PORPHYRINS THROUGHOUT THE CHEMISTRY CURRICULUM

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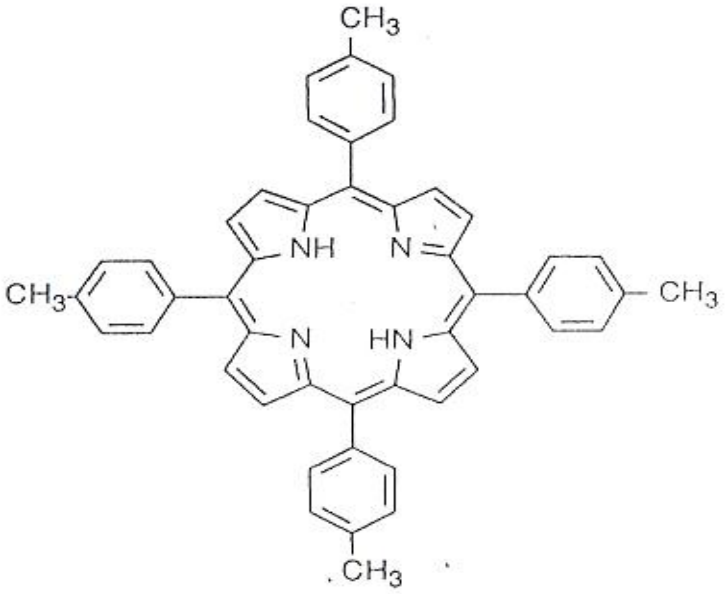
ABSTRACT

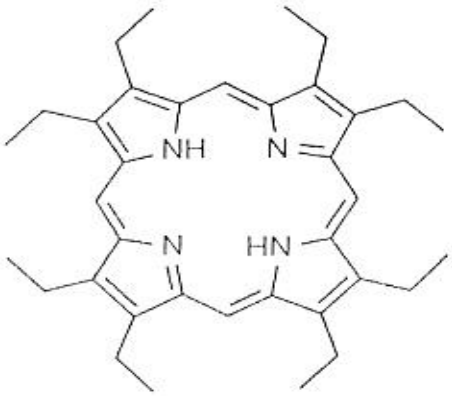
Porphyrins are ubiquitous compounds with many useful chemical, physical, and biological properties. This presentation will provide examples of the use of porphyrins in teaching chemistry in a variety of courses at Glenville State College and Edgewood College. The goal of this approach is to provide continuity from one chemistry course to another.

PORPHYRINS



H_2TTP

meso-tetra-p-tolylporphyrin



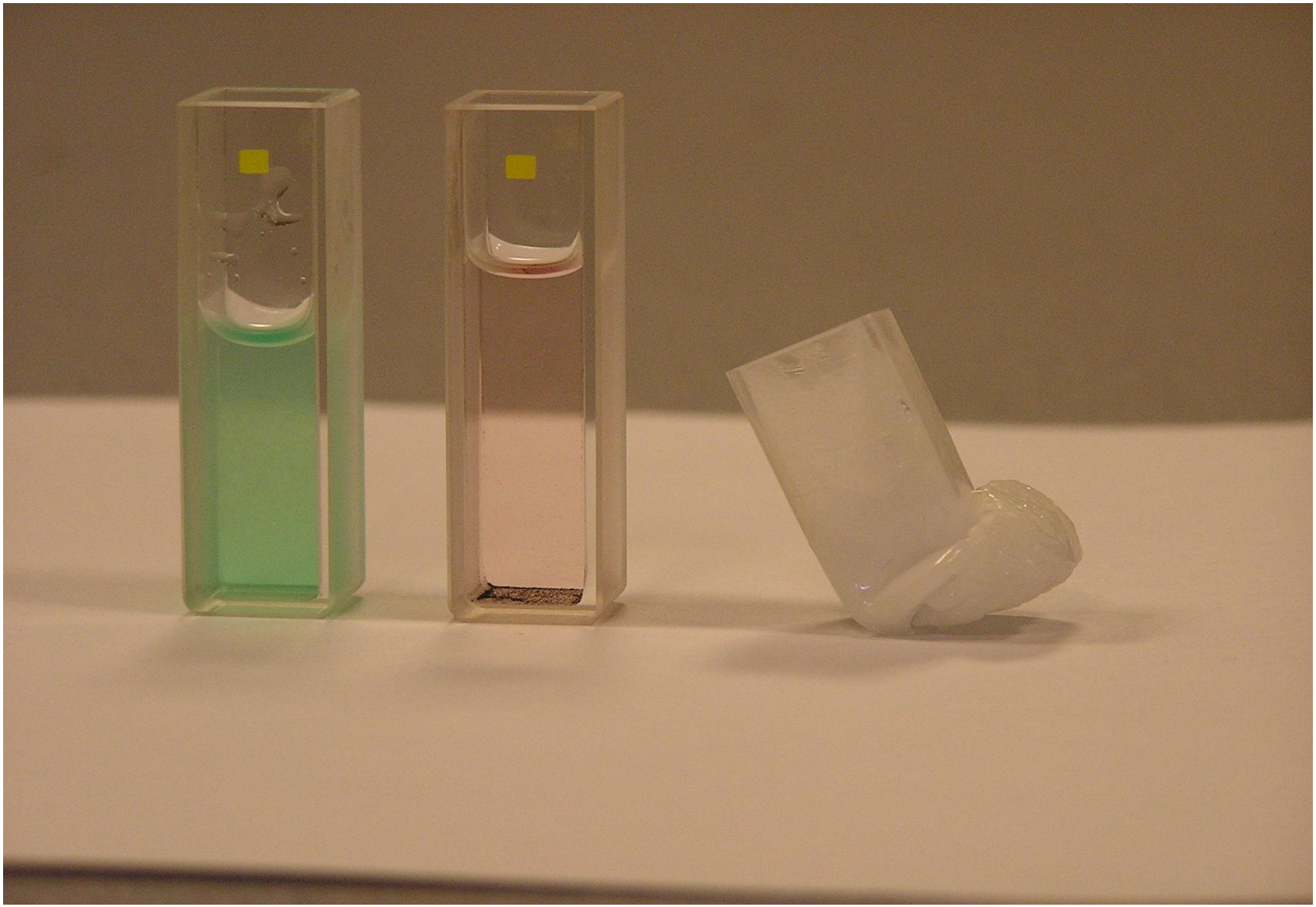
H_2OEP

octaethylporphyrin

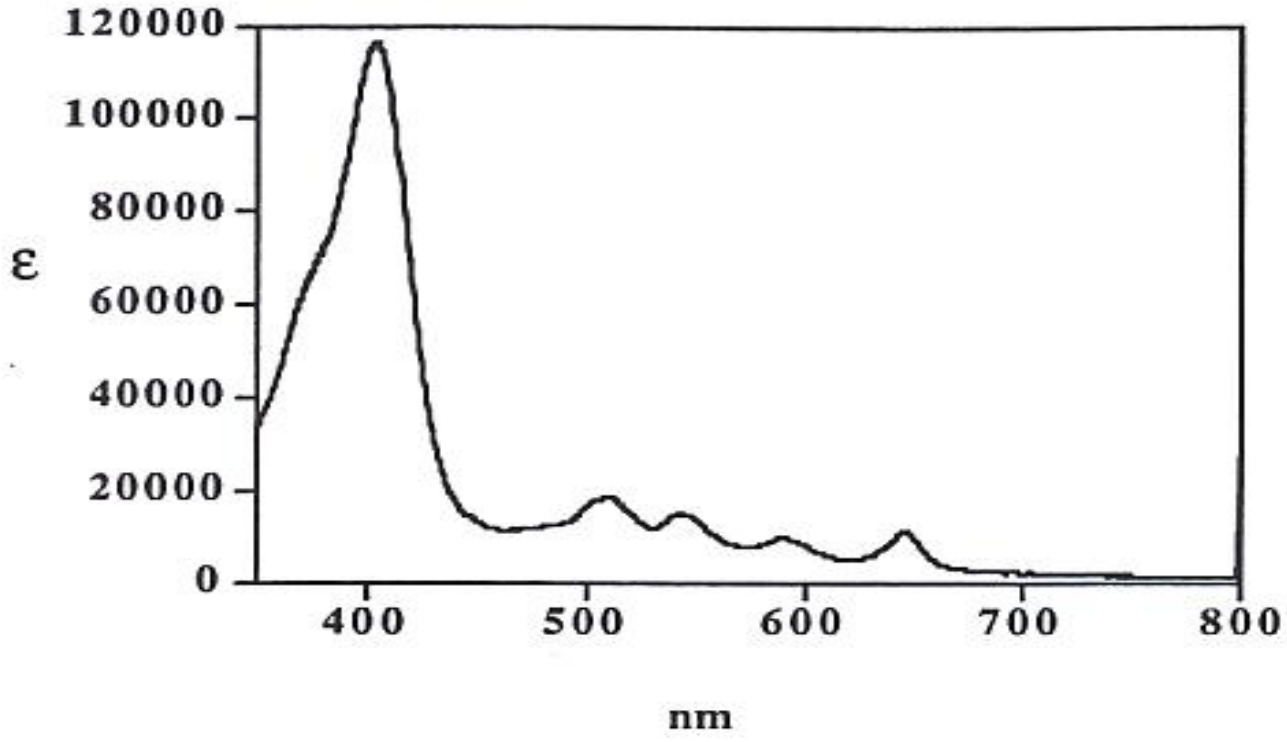
GENERAL CHEMISTRY

Spectroscopy is introduced by giving students a colored sample. The students are then are asked to obtain a visible spectra of the compound. The students are divided into groups of four and they discuss what needs to be done. After they determine what is a spectra, they start to think about what equipment is needed. After they discover a spectrometer is required, they must determine how to put a sample in the spectrometer. The samples given include transition metal compounds, organic dyes, and of course porphyrin. Students typically work with water soluble materials and the porphyrin compound given is not water soluble. After the student finds a suitable solvent, acetone, they then place the sample in an acrylic cuvette. The students then discover that the container should not interact with the solvent as the cuvettes become cloudy and eventually soften. Once the students obtain glass cuvettes, they learn about the absorptivities of different samples. An acceptable spectra of a porphyrin requires a very dilute solution that is nearly colorless to the naked eye. This is contrasted with transition metal ions that are highly colored but still yield a good quality spectrum. After several dilutions students learn that highly concentrated porphyrins solutions do not response linearly with the amount of dilution.

SAMPLES



PORPHYRIN UV-VISIBLE SPECTRA



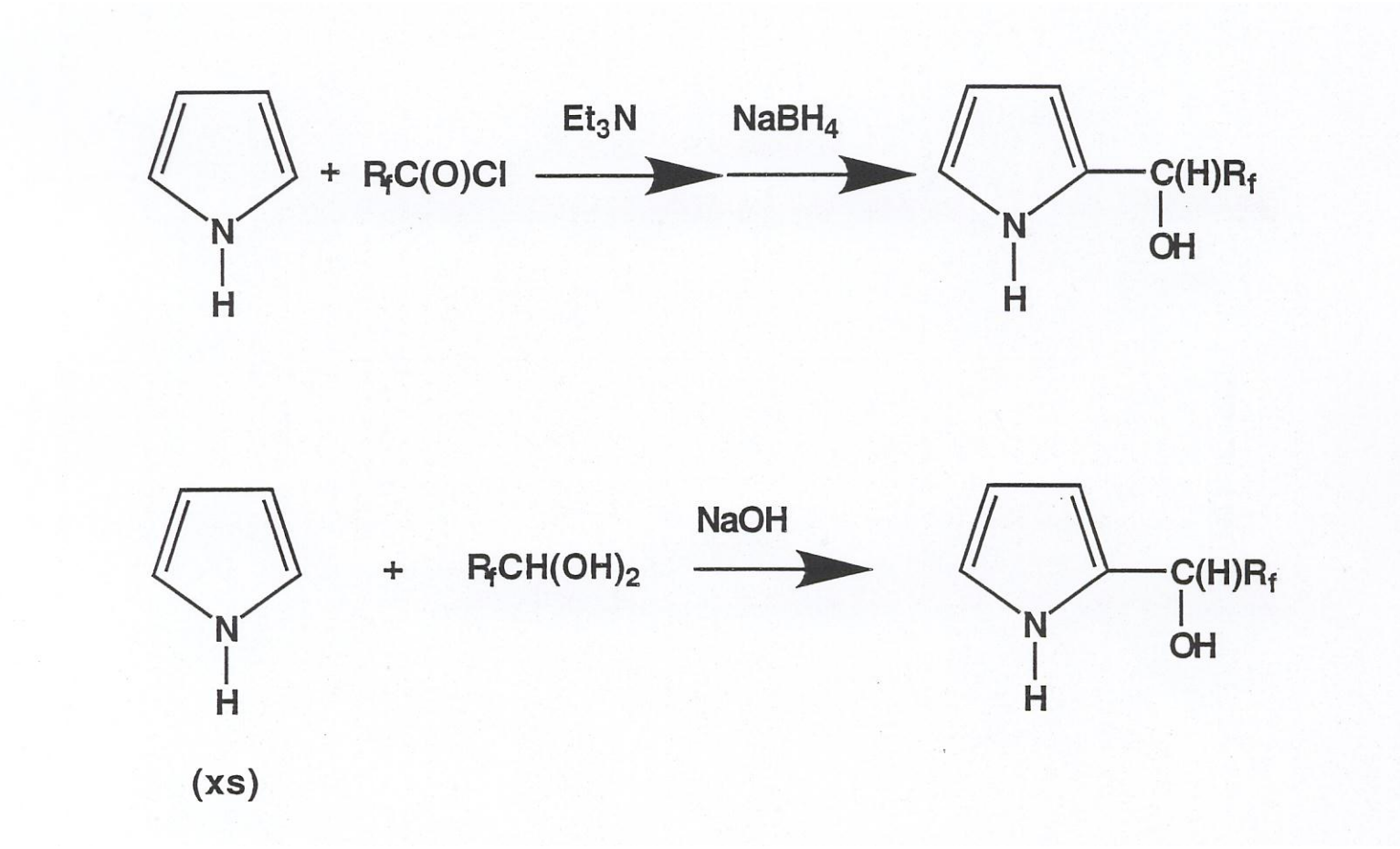
ORGANIC CHEMISTRY

The fabrication of porphyrins involve reactions taught as part of an organic chemistry course. One of the reactions is electrophilic aromatic substitution. This reaction is demonstrated by treating either an aldehyde or acid chloride with the aromatic hetereocycle, pyrrole. Simple aryl porphyrins are synthesized by treating an aryl aldehyde with pyrrole in refluxing proprionic acid commonly called the Alder-Longo method.

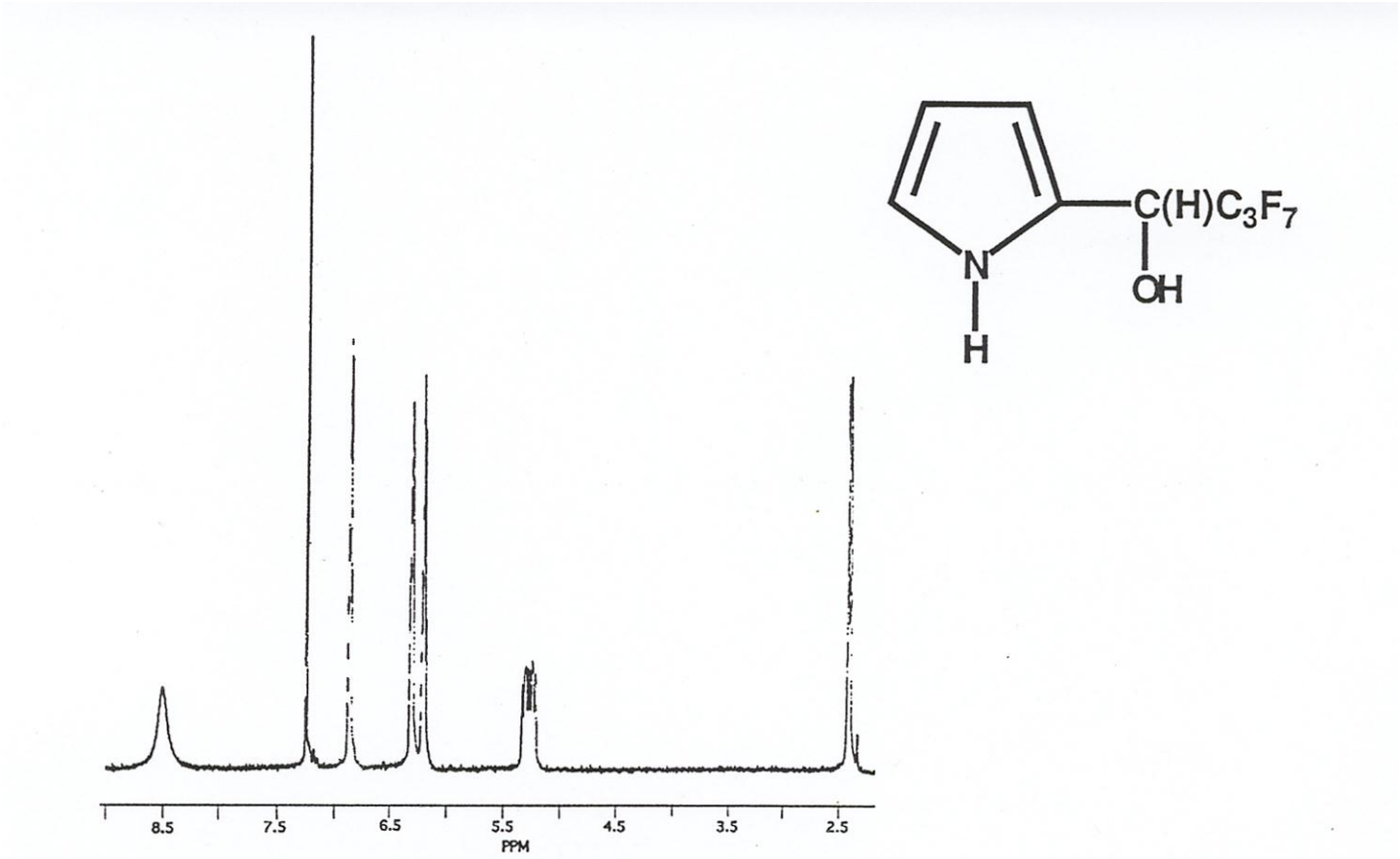
The reaction is also used in the preparation of a porphyrin precursor commonly known as a hydroxymethylpyrrole. This preparation may be done using acid chlorides to yield a ketonic product. The carbonyl may be reduced to an alcohol using sodium borohydride, another common organic reaction.

A porphyrin is an example of an aromatic molecule. The shielding and deshielding properties of the ring current can be observe in ^{1}H Nuclear Magnetic Resonance Spectroscopy (NMR). Hydroxymethylpyrrole provides an example of a compound containing diastereotopic hydrogens. This property can be observed in the ^{1}H NMR spectra. When fluoroalkyl groups are part of the molecule, coupling between fluorine and hydrogen is observed. Using NMR simulation software, the effect of field strength and decoupling can be demonstrated.

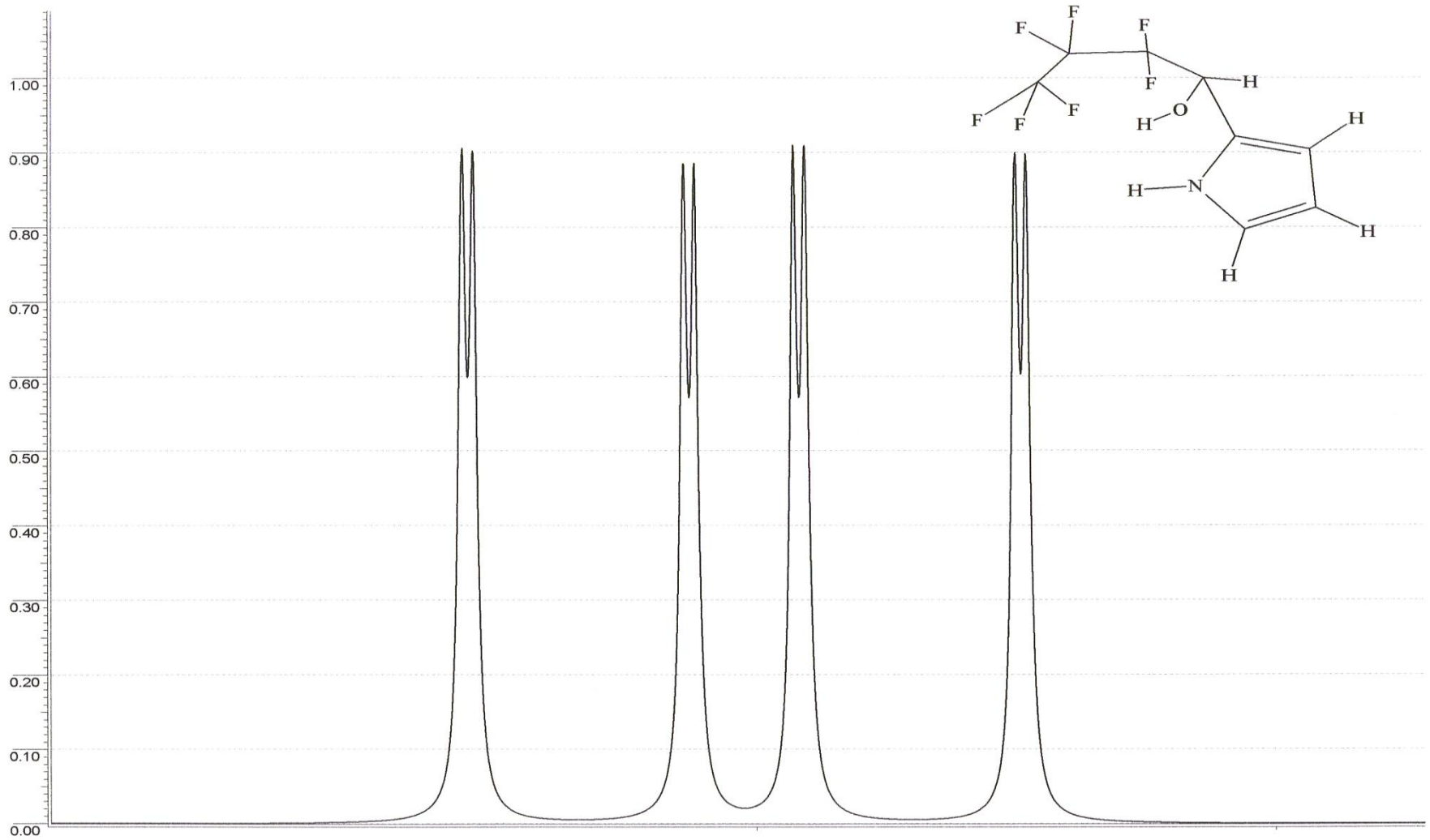
SYNTHESIS OF HYDROXYMETHYLPYRROLE



^{1}H NMR SPECTRA OF A HYDROXYLMETHYLPYRROLE



SIMULATED NMR SPECTRA



INORGANIC CHEMISTRY

Porphyrins are naturally occurring macrocycles found in animal and plant tissue. Several synthetic porphyrins are readily prepared. They are fairly rigid are macrocyclics that are excellent ligands that can coordinate a wide variety of metals and even some nonmetals. Porphyrins are able to complex with metals in a variety of oxidation states. In the laboratory portion of the course, students prepare and characterize manganese porphyrins coordination compounds to multiple oxidation states.

Synthetic porphyrins and metalloporphyrins are highly symmetrical compounds. These provide excellent examples for instruction in the assignment of point groups. Often changes in symmetry upon metallation of a porphyrin will manifest itself in the change in the UV-visible spectra. Porphyrin compounds of iron are commonly known as heme. Heme is ubiquitous in many metalloprotiens and provide an excellent example of the importance of inorganic compounds that are biologically active.

REACTIONS

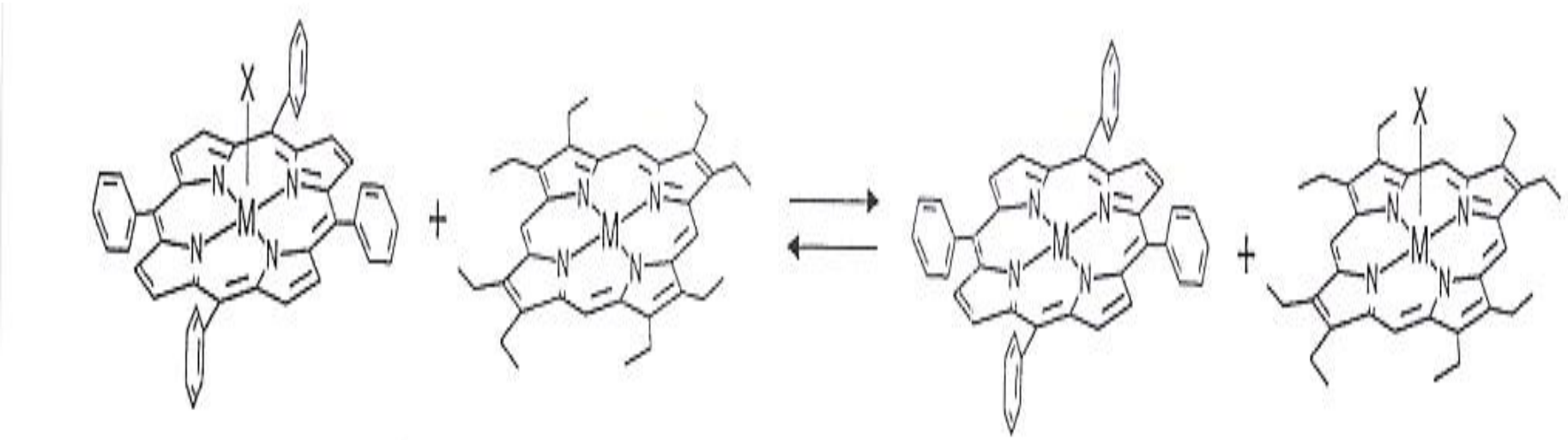
ANALYTICAL CHEMISTRY

The purification of porphyrinatomangansesethiol was developed by analytical chemistry courses. The compound can be separated from any porphyriatomanganese nitride starting material using column chromatography by elution with acetone. The product can be eluted with methanol. Alumina was found to decompose the product but silica gel was found to be useful. Future Analytical classes will work on a band broadening problem. Elemental analysis have been high in sulfur. Sulfur elutes with the product but it may be possible to remove the excess via sublimation. They are also used to discuss fluorescence spectroscopy and electrochemistry.

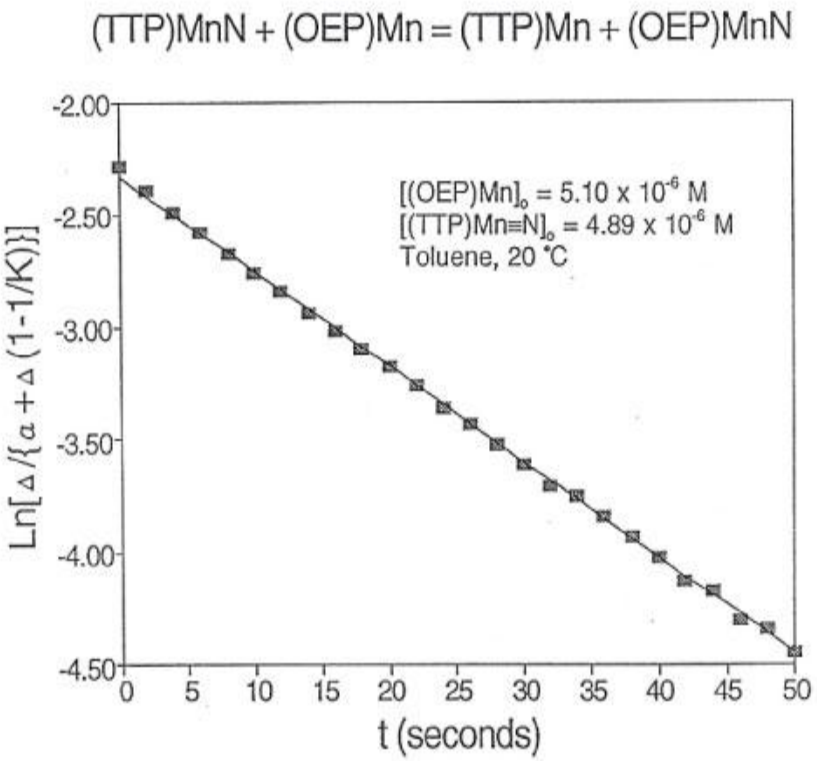
PHYSICAL CHEMISTRY

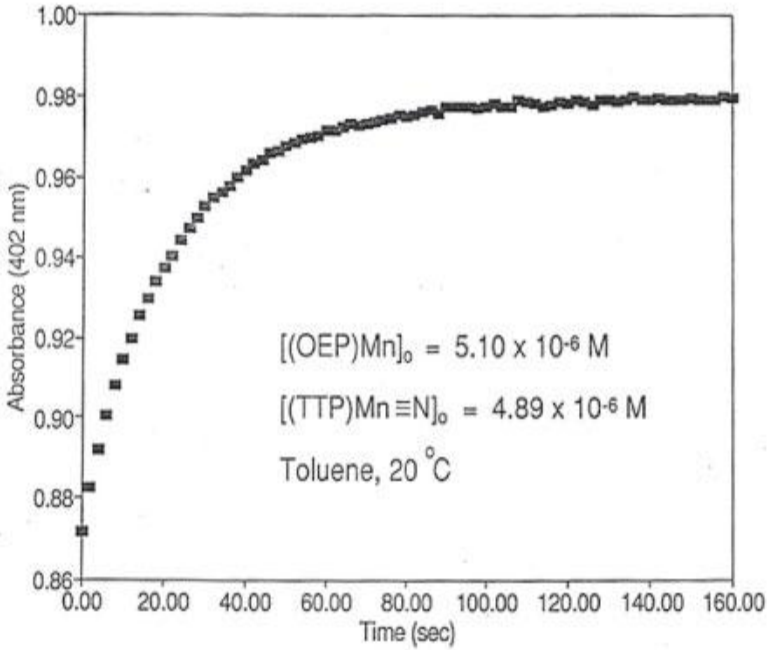
In the physical chemistry course, students determine the equilibrium and rate constants of atom transfer reactions of metalloporphyrins. Temperature studies of the rate and equilibrium constants are used to determine thermodynamic and activation parameters using van't Hoff and Eyring plots respectively.

Edgewood College has an integrated laboratory course in the chemistry curriculum. The preparation of porphyrins, metalloporphyrins, study of reactivities, and determination of thermodynamic and kinetic properties will be the basis of a project for this course.



KINETIC PLOTS





BIOCHEMISTRY

Iron porphyrins commonly known as heme are prosthetic groups for a wide variety of metalloprotiens. These metalloprotiens are used to transport and store oxygen, activate oxygen for use in detoxification and biosynthesis, and participate in electron transport processes. At Edgewood College, the biological importance of heme based metalloprotiens are part of Inorganic Chemistry I, a course that emphasizes bioinorganic chemistry. This course is required of chemistry majors and minors.

The heme containing metalloenzymes, catalase and horseradish peroxidase, are readily available for study. These enzymes are commonly used to explore enzyme kinetics and the effects of condition on activity.