Experiment

KINETIC STUDIES OF THE FERROIN COMPLEX

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, you will determine the rate and experimental rate laws of several reactions involving the ferroin 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. For example, the rate at which dinitrogen pentoxide decomposes can be expressed as the number of moles of N_2O_5 per liter that decompose per second.

$$2\ N_2O_{5(g)} \ ==>\ \ 2\ N_2O_{4(g)} \ +\ O_{2(g)} \qquad (1)$$

This rate could just as easily be defined in terms of the rate of production of dinitrogen tetroxide or molecular oxygen. Using the stoichiometry of the balanced equation, one can relate the rates of change in the following way:

$$\frac{-d[N_2O_5]}{dt} \ ==>\ \frac{d[N_2O_4]}{dt} \ ==>\ \frac{2\ d[O_2]}{dt} \qquad (2)$$

The minus sign indicates the decreasing concentration of N_2O_5 with time, and the positive signs indicate the increasing concentrations of the products. Note that the rate of reaction in terms of N_2O_5 is twice the rate in terms of oxygen. This is expected, because only one mole of oxygen is formed when two moles of N_2O_5 are reacted. It is clear that one must indicate what species is being followed when stating the rate of reaction.

Normally, 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 => C, the rate law would have the form:

$$\text{Rate} \;\Longrightarrow\; \frac{-d[A]}{dt} \;\Longrightarrow\; k[A]^x[B]^y \qquad (3)$$

where [A] and [B] are molar concentrations, and *x* and *y* are experimentally determined integers, fractions, or zero (usually 0, 1, or 2). If doubling the concentration of A doubles the rate, $x = 1$; if the rate increases fourfold, then $x = 2$. If doubling A has no effect on the rate, $x = 0$. The same is true for the concentration behavior of B. The value of *x* is the **order** of the reaction for A, and *y* is the order for B. The sum of x and y is termed the **overall order** of the reaction.

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 value of the rate constant can be 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. The slope of the line is related to the rate constant. Once a rate law has been established, the next step is to propose a mechanism for the reaction that not only makes sense from a chemical standpoint, but also predicts the observed rate law. A mechanism consists of a series of elementary steps and is an informed guess of the individual chemical steps occurring in the course of the reaction. The sum of the elementary steps must give the correct stoichiometry of the reaction. An elementary step is one that involves either a collision between two species (a bimolecular reaction) or the decomposition of a single species (unimolecular). The overall mechanism consists of one or more elementary steps in sequence.

The rate law is closely related to the proposed reaction mechanism. If the mechanism contains several elementary steps, the rate law provides information about those steps up to and including the slowest step. The slowest step is called the **rate determining step**, because the overall reaction cannot be faster than the slowest step.

A reaction system that will serve as an example of some of these ideas is the hydrolysis of tertiary-butyl chloride, $(CH_3)_3$-C-Cl, abbreviated t-BuCl, carried out with isopropyl alcohol (rubbing alcohol) as the solvent. The reaction of t-BuCl with water produces tertiary-butyl alcohol (t-BuOH) and hydrochloric acid (HCl):

$$\text{t-BuCl} + H_2O \quad \text{t-BuOH} + \text{HCl} \qquad (4)$$

The observed rate law for the reaction is first order in t-BuCl:

$$\text{Rate} \;\Longrightarrow\; \frac{-d[\text{t-BuCl}]}{dt} \;\Longrightarrow\; k[\text{t-BuCl}] \qquad (5)$$

Two of the several mechanisms that could be proposed for the reaction are given below. Mechanism I is termed a **dissociative** mechanism, because the rate determining step is the dissociation of the chloride ion from t-BuCl. Mechanism II is **associative**, because the rate determining step is the association of t-BuCl with another species (OH) to produce a complex intermediate:

Mechanism I:

$$\text{t-BuCl} \;\Longrightarrow\; \text{t-Bu}^+ + \text{Cl}^- \text{ (slow) (rate determining)} \qquad (6)$$

$$\text{t-Bu+} + H_2O \;\Longrightarrow\; \text{t-BuOH} + H^+ \text{ (fast)} \qquad (7)$$

Mechanism II:

$$H_2O \;\Longleftrightarrow\; H^+ + OH^- \text{ (fast equilibrium)} \qquad (8)$$

$$\text{t-BuCl} + OH \;\Longrightarrow\; \{\text{ t-Bu(Cl)(OH) }\} \text{ (slow)} \qquad (9)$$

$$\{\text{t-Bu(Cl)(OH) }\} \;\Longrightarrow\; \text{t-BuOH} + Cl \text{ (fast)} \qquad (10)$$

In Mechanism I, because the overall rate of reaction is determined by the rate at which t-BuCl dissociates,

the rate depends directly on the concentration of t-BuCl. This is expected because the number of dissociations per second will be directly proportional to the concentration of t-BuCl. Once formed, the tertiary carbocation, t-Bu$^+$, reacts quickly with water. Because the second step comes after the rate determining step, it does not affect the rate of the reaction, and therefore is not expressed in the rate law. The rate law for Mechanism I would be the same as that observed experimentally.

A rate law derived from Mechanism II would show a concentration dependence on water as well as t-BuCl, because the slow step involves two reactants, one of which is dependent on the water concentration. Obviously, a rate law derived from this mechanism would not agree with the one observed experimentally.

An organic chemist would predict the first mechanism by inspection of the species involved and their chemical reactivities. Tertiary carbocations like t-Bu$^+$ are relatively stable and could easily exist as an intermediate in a reaction. Species like {t-Bu(Cl)(OH)}, in the second mechanism, would be unlikely because of the steric hindrance involved in attaching five groups to the central carbon (there is simply not enough space). You are not expected to be able to draw these types of reactivity conclusions now, but this is an example of the types of evidence that a chemist would use to corroborate a proposed mechanism.

All of this information does not mean that Mechanism I is absolutely correct, because it can only be a proposed mechanism. There is no way to prove a mechanism absolutely, short of watching the individual molecules as they react, which is obviously impossible. Further study, however, could be used to develop confidence in the mechanism, and many mechanisms are widely believed to be correct, even though they cannot be proven.

SAFETY PRECAUTIONS

Safety goggles must be worn in the lab at all times. Any skin contacted with chemicals should be washed immediately.

BEFORE PERFORMING THIS EXPERIMENT . . .

Discussion of the experiment

In this experiment, the kinetics of a series of reactions involving the tris-(1,10-phenanthroline) iron(II) ion, commonly called **ferroin**, will be studied. This iron(II) complex ion is composed of three 1,10-phenanthroline molecules that are arranged around the Fe^{2+} such that the six nitrogen donor atoms are located at the corners of an octahedron. In the schematic structure below, Figure 1, each N----N represents one ligand molecule:

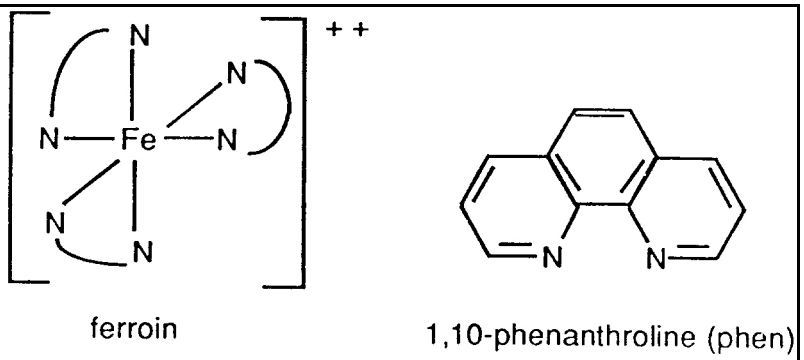

Figure 1. The octahedral structure on the Ferroin complex with iron(III) ion at the center, complexed to three 1,10 phenanthroline ligands, whose structure is also shown.

Since ferroin, 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. Ferroin absorbs the green light strongly, and the products of the reactions absorb very little of the green light. The Spectrum Profile for the Ferroin on the ***MicroLAB* Colorimeter** is shown in the following Figure 2.

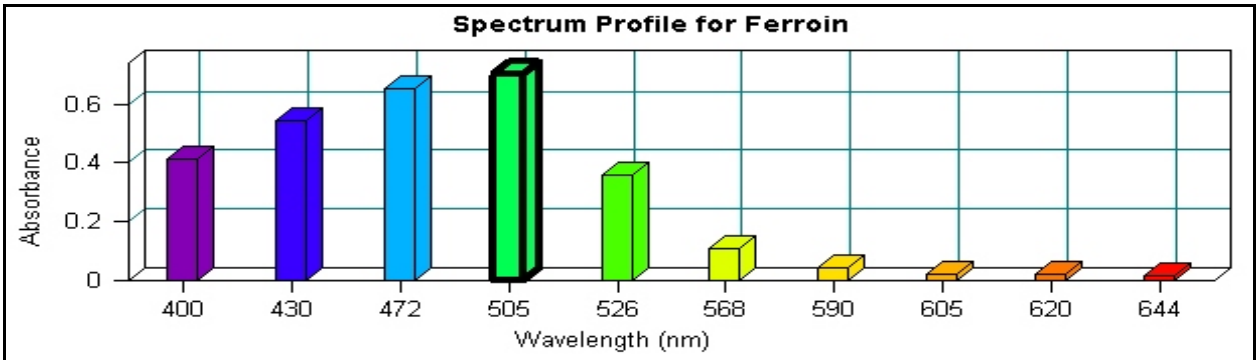

Figure 2. Absorbance Spectrum Profile for Ferroin showing maximum absorbance at the 505 nm wavelength.

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:

A. $Fe(phen)_3^{2+} + 3\ Cu^{2+} \Longrightarrow Fe^{2+} + 3\ Cu(phen)^{2+}$ (11)

B. $Fe(phen)_3^{2+} + P_2O_7^{4-} \Longrightarrow [Fe(phen)_2P_2O_7]^{2-} +$ phen (12)

C. $Fe(phen)_3^{2+} + 6\ H_2O + 3H^+ \Longrightarrow Fe(H_2O)_6^{2+} + 3$ H-phen$^+$ (13)

For each reaction system, you 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. The order of reaction for ferroin can then be determined by graphing the appropriate data. If [ferroin] vs. time is a horizontal straight line, the reaction is zero order for ferroin. If a plot of ln[ferroin] vs. time is straight, the reaction is first order, and if 1/[ferroin] vs. time gives a straight line, the reaction is second order. (See your textbook for more details.) The rate constant can also be determined from these plots. For zero and first order plots, k equals the negative of the slope. For second order plots, k equals the slope.

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. When you double the concentration of the non-ferroin reaction, if the rate constant does not change, the reaction is zero order in that reactant. If the rate constant doubles, the reaction is first order, and if the rate constant increases fourfold, the reaction is second order in that reactant. This procedure is called a pseudo-order process, and is discussed more fully in your text.

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

$$k = A\, e^{(-Ea / RT)} \qquad (14)$$

or

$$\ln (k) = (E_a / RT) + \ln A \qquad (15)$$

where A is the pre-exponential factor, E_a is the activation energy, T is the Kelvin temperature, and R is the gas constant, 8.314 J/K mol. 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

You will work in groups for this experiment, and each group will be assigned one of the three reaction series. You will then be responsible for obtaining data about the other reaction series from the other groups. See your instructor for group and series assignments.

The experiment will be done using the ***MicroLAB*** colorimeter and software program.

You will complete the experiment at two Temperatures, 40 °C and 50 °C. Comparing the rates at the two temperatures will allow you to estimate the activation energy for the reaction. Following are the concentrations that you should use:

Series	***Experiment***	***Makeup of the reaction solutions before the addition of ferroin***
A	1	2.0 ml of 0.02 *M* $Cu(NO_3)_2$ + 7.0 ml H_2O
	2	4.0 ml of 0.02 *M* $Cu(NO_3)_2$ + 5.0 ml H_2O
B	1	2.0 ml of 0.10 *M* Na_4P_2O7 + 7.0 ml H_2O
	2	4.0 ml of 0.10 *M* Na_4P_2O7 + 5.0 ml H_2O
C	1	2.0 ml of 1.0 *M* HNO_3 + 7.0 ml H_2O
	2	4.0 ml of 1.0 *M* HNO_3 + 5.0 ml H_2O

Note that experiment 2 of each series contains twice the concentration of the non-ferroin reactant as experiment 1.

An additional study will be carried out to determine if the solvent (water) reacts directly with ferroin, an effect which would complicate the kinetic studies. For this experiment, 9.0 ml of water will be used.

For each reaction series which you study, you will need to complete 4 determinations:

Experiment 1 at 40 °C
Experiment 2 at 40 °C
Experiment 1 at 50 °C
Experiment 2 at 50 °C

You will also complete the water blank at both temperatures, for a total of six runs.

The colorimeter works by reading the current of a photomultiplier on the opposite side of the sample from the light source. This current is directly proportional to the light transmitted by the sample. To convert from this current to the absorbance of the solution, the following equation is used:

$$A = \log (I_0/I_t)$$

where I_0 is the current of the blank solutions (before ferroin has been added), and I_t is the current at a specific time later. The absorbance can then be converted to ferroin concentration using Beer's Law, $A = \epsilon bc$. The pathlength, b, for this colorimeter is 2.54 cm, and the molar absorbtivity constant, ϵ, for ferroin is 11,000 cm^{-1}.

Detailed procedure

1. It is suggested that you complete one series at 40 °C (both concentrations) first, then the other series at 50 °C. Finally, you will run the water blanks. Make sure to record the exact temperature of the water baths in your lab notebook.

2. Turn on the computer and open the ***MicroLAB*** **Kinetics Experiment** program. Make sure the ***MicroLAB*** interface is connected properly to the computer.

3. Add 10 ml of distilled water to the colorimeter vial, place a vertical line near the top with a marker pen, wipe the outside of the vial to remove any drops of water or fingerprints, and insert the vial into the colorimeter chamber with the mark directly forward.

4. Make the title of the data file in the following format: group number, series, temperature, concentration. For example, group 2 completing series B at 40 °C , concentrations 1, should use the file name: *g2B40c1.dat*. This title is rather cryptic, but it is necessary to make sure that all of the data can be located for analysis.

5. Place three large test tubes in a 400 ml beaker. Fill one test tube with deionized water, one with the reactant, and one about half full with ferroin. Fill the beaker with water from the water bath to above the level of the liquids in the test tubes, then place the beaker back into the water bath to equilibrate. Allow the temperature to equilibrate by leaving the solutions in the water bath for about ten minutes. Because the rate constant is dependent on the temperature of the reaction, maintaining a constant temperature is vital, so the solutions must be at the reaction temperature before the ferroin is added.

6. After the reactants have equilibrated, remove the beaker from the bath and take it to your workstation. The heat capacity of the water in the beaker acts as a "mini-water bath," greatly slowing the cooling of the solutions in the test tubes to room temperature, so do not remove the test-tubes from the beaker. Mix the solutions to the point of adding the ferroin. **Do not add the ferroin until the solutions are completely mixed and re-equilibrated thermally.** To mix the solutions, use a 10.0 ml Mohr pipet to deliver the exact amounts directly to the colorimeter vials. Return the test tubes and beaker to the water bath.

7. Add about 20 ml of water from the water bath to labeled 50 ml beakers and place the colorimeter vials in the beakers. Make sure that the water level in the 50 ml beaker is essentially at the same level as the solution in the vial. Place the beaker back into the water bath for a couple of minutes to re-equilibrate.

8. When the vial is thermally re-equilibrated, the next few steps should be done as quickly as possible to minimize the uncertainty in the temperatures of the solutions. Have one person in the group add exactly 1.0 ml of ferroin to the vial using a 1.0 ml Mohr pipet.

9. Cap the vial, invert twice to mix fully, quickly wipe of the outside, place the vial in the colorimeter, place the colorimeter cap and click on the **Collect Data** button to make the first reading. This should all be accomplished as quickly as possible in order to catch the reaction at its earliest stage.

10. The samples will be taken every 100 seconds. Since the ***MicroLAB*** **Kinetics** program currently does not keep track of time between samplings, you will need to time this yourself. Watch it carefully, so you can get your sample from the water bath, dry it off, and place it back in the colorimeter before it reaches 100 seconds. This process should take less than 20 seconds, so start it at about 75 seconds to be sure your sample is in the colorimeter and capped before the 100 seconds. It is important to keep the samples in the water bath when they are not being measured, to make sure that the temperatures remain constant. To do this, make sure that you do not get your samples from the water bath too soon, or you risk cooling.
11. Replace the vial in the proper beaker in the water bath as soon as the sample has been read by the kinetics program.
12. Let the reaction run for approximately 60 minutes for a 40 °C run, and 30 minutes for a 50 °C run. The water blanks need only be run long enough to determine if the concentration of ferroin is changing (about 10-15 minutes). You can stop the program by clicking on the **Stop** button.

Calculations

1. You should **Print** the spreadsheet once for each sample.

2. You can then use the tabs at the bottom of the **Graph** to determine the order in ferroin for the reaction. Use the **Linear regression** equation to determine the value of the rate constant. Note that the first one or two data points may be out of line. Despite your valiant efforts to keep the temperature constant while mixing solutions, it is likely that the solutions will cool slightly, so the first few readings are effectively taken at a lower temperature. If this is the case, throw out the first few points, and note it in your lab report.

The report

For each of the reaction series A, B and C at the two temperatures, you should determine and report the following:

1. the experimental rate law
2. the value of the rate constant, k
3. the initial rate of reaction
4. the activation energy, E_a
5. the value of the pre-exponential factor, A
6. a proposed mechanism for the reaction

You should also include the appropriate printouts of data tables and graphs to support your answers. Further considerations/questions:

1. Compare your results for all three reactions. Describe your findings and the conclusions to which they lead you about the mechanisms for the three reactions which you have studied.

2. According to the absolute rate theory, the rate constant can be represented by the following expression, commonly called the **Eyring equation**:

$$k \quad ==> \quad \frac{k_B T}{h} \exp(-\Delta H^*/RT)\exp(\Delta S^*/R)$$

where k_B is the Boltzmann constant, h is Planck's constant, and H^* and S^* are the enthalpy and entropy of activation for the process. Calculate the values of H^* and S^* for the $P_2O_7^{4-}$ reaction. Do these values support the mechanism that you have postulated? **Hint:** a plot of ln (k/T) vs. 1/T is needed.