Determining the Oxidation Potentials of Aniline and its Derivatives via Aqueous Cyclic Voltammetry to Model the Photocatalyzed Electrochemistry of Organic Pollutants
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Understanding the fate of organic pollutants in the environment due residential, commercial, and industrial pollutants is essential to determining the potential hazards of existing and new chemicals. Ideally, all pollutants would quickly degrade into harmless chemicals; however, it is impossible to tell if this will happen without rigorous experimental and theoretical studies. Many pollutants find their way into natural waters where they are exposed to sunlight and the possibility of degradation via the absorption of ultraviolet radiation from the sun. One such pathway involves the excitation of naturally occurring dissolved organic matter in the water into a excited electronic triplet state, creating the opportunity for pollutants to “quench” these excited states via the transfer of electrons. This kind of process is a photochemically-catalyzed reduction/oxidation reaction. Once they have “quenched” the excited states in dissolved organic matter, the pollutants themselves become radicals, and these excited radicals can react via numerous pathways and transform or degrade in many ways.

Unfortunately, dissolved organic matter and organic pollutants can be fantastically complex and difficult to study, so it is useful to model these reactions with simpler compounds and to then apply the knowledge obtained from these simplified conditions to more complex systems. To model photochemically catalyzed reduction/oxidation reactions, it is useful to excite a photosensitizing compound which is readily excited by ultraviolet light and to “quench” these excited compounds with small organic molecules. The Environmental Chemistry Modeling Laboratory at the Swiss Federal Polytechnical Institute in Lausanne, Switzerland and the Environmental Chemistry Group at the Swiss Federal Technical Institute in Zürich, Switzerland have conducted experiments where they excite the photosensitizers Rose Bengal and Methylene Blue and quench them with aniline and various aniline derivatives. They have determined the rate of this quenching reaction using Laser Flash Photolysis, and using Sandros-Bloltzman theory, have shown a relationship between the rate of the quenching reaction and the energy of the electron transfer that quenches the excited photosensitizers.

In order for their calculations to be accurate, it is essential to know the oxidation potential, or energy of removing an electron, of aniline and its derivatives. Current literature values for the oxidation potential of aniline are incomplete or have been collected in non-aqueous solvents such as acetonitrile or methanol. Since environmentally relevant reactions and the study conducted in Switzerland occur in water, it is necessary to have aqueous oxidation potentials. Since using computer models to calculate these values from quantum theory is very difficult, we have collaborated with the Swiss group in order to provide accurate experimental values.

Aniline, 4(tert-butyl)aniline, p-toluidine, benzene-1,4-diamine, 3-fluoroaniline, N-methylaniline, 4-chloroaniline, 4-fluoroaniline, 3-methoxyaniline, 3-ethylaniline, 3-ethoxyaniline, 3-aminophenol, 3-chloroaniline, m-toluidine, 3-iodoaniline, and N,N-dimethylbenzene-1,4-diamine were selected as the focus of this summer project. All of these compounds were purified via distillation or recrystallization in order to remove a polymer that forms when anilines are exposed to oxygen. Once purified, the anilines were dissolved in an aqueous system and their oxidation potentials were determined via a technique called cyclic voltammetry. These values will be critical to the work done in Switzerland and the Eustis Lab. Continuing work in this area will greatly increase our knowledge of the behavior of organic pollutants in natural bodies of water and help us better predict their fate.

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