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Experimental Analysis of Bromonaphthol Triplet States

A photoacid is a compound that, upon photoexcitation, becomes more acidic and is more likely to donate its proton through excited state proton transfer (ESPT). In photoacids like 2-naphthol, the mechanisms behind ESPT remain in the singlet state, where the electron accessing the excited state maintains its spin orientation from the ground state (Fig. 1[1]). The limitation with photoacids restricted to ESPT in the singlet state is their short lifetime, lasting a few nanoseconds.[2] A short lifetime can prevent other photochemical pathways, as a photoacid may not have enough time to donate a proton to another molecule. This project focuses on extending the lifetime via the triplet state.

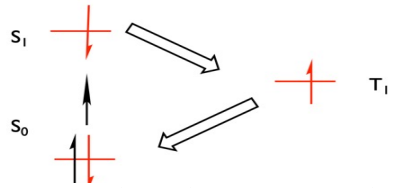

Figure 1: The singlet state, represent by S_0, the ground state, and S_1, the singlet excited state. Through intersystem crossing, the triplet excited state is accessed (T_1).

The triplet state can be accessed by adding an atom with a high atomic number, like bromine, to a photoacid. Due to the heavy atom effect, the presence of the bromine atom increases the likelihood of intersystem crossing.[3] Two brominated photoacids of interest in this project are 1-bromo-2-naphthol (1Br2OH) and 6-bromo-2-naphthol (6Br2OH). The impact of the bromide’s position on the photoacids’ excited state mechanisms is observed by comparing the lifetimes of the two compounds. This project also examines how solvents may influence triplet formation.

To compare the excited state lifetimes of 1Br2OH and 6Br2OH, I utilized time-correlated single photon counting (TCSPC) emission spectroscopy and transient absorption spectroscopy (TAS). For each bromonaphthol, samples were prepared in acetonitrile, methanol, and deionized water. Samples were also prepared with and without degassing with argon gas for at least 15 minutes to remove ambient molecular O_2. The TCSPC emission data for a degassed sample of 1Br2OH in acetonitrile at 450 nm was fit to a triexponential decay from the excited state (Fig. 2A) using DAS6. The longest of the three lifetimes was about 8.863 nanoseconds (T2). This is consistent with lifetimes associated with the singlet excited state.[2] In contrast, the corresponding TAS data was fit to a monoexponential decay using a MatLab program developed by a senior lab member which indicated a longer lifetime value of 131 ns (Fig. 2B).

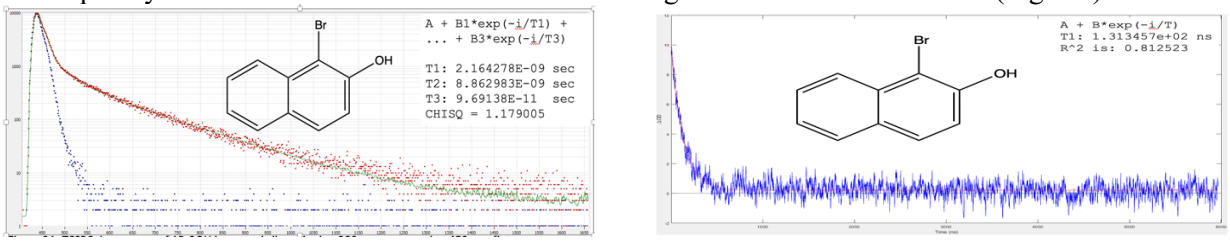

Figure 2: (A) TCSPC decay curve of 1Br2OH in acetonitrile excited at 280 nm, measured at 450 nm, fit to a triexponential curve. Sample has been degassed. (B) TAS ΔOD decay curve of 1Br2OH in acetonitrile excited at 266 nm, measured at 450 nm, fit to a monoexponential curve. Sample has been degassed.

Given the difference in lifetime values between the TAS and TCSPC decay curves, the kinetics allude to the existence of multiple decay pathways from the singlet excited state. The TCSPC data corresponds to the fluorescence of the sample’s singlet excited state as it decays back to the ground state, as evidenced by the short lifetime of around 8.863 ns. Unlike TCSPC, TAS data can reveal non-emissive species, such as 1Br2OH’s triplet state. This explains the longer lifetime present in Fig. 2B’s decay. Analysis of TAS data for 6Br2OH under the same conditions yields a longer lifetime value of around 2.48 microseconds. As I aim to compare the two bromonaphthols in other solvents, I will continue to use TAS to study the effect of bromide position on triplet formation.

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[1] Frackowiak, Danuta. “The Jablonski Diagram.” Journal of Photochemistry and Photobiology B: Biology, vol. 2, no. 3, Nov. 1988, p. 399. ScienceDirect, https://doi.org/10.1016/1011-1344(88)85060-7.

[2] Wang, Zhijia, et al. “Insight into the Drastically Different Triplet Lifetimes of BODIPY Obtained by Optical/Magnetic Spectroscopy and Theoretical Computations.” Chemical Science, vol. 12, no. 8, Mar. 2021, pp. 2829–40. pubs.rsc.org, https://doi.org/10.1039/D0SC05494A.

[3] Chemistry (IUPAC), The International Union of Pure and Applied. IUPAC - Heavy Atom Effect (H02756). https://doi.org/10.1351/goldbook.H02756. Accessed 20 July 2023.