

KINETIC STUDIES OF THE FERROIN COMPLEX (#8.3)

The CCLI Initiative Computers in Chemistry Laboratory Instruction

Learning Objectives

The objectives of this experiment are to ...

- determine the rate of a chemical reaction.
- determine the rate law for a chemical reaction.
- propose a mechanism for the reaction under study.
- determine the activation energy for the reaction.

Background

Chemical kinetics is the study of the rates of chemical reactions and the mechanisms by which they occur. By carefully observing how the concentrations of the reactants and products vary with time, it is possible to determine a rate law for the reaction. This rate law can then be used to either support or disprove a suggested mechanism for the reaction. In this experiment, students will determine the rate and experimental rate laws of several reactions involving the ferriin complex, and then propose a mechanism, i.e., the detailed pathway from reactants to products.

The rate of a chemical reaction is defined as the change in the concentration of a reactant or product per unit time. The first goal of a kinetic study is to determine the effect of reactant concentrations on the reaction rate, and to state this in the form of a **rate law** for the reaction. Rate laws are always experimentally determined. For the hypothetical elementary reaction $A + B \Rightarrow C$, the rate law would have the form:

$$\text{Rate} \Rightarrow \frac{-d[A]}{dt} \Rightarrow k[A]^x[B]^y$$

where $[A]$ and $[B]$ are molar concentrations, and x and y are experimentally determined integers, fractions, or zero (usually 0, 1, or 2). The **order** of the reaction for individual reactants and the **overall order** of the reaction is discussed.

The **rate constant**, k , is a function of temperature for a specific reaction, but it is completely independent of the concentrations of A and B. The rate constant is determined by following the concentration of a species in the reaction with time, and then plotting the appropriate functions of the data to obtain a straight line. Once a rate law has been established, the next step is to propose a mechanism which makes sense from a chemical standpoint, and also predicts the observed rate law.

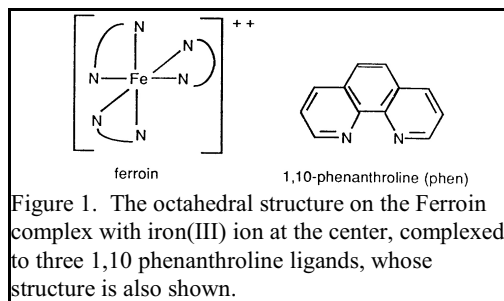


Figure 1. The octahedral structure on the Ferriin complex with iron(III) ion at the center, complexed to three 1,10 phenanthroline ligands, whose structure is also shown.

Since ferriin, like many coordination complexes, is intensely colored (a deep red), the concentration of the complex can be determined spectrophotometrically using green light, at 505 nm on the **MicroLAB Colorimeter**. By following the absorbance vs. time, data can be obtained which can be used to determine rate laws and calculate rate constants. Ferriin absorbs the green light strongly, and the products of the reactions do not absorb the green light at all. The Spectrum Profile for the Ferriin on the **MicroLAB Colorimeter** is shown in the following Figure 2.

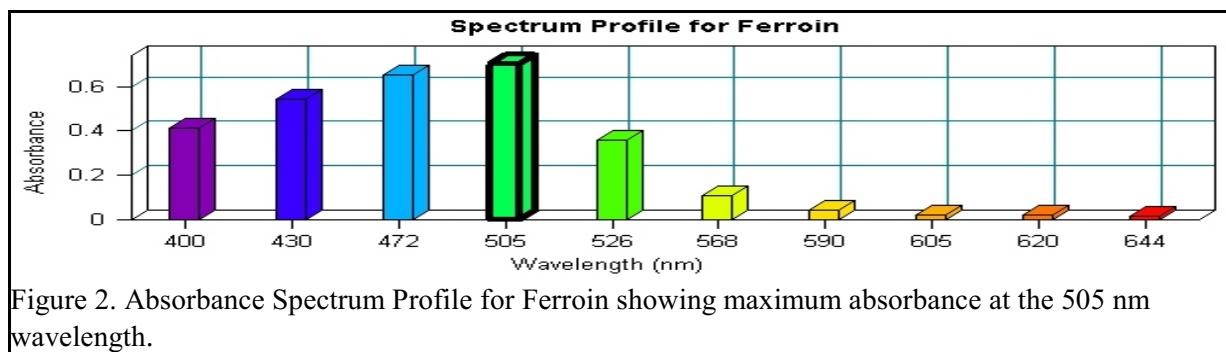


Figure 2. Absorbance Spectrum Profile for Ferriin showing maximum absorbance at the 505 nm wavelength.

The most common types of reactions involving coordination complexes are oxidation-reduction reactions and ligand substitution reactions. The latter reaction type will be studied in this experiment by employing the following reaction systems:



For each reaction system, students will determine the rate law and the rate constant at two temperatures, then attempt to formulate the mechanism for each. By studying each reaction at two temperatures, estimates can be made of the activation energies.

In each reaction, the concentration of ferroin will be much smaller than the concentrations of the other reactants. This has the effect of making the concentration of the non-ferroin reactants essentially constant and the order of reaction for ferroin can then be determined by graphing the appropriate data. You will follow each reaction at two different concentrations of the non-ferroin reactant. This will allow you to determine the order of reaction for the non-ferroin reactant by comparing the rate constant k for the two reactions.

Rate constants can be expressed as a function of temperature in terms of the Arrhenius equation:

$$k = A \exp(E_a / RT)$$

or

$$\ln(k) = (E_a / R)(1/T) + \ln A$$

where A is the pre-exponential factor, E_a is the activation energy, T is the Kelvin temperature, and R is the gas constant. The pre-exponential factor relates the collision or dissociation behavior to the rate, and the activation energy is a measure of the minimum energy required in the rate determining step of the reaction. By graphing $\ln(k)$ vs. $1/T$ for a reaction, it is possible to determine both of these constants: E_a/R equals the slope of the line, and $\ln(A)$ is the y-intercept.

Experimental Procedure

students will work in groups for this experiment, and each group will be assigned one of the three reaction series and will be responsible for obtaining data about the other reaction series from the other groups

Calculations

Students will determine the order of the reaction from their various graphs, and print out the appropriate graphs. The values of ΔH and ΔS are also calculated from the Eyring equation, given in the experiment.

Instructor Resources Provided

- Sample Report Sheets providing the format to organize the data collection with sample data.
- Questions to consider, answer and turn-in with suggested answers.
- Tips and Traps section to assist the instructor with potential problems and solutions.
- Sample *MicroLAB* screen shots and graphs.
- Laboratory preparation per student station.

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