Quantum Yield and Rate Constants for H/HTFAA

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Gas-phase hexa/trifluoro-acetylacetone exists in the enol form with a strong intramolecular hydrogen bond. The compound reacts to close a ring, forming methylfuranones, and eliminate HF in a remarkable UV-photochemical pathway. We measured the relative efficiency of this pathway and determined a rate constant and lifetime for both molecules.

My summer research began with a literature study and acclimation to the years’ worth of data already collected on these two molecules. In doing so, I found that the methods used to determine the peak area were not accurate, so I recalculated them. I used OMNIC software to quantify ½ of the peak (the left side) because the upper wavenumber side had some interference. I manually estimated baselines for each individual pressure studied in order to ensure accuracy of relative quantum yield values. I also quantified the areas of some smaller molecule photoproducts for future research.

Since data was collected by multiple people on different days, slight discrepancies arose in the data analysis spreadsheets. I made concise, accurate spreadsheets that synthesized both sets of data in a single analysis process. For example, correction of the cell’s pressure was done at a certain time using the UV-Vis spectrometer, and the values were extrapolated. However, these values were extrapolated using different methods, so I chose the most accurate method and applied it to both data sets. Also, one experimenter corrected for UV laser light reflecting off the front window of the cell before it entered, and the other did not. I made sure to make the same correction, which improved the linear fit of the data significantly.

The relative quantum yield was established by dividing IR absorption $I_{IR}$ (measured by peak area) by the UV laser light absorbed $I_{UV}$.

$$\Phi_R = \frac{I_{IR}}{I_{UV}}$$

We wanted to find an absolute quantum yield from our relative QY because an absolute QY can be compared across literature to other similar molecules. Unfortunately, the disappearance of the parent molecule that would provide us with an absolute QY did not prove to be quantitatively sound. This caused us to try another method, using Wolfram Mathematica 9 to fit a non-linear curve to the log-scaled data. I learned the syntax of the program and successfully fit the least squares curve, giving us a horizontal asymptote and a curvature value. This allowed us to scale our relative QYs to something very similar to absolute QYs. The curvature value also allowed us to accurately calculate a dissociation rate constant for the photochemical process.

First, though, I had to calculate a collision rate constant using the mean relative speed, collision diameter, and number density. I found the correct mean relative speed equation and had to estimate hard sphere collision diameters from the literature. I did this by finding similar molecules and comparing them to other molecules with or without functional groups in order to estimate the effect of these groups. I also calculated error values for rate constants and lifetimes by considering all the possible sources of error and assigning percentage values to them. I compared this error with the linearity of the slopes and found that my estimated error was likely too large. This validated the choice of scaled relative quantum yields and provided support that our rate constants were accurate within about 10%.

The last part of the summer was spent creating a manuscript for publication in the Journal of Physical Chemistry A. I wrote large sections of the manuscript, assisted in the editing process, curated the figures and graphs, and found some valuable literature citations. At the end of the summer, the manuscript was sent off to be read over by colleagues of Prof. Muyskens.