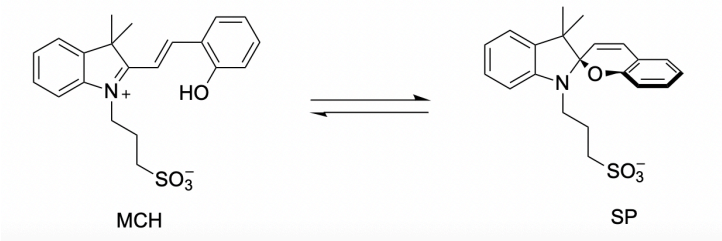

Figure 1. Schematic representation of MCH conversion to SP. After irradiation from light, MCH undergoes a ring-closing reaction and releases a proton (H^+)

Faculty Mentor: Kana Takematsu
Funded By: Surdna Foundation Undergraduate Research Fellowship Program