Accessing the Triplet Excited State of Bromonaphthols to Extend Proton Lifetimes

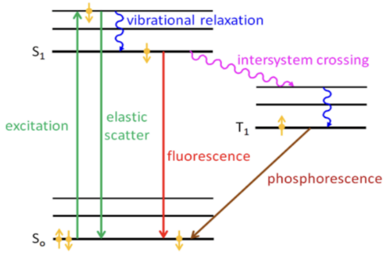

Figure 1. Jablonski diagram of singlet and triplet excitation/relaxation. The singlet state, the electron gets excited and relaxes back down. Through intersystem crossing (pink), the triplet state can be accessed.

Photoacids are compounds that become more acidic, or lose protons more easily, after excitation with light through excited state proton transfer (ESPT).[1] Most photoacids undergo ESPT in the short-lived singlet state that only lasts for a few nanoseconds (Fig.1).[2] This limits the proton from interactions with surrounding molecules. To extend the lifetime, a heavy atom such as bromine can be added to the photoacid to induce intersystem crossing (ISC) to access the triplet state.[3] 1-bromo-2-naphthol (1Br2OH) and 6-bromo-2-naphthol (6Br2OH) in the presence of an external proton acceptor, triethylamine (TEA),were used to examine the impact of the bromine's position on ESPT and proton transfer dynamics. Transient absorption spectroscopy (TAS) was used to measure and compare excited state lifetimes of the samples in acetonitrile. 1Br2OH and 6Br2OH samples were prepared with and without degassing in argon gas for at least 25 minutes to remove molecular O_2. TAS data for degassed samples of 6Br2OH and 1Br2OH (Fig. 2) were vastly different, indicating that the position of bromine plays a significant impact on triplet formation. 1Br2OH (Fig. 2A) had a lifetime of 247 ns, consistent with singlet decay, while 6Br2OH (Fig. 2B) showed a lifetime of 4.498 µs, characteristic of triplet formation. The data was fitted to a monoexponential decay using a MatLab program developed by a senior lab member.

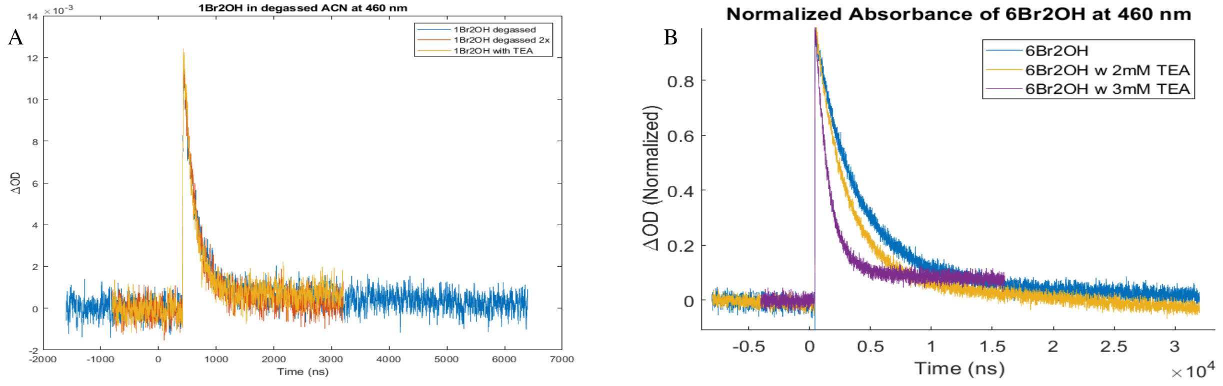

Figure 2. TAS ΔOD curve of 1Br2OH (A) and 6Br2OH (B) in degassed acetonitrile excited at 266 nm, measured at 460 nm, fit to a monoexponential curve.

Proton transfer efficiency was probed by adding TEA (2 mM). For 1Br2OH, TEA had little effect, reducing the lifetime from 247 ns to 170 ns. In contrast, 6Br2OH showed a marked reduction from 4.50 µs to 3.07 µs, indicating significant interaction with the proton acceptor.

These results demonstrate that bromine substitution position critically influences ISC efficiency and ESPT pathways. While 1Br2OH remains mostly in the singlet state, 6Br2OH efficiently accesses the triplet state and engages in proton transfer. Future work will explore mixed water-acetonitrile solvents to better control hydrogen bonding and proton mobility.

[1] Agmon, Naom. *J. Phys. Chem. A.,* 2005, 109, 13-35

[2] Mobely, Chris. "Theory of Fluorescence and Phosphorescence". *Ocean Optics Web Book*. Mar. 2021

[3] Chemistry (IUPAC), IUPAC - Heavy Atom Effect (H02756).