Experiment 13D

FV-1/7/01

THE KINETICS OF A NITROFERROIN REACTION[1]

MATERIALS: Spectronic 20, three cuvettes, 1.5 x 10^{-4} M nitroferroin solution, 0.50 M HCl, 1.0 M HCl, 0.010 M $CuSO_4$, 0.020 M $CuSO_4$, two 50 mL Erlenmeyer flasks, two 50 mL beakers, 10 mL volumetric pipet, pipet bulb, 10 mL graduated cylinder.

PURPOSE: The purpose of this experiment is to determine the rate law for a chemical reaction and to use this information to decide which of two mechanisms is more likely to be correct.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Convert between units of percent transmittance and absorbance.
2. Perform a graphical determination of a reaction order and rate constant.
3. Determine the order of a reaction in a specific reactant by varying the initial concentration of that reactant.
4. Determine which of several mechanisms is supported by the experimental rate law.

DISCUSSION:

Review Appendix I before proceeding with the experiment.

In this experiment, the kinetics of nitroferroin reactions (1) and (2) will be investigated. Nitroferroin, $Fe(phen)_3^{2+}$, is the iron(II) ion complex of 5-nitro-1,10-phenanthroline, abbreviated as "phen." The stoichiometries of these two reactions are shown below.

$$Fe(phen)_3^{2+}\ (aq) + 3\ H^+\ (aq) \rightarrow Fe^{2+}\ (aq) + 3\ Hphen^+\ (aq) \qquad (1)$$

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

The reactions can be followed spectrophotometrically since nitroferroin is the only species present that absorbs light at 510 nm. Thus, the course of the reaction can be followed by observing the rate at which the color of the nitroferroin complex disappears. Such an experiment will provide the information needed to determine the order of the reaction in nitroferroin. The order of the reaction in the second reactant, H^+ (aq) or Cu^{2+} (aq), can be deduced by running the reaction at different initial concentrations of those reactants and observing the effect of the concentration changes on the rate of reaction.

The general rate law for reaction (1) is

$$\text{rate} = \frac{-d[Fe(phen)_3^{2+}]}{dt} = k_1[Fe(phen)_3^{2+}]^a[H^+]^b$$

where *a* and *b* are the orders of the reaction to be determined in this experiment. In order to simplify the analysis, the reaction will be run in the presence of a large excess of hydrogen ion. Under these conditions, only a negligible amount of the hydrogen ion initially present will be consumed by the reaction, so the hydrogen ion concentration can be considered to remain constant. Therefore the hydrogen ion

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

concentration can be combined with k, the rate constant, to give a so-called "pseudo order" rate constant, $k_{1,obs}$, for the reaction:

$$k_{1,obs} = k_1 [H^+]^b$$

Substituting this expression into the rate law, the rate law then simplifies to:

$$\text{rate} = k_{1,obs} [Fe(phen)_3^{2+}]^a$$

Reaction (2) will be studied in a similar manner. The general rate law for reaction (2) is

$$\text{rate} = \frac{-d[Fe(phen)_3^{2+}]}{dt} = k_2[Fe(phen)_3^{2+}]^c[Cu^{2+}]^d$$

Again carrying out the reaction in the presence of a large excess of copper(II) ions, similar algebraic manipulations will lead to:

$$\text{rate} = k_{2,obs} [Fe(phen)_3^{2+}]^c$$

In this case, $k_{2,obs} = k_2 [Cu^{2+}]^d$.

Part A. Determining the Order in Nitroferroin[2]

The order of each reaction with respect to nitroferroin concentration, a and c, will be determined graphically. Since the absorbance of nitroferroin is directly proportional to its concentration, according to Beer's Law, absorbances can be used instead of concentrations in the plots. Plots of absorbance versus time, ln(absorbance) versus time, and 1/(absorbance) versus time will be made to determine if the reaction is zero, first, or second order, respectively, in nitroferroin.

Part B. Determining the Order in Hydrogen Ions and Copper(II) Ions

The order of the reaction, b or d, for the second reactant, (H^+ or Cu^{2+} respectively) will be determined by inspection. The procedure from Part A will be repeated with the exception that the concentration of the second reactant will be doubled. Under the pseudo order conditions of the experiment, the rate constants, k_{obs}, are dependent on $[H^+]^b$ or $[Cu^{2+}]^d$, and the order of the reaction in each reagent can be determined by comparison of the k_{obs} values at different H^+ and Cu^{2+} concentrations.

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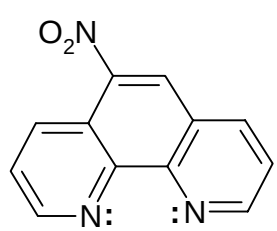
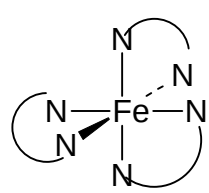
[2]Another name for nitroferroin is Tris-(5-nitro-1,10-phenanthroline)-iron(II). 5-nitro-1,10-phenanthroline is particularly well suited for complex formation since the unshared electron pairs on the nitrogen atom are directed so that both nitrogen atoms can participate in bonding to a metal ion such as iron. The iron(II) ion, Fe^{2+}, binds three molecules of 5-nitro-1,10-phenanthroline to form a distorted octahedral complex, shown schematically below (the arcs ending in N's are a shorthand way of representing the nitro-phenanthroline molecule).



1,10 phenanthroline



ferroin

PROCEDURE:

Part A. Determining the Order in Nitroferroin

READ THROUGH THIS ENTIRE PROCEDURE BEFORE YOU BEGIN.

1. Make sure all of your glassware is clean. Contaminants can affect your results.

2. Insure that the Spectronic 20 wavelength is set to 510 nm and that the zero and 100% Transmittance have been adjusted properly. Use distilled water as a blank.

3. Pipet 10 mL of the nitroferroin solution into each of the two Erlenmeyer flasks. To one flask, add 10 mL of 0.50 M hydrochloric acid, record the initial time, and swirl to mix. Rinse and fill a cuvette (to ¾ full) with this solution and then measure its percent transmittance, %T, at 510 nm. Record the time of this measurement in the Data Section, and continue to record the time and %T every 5 minutes.

4. Follow the same procedure with a second flask, but substitute 10 mL of the 0.010 M copper(II) sulfate for the hydrochloric acid.

5. Measure the percent transmittance for each solution at 5 minute intervals until the measured transmittance of each solution rises to approximately 75 %T.

✍ Answer In-Lab Questions #1-4 on page E13D-9 in the time between measurements.

Part B. Determining the Order in Hydrogen Ions and Copper(II) Ions

1. Repeat the above procedure using 10 mL of the more concentrated form of the same solutions (i.e., 1.0 M HCl and 0.020 M $CuSO_4$). Record this data in the appropriate table in the Data Section.

Clean Up:

1. All solutions are dilute and may be disposed of in the sink.

2. Return all equipment to their proper locations.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 13D

Part A. Determining the Order in Nitroferroin

Flask 1 **0.50 M HCl**	
Initial Time of mixing _____	
Time	%T

Flask 2 **0.010 M $CuSO_4$**	
Initial Time of mixing _____	
Time	%T

Part B. Determining the Order in Hydrogen Ions and Copper(II) Ions

Flask 3 **1.0 M HCl**	
Initial Time of mixing _____	
Time	%T

Flask 4 **0.020 M $CuSO_4$**	
Initial Time of mixing _____	
Time	%T

DATA TREATMENT
Experiment 13D

Part A. Order in Nitroferroin

Set up a spreadsheet to show the results of the following calculations and the linear regression of each plot. The spreadsheet should contain columns for elapsed time (in minutes), %T, Abs, ln (Abs), and 1/Abs. Submit all spreadsheets and graphs with your lab report.

(A.1) Calculate the absorbance (Abs) of each solution from the %T values.

(A.2) For each solution, calculate ln (Abs) and 1/Abs.

(A.3) Construct graphs of Abs vs. time, ln (Abs) vs. time, and 1/Abs vs. time for each reagent (H^+ and Cu^{2+}).

(A.4) Perform a linear regression analysis for each plot. Record the R^2 (correlation) values below:

	R^2 value for H^+ reagent	R^2 value for Cu^{2+} reagent
Abs vs. time		
ln (Abs) vs. time		
1/Abs vs. time		
Which plot was the most linear?		

Show the regression line only on the *most linear* plot for each reagent. Include the equation of the line and the R^2 value on the plot.

(A.5) From these plots, determine the order of each reaction with respect to nitroferroin.

The reaction with H^+ is _____ order with respect to nitroferroin.

The reaction with Cu^{2+} is _____ order with respect to nitroferroin.

Part B. Determining the Order in Hydrogen Ions and Copper(II) Ions

Order in [H^+]

(B.1) Set up a spreadsheet for the 1.0 M hydrogen ion data collected in Part B of this experiment. The spreadsheet should include columns for elapsed time (in minutes), %T, Abs, and the function, (Abs, ln (Abs) or 1/Abs), *that was determined to be linear in Part A.* Construct a graph and perform a linear regression for *that function* vs. time.

(B.2) Determine $k_{1,obs}$ from the slope of the regression data for both Part A and Part B and enter the values in the table below.

	[H^+]	$k_{1,obs}$	k_1
Part A	0.50 M		
Part B	1.00 M		

By inspection of the data in the table above, determine the order of the reaction with respect to [H^+], *b*.

The reaction with H^+ is _____ order with respect to [H^+].

Write the overall rate law for reaction (1): Rate = _____

Determine the value of k_1 for each reaction and write it in the table above. Include units!

Order in [Cu^{2+}]

(B.3) Set up a spreadsheet for the 0.020 M copper(II) ion data collected in Part B of this experiment. The spreadsheet should include columns for elapsed time, % T, Abs, and the function, (Abs, ln (Abs), or 1/Abs), *that was determined to be linear in Part A.* Construct a graph and perform a linear regression for *that function* vs. time.

(B.4) Determine $k_{2,obs}$ from the slope in the regression data for both Part A and Part B and enter the values in the table below.

	[Cu^{2+}]	$k_{2,obs}$	k_2
Part A	0.010 M		
Part B	0.020 M		

By inspection of the data in the table above, determine the order of the reaction with respect to [Cu^{2+}], *d*.

The reaction with Cu^{2+} is _____ order with respect to [Cu^{2+}].

Write the overall rate law for reaction (2): Rate = _____

Determine the value of k_2 for each reaction and write it in the table above. Include units!

QUESTIONS
Experiment 13D

1. Consider these possible mechanisms for the nitroferroin reaction (1).

Mechanism A

$Fe(phen)_3^{2+}$ (aq) + H^+ (aq) → $[Fe(phen)_2phenH]^{3+}$ (aq)	(Slow)
$[Fe(phen)_2phenH]^{3+}$ (aq) → $Fe(phen)_2^{2+}$ (aq) + $Hphen^+$ (aq)	(Fast)
$Fe(phen)_2^{2+}$ (aq) + H^+ (aq) → $[Fe(phen)phenH]^{3+}$ (aq)	(Fast)
$[Fe(phen)phenH]^{3+}$ (aq) → $Fephen^{2+}$ (aq) + $Hphen^+$ (aq)	(Fast)
$Fephen^{2+}$ (aq) + H^+ (aq) → $[FephenH]^{3+}$ (aq)	(Fast)
$[FephenH]^{3+}$ (aq) → Fe^{2+} (aq) + $Hphen^+$ (aq)	(Fast)

Mechanism B

$Fe(phen)_3^{2+}$ (aq) → $Fe(phen)_2^{2+}$ (aq) + phen (aq)	(Slow)
phen (aq) + H^+ (aq) → $Hphen^+$ (aq)	(Fast)
$Fe(phen)_2^{2+}$ (aq) → $Fephen^{2+}$ (aq) + phen (aq)	(Fast)
phen (aq) + H^+ (aq) → $Hphen^+$ (aq)	(Fast)
$Fephen^{2+}$ (aq) → Fe^{2+} (aq) + phen (aq)	(Fast)
phen (aq) + H^+ (aq) → $Hphen^+$ (aq)	(Fast)

a. What overall rate law would be consistent with mechanism A? Rate = _____

b. What overall rate law would be consistent with mechanism B? Rate = _____

c. Which mechanism is better supported by your experimental data? Explain your answer.

2. Compare the rate laws and rate constants for the two reactions studied. Look for similarities and differences between the results. Based upon these comparisons, what conclusions can be drawn about the mechanisms for the reaction of nitroferroin with copper(II) ions? Explain your answer.

Name _____ Section _____

Partner _____ Date _____

IN-LAB QUESTIONS
Experiment 13D

TURN IN THIS PAGE BEFORE YOU LEAVE LAB.

1. How accurate do the volume measurements for HCl and $CuSO_4$ have to be in steps 3 and 4 of the procedure? Explain your answer.

2. a. What color of light does the chosen wavelength of 510 nm correspond to? Why is 510 nm a sensible wavelength choice for the red nitroferroin solution?

   b. Approximately what wavelength would you expect the blue $CuSO_4$ solution to absorb?

3. Why is distilled water an appropriate blank to use for the experiment?

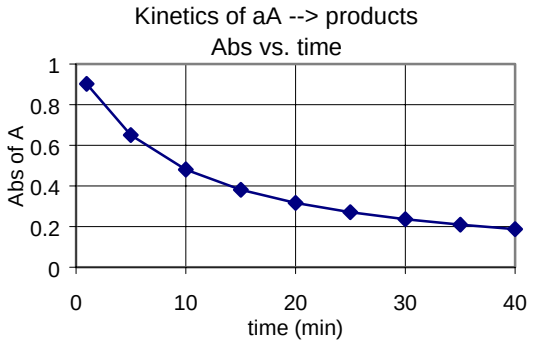
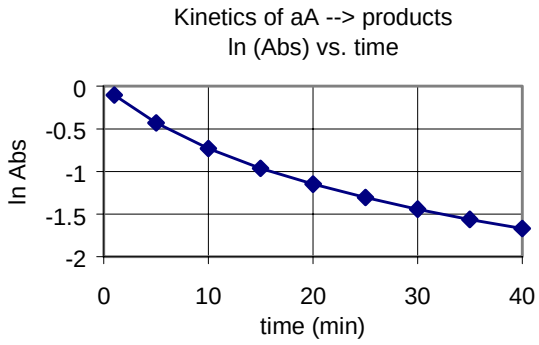
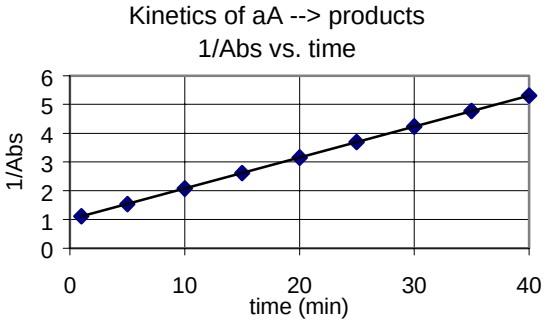
4. On the Spectronic 20, why do you record % Transmittance values and later calculate Absorbance from these values, rather than read Absorbance directly from the display? (Hint: Compare the two scales on the Spec. 20)

Name _____ Section _____ Date _____

PRE-LAB EXERCISES
Experiment 13D

1. Write the algebraic relationship between %T and absorbance.

2. Can you predict the values for the order in nitroferroin and copper(II) ions based on the stoichiometry? Explain your answer.

3. Kinetics data for the following reaction were obtained and plotted below. From these data, predict the order of the reaction with respect to [A]. (Hint: which plot is most linear?)

Reaction: $a\,A \rightarrow$ products