Experiment 13C

THE KINETICS OF A NITROFERROIN REACTION[1]

MATERIALS:

B & L Spectronic 20, three cuvettes, 1.5×10^{-4} M nitro-ferroin solution, 0.010 M, 0.020 M, and 0.0050 M $CuSO_4$ solutions, three 50 mL Erlenmeyer flasks, four 50 mL beakers, two 10 mL volumetric pipets.

DISCUSSION:

In this experiment, you will investigate the kinetics of the following reaction involving nitroferroin, $Fe(phen)_3^{2+}$. Nitroferroin is a complex ion in which three molecules (called ligands) of 5-nitro-1,10-phenanthroline, (abbreviated "phen") are bonded to the iron(II) ion.[1]

$$3\ Cu^{2+}_{(aq)} + 2\ Fe(phen)_3^{2+}{}_{(aq)} \rightarrow 3\ Cu(phen)_2^{2+}{}_{(aq)} + 2\ Fe^{2+}_{(aq)}$$

This reaction will be followed spectrophotometrically. *Review Appendix I for a discussion of spectrophotometry before proceeding*. We will take advantage of the fact that nitroferroin is the only species present which absorbs green light at 510 nm (hence, nitroferroin appears red in color). As the nitroferroin complex reacts, the color disappears and absorbance decreases. Thus we can follow the course of the reaction by observing the decrease in absorbance. This will provide sufficient information to determine the rate law for the reaction and to make some deductions about a possible reaction mechanism.

"Pseudo-order" Conditions

The rate law for the nitro-ferroin reaction may be expressed as:

(1) $$\text{rate} = k\left[Cu^{2+}\right]^a\left[Fe(phen)_3^{2+}\right]^b$$

We will perform this reaction in the presence of a large excess of copper(II) ions. A negligible amount of the copper(II) will actually be consumed in the reaction so the $[Cu^{2+}]$ can be assumed to remain virtually constant throughout the reaction. Therefore, the copper(II) ion concentration term can be combined with the rate constant k to give a so-called "pseudo" rate constant, k_{obs}, for that particular $[Cu^{2+}]$:

(2) $$k_{obs} = k\left[Cu^{2+}\right]^a$$

Substituting into equation (1), we get:

(3) $$\text{rate} = k_{obs}\left[Fe(phen)_3^{2+}\right]^b$$

where b is the reaction order for the experimental condition of a large excess of copper(II) ions, the "pseudo-order".

Part A: Determining the order in nitroferroin

The rate expression for nitroferroin is:

(4) $$\text{rate} = -\frac{d\left[Fe(phen)_3^{2+}\right]}{dt}$$

The order of the reaction determines whether $[Fe(phen)_3^{2+}]$ decreases linearly, exponentially, or inversely with time. From Beer's Law: Absorbance α $[Fe(phen)_3^{2+}]$. Therefore, absorbance will decrease in the same manner as the $[Fe(phen)_3^{2+}]$. Plots of Abs vs. time, ln(Abs) vs. time, and 1/Abs vs. time will be used to graphically determine "b", the order in nitro-ferroin.

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[1] Adapted from the original work of A. A. Green, J. O. Edwards and P. Jones, **Inorganic Chemistry**, **1966,** *5*,1858.

Part B: Determining the order in Cu^{2+}

The order in copper(II) ions, "a", will be obtained by determining k_{obs} for different concentrations of copper(II) ions. By doubling the $[Cu^{2+}]$ and observing the effect on k_{obs}, the order "a", which is the exponent in equation (2), can be obtained by inspection.

PROCEDURE: (work in pairs)
READ THROUGH THIS ENTIRE PROCEDURE BEFORE YOU BEGIN.

1. Set the Spectronic 20 is to 510 nm and adjust the zero and 100 percent transmittance (%T) properly. Use distilled water as a blank.

2. Clean and rinse a 10 mL pipet with 0.010 M copper(II) sulfate solution and then pipet 10 mL of this solution into a clean, clearly labeled 50 mL Erlenmeyer flask. Similarly, pipet 10 mL of 0.020 M copper(II) sulfate solution into a second Erlenmeyer flask. Pipet 10 mL of 0.0050 M copper(II) sulfate solution into the third Erlenmeyer flask.

3. Place approximately 40 mL of nitroferroin solution in a clean 50 mL beaker. Clean and rinse a pipet with the nitroferroin solution

The next steps will be performed so that 3 reactions are started at staggered times and run simultaneously. The %T of each solution is recorded periodically, on a rotating basis. DO NOT worry about taking every measurement at an even interval; just record accurately the time at which each measurement is taken.

Part A: The Order in $Fe(phen)_3^{2+}$

4. Pipet 10 mL of the nitroferroin solution into the Erlenmeyer flask containing the 0.010 M copper(II) sulfate solution, <u>record the clock time to the nearest 0.1 minute</u>, and swirl to mix.

5. Quickly rinse and fill a cuvette with this solution and then measure its percent transmittance at 510 nm. <u>Record the clock time</u> of the measurement to the <u>nearest 0.1 minute</u>. Record your data in the table in the Data Section. Place the cuvette in a labeled position in the test tube rack immediately after obtaining the transmittance measurement.

Part B: The Order in Cu^{2+}

6. Pipet 10 mL of the nitroferroin solution into the Erlenmeyer flask containing the 0.020 M copper(II) sulfate solution, <u>record the clock time</u>, and swirl to mix.

7. Quickly rinse and fill a cuvette with this solution and then measure its percent transmittance at 510 nm. <u>Record the clock time</u> of the measurement. Record your data in the table below. Place the cuvette in a labeled position in the test tube rack immediately after obtaining the transmittance measurement.

8. Pipet 10 mL of the nitroferroin solution into the Erlenmeyer flask containing the 0.0050 M copper(II) sulfate solution, <u>record the clock time</u>, and swirl to mix.

9. Quickly rinse and fill a cuvette with this solution and then measure its percent transmittance at 510 nm. <u>Record the clock time</u> of the measurement. Record your data in the table below. Place the cuvette in a labeled position in the test tube rack immediately after obtaining the transmittance measurement.

10. Repeat the measurement of %T for each solution, alternating among all three, at 6-8 minute intervals until the percent transmittance of ALL solutions increases to approximately 70%. This should take 45-60 minutes. A minimum of 8 data points for each solution is required. Record your data in the appropriate table in the Data Section.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 13C

Part A 0.010 M $CuSO_4$

Clock time	Elapsed time	% Transmittance
	0.0 min	(initial mixing)

Part B: The Order in Cu^{2+}

0.020 M $CuSO_4$			**0.0050 M $CuSO_4$**		
Clock time	Elapsed time	% Transmittance	Clock time	Elapsed time	% Transmittance
	0.0 min	(initial mixing)		0.0 min	(initial mixing)

DATA TREATMENT
Experiment 13C

Part A: The Order in $[Fe(phen)_3^{2+}]$

1. Calculate the "elapsed time" for each %T measurement. This is the total time (to the nearest 0.1 min) since the mixing of a particular solution.

2. Use Quattro Pro to set up a spreadsheet for this experiment. For Part A, this spreadsheet should include columns for: elapsed time; % transmittance; Absorbance; ln(Abs); 1/Abs; and Linear Regression (for the appropriate function of Abs). Perform a linear regression analysis for Abs. vs. time, ln(Abs) vs. time and 1/Abs vs. time. The value of R squared closest to 1.0 indicates the linear regression of the data which best approximates a straight line.

3. Plot graphs of Abs vs. time, ln(Abs) vs. time and 1/Abs vs. time. Determine "b", the reaction order in nitro-ferroin. (Hint: the plot that is most linear indicates what the reaction order is.) Use the markers and lines option to eliminate lines between raw data points. Show a regression straight line on the linear plot <u>only</u>.

The reaction is _____ order in nitro-ferroin.

Part B: The Order in Cu^{2+}

1. Set up a spreadsheet for Parts B of this experiment. For each concentration of $CuSO_4$, this spreadsheet should include columns for: elapsed time; % transmittance; Absorbance; and Linear Regression value of the function (1/Abs or ln(Abs) determined to be linear in Part A. Perform the appropriate linear regressions for the two runs of Part B.

2. Determine k_{obs} from the slope of the <u>linear</u> graph in Part A. Similarly, determine k_{obs} from the regression data for the two runs of Part B and complete the following table:

$[Cu^{2+}]$	k_{obs}

From the data in the above table, determine "a", the order in copper(II) ions by inspection. See equation (2) on page E13C-1.

The reaction is _____ order in copper(II) ions.

3. Write the rate law for the nitroferroin reaction:

rate = k _____

4. Determine k for each run from k_{obs}. (See equation (2) above.) Calculate the average value of k.

k = _____ (units?)

Conclusions:

From the rate law obtained, what conclusions can you draw about the rate determining step in this reaction?

Problems:

1. When the following nitroferroin reactions are investigated spectrophotometrically, the rate law is found to be first order in nitroferroin and zero order in the other reactant. The rate constants, k, for these reactions, determined at room temperature, are nearly identical to the measured rate constant for the reaction studied in this experiment (i.e., 2 $Fe(phen)_3^{2+}(aq) + 3Cu^{2+}(aq)$). What conclusions can be drawn from this information?

$$Fe(phen)_3^{2+}{}_{(aq)} + 3H^+{}_{(aq)} \rightarrow Fe^{2+}{}_{(aq)} + 3H(phen)^+{}_{(aq)}$$

$$Fe(phen)_3^{2+}(aq) + EDTA(aq) \rightarrow Fe(EDTA)^{2+}(aq) + 3phen(aq)$$

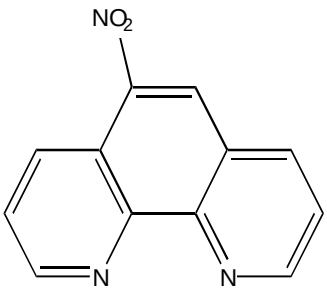
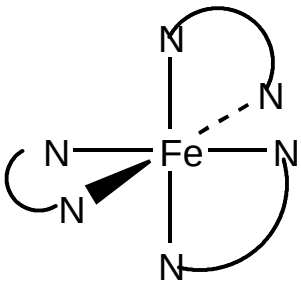
2. The first-order rate constant (k) for the reaction between nitroferroin and EDTA (shown below) has been measured at two temperatures. At 22.0°C, k was 0.0286 min^{-1} and at 31.5°C, it was 0.148 min^{-1}. Calculate the activation energy (E_a) for this reaction.

$$Fe(phen)_3^{2+}{}_{(aq)} + EDTA^{4-}{}_{(aq)} \rightarrow FeEDTA^{2-}{}_{(aq)} + phen_{(aq)}$$

$EDTA^{4-}$, a strong complexing agent, is the conjugate anion of ethylenediaminetetraacetic acid.

1. Another name for nitroferroin is tris-(5-nitro-1,10-phenanthroline)-iron(II). 5-nitrophenanthroline is particularly well suited for complex ion formation since the nitrogen lone electron pairs are directed so that both nitrogen atoms can participate in bonding to a metal ion such as iron. The Fe^{2+}, binds to three molecules of 5-nitrophenanthroline to form a distorted octahedral complex (the arcs ending in N's represent the 5-nitrophenanthroline molecules).

Nitro-phenanthroline



Nitroferroin