Experiment 13B

THE KINETICS OF FERROIN REACTIONS[1]

MATERIALS:

B & L Spectronic 20, cuvettes, constant temperature bath set at 40°C, ferroin solution, 1.0 M HCl, 0.10 M $CuSO_4$, 0.10 M Na_3EDTA, two 125 mL Erlenmeyer flasks, 50 mL graduated cylinder, two (1-5 mL) graduated pipets, thermometer, two 50 mL beakers.

DISCUSSION:

In this experiment you will investigate the kinetics of two reactions of ferroin, the Fe^{2+} complex of o-phenanthroline (phen).

The stoichiometries of the ferroin reactions are quite different. For example,

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

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

3. $Fe(phen)_3^{2+}{}_{(aq)} + EDTA^{4-}{}_{(aq)} \rightarrow FeEDTA^{2-}{}_{(aq)} + 3\ phen_{(aq)}$

(Note: $EDTA^{4-}$ is the anionic form of ethylenediaminetetracetic acid. This ion is a very powerful complexing agent.)

These reactions will be followed spectrophotometrically. We will take advantage of the fact that ferroin absorbs light at 510 nm, whereas none of the other species do. Thus we will follow the course of each reaction by observing the rate at which the color of the ferroin complex disappears. Such an experiment will provide sufficient information to determine the rate law for each reaction and to make some deductions with regard to the possible reaction mechanism.

PROCEDURE: (work in pairs)

We shall investigate the above reactions under pseudo-order conditions by running two of three (your choice) in the presence of a large excess of H^+, Cu^{2+} or Na_3EDTA. Under these conditions the general rate expression may be represented as follows:

$$\frac{-d\left[Fe(phen)_3^{2+}\right]}{dt} = \frac{-dAbs}{dt} = k_{obs}\left[Fe(phen)_3^{2+}\right]^a$$

where $k_{obs} = k[H^+]^b$ for the case of the H^+ reactions. (The same will be true of the other reagents.). Note, that since H^+ will be present in a large excess, its concentration will remain virtually constant throughout the reaction. Therefore, its concentration times the true rate constant, k, will be another constant, k_{obs}, the so-called "pseudo" rate constant.

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

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

READ THROUGH THIS ENTIRE PROCEDURE BEFORE YOU BEGIN.

Place 50 mL of the ferroin[b] solution into two separate, clean 125 mL Erlenmeyer flasks. Place the flasks and contents into a constant temperature bath (40°C) and wait until these solutions equilibrate with the bath. (This should take no longer than 5 minutes but check the temperatures with a thermometer before continuing further.) Next, add 1 mL of 1.0 M hydrochloric acid solution to one flask, swirl the resulting solution, record the time, quickly withdraw 4+ mL of the solution and measure its absorbance at 510 nm. Now add 1 mL of the Cu^{2+} or Na_3EDTA solution to the other flask and repeat the above operations. Continue to withdraw 4+ mL of each solution at 5 minute intervals for at least 25-30 minutes, recording your times and absorbances as you go.

Part B: The order in $[H^+]$, $[Cu^{2+}]$ or $[Na_3EDTA]$

Repeat the above procedure using the same solutions, except this time use 2 mL of each solution. Record the data collected in the appropriate section of the Data page.

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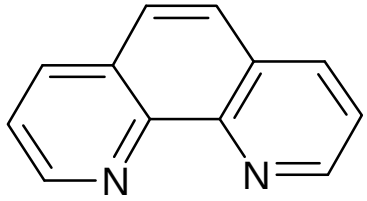
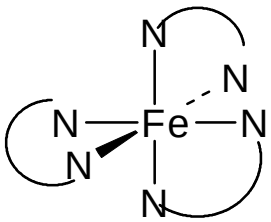
[b]Another name for ferroin is Tris-(1,10-phenanthroline)iron(II). Phenanthroline is particularly well suited for complex formation since the nitrogen unshared electron pairs are directed so that both nitrogens can participate in bonding to a metal ion such as iron. The Fe^{2+} binds three molecules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



1,10 phenanthroline



ferroin

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 13B

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

Conc. of ferroin solution_____

1 mL of	Time	Abs.	1mL of	Time	Abs.
_____	_____	_____	_____	_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____

Data:

Part B: The order in $[H^+]$, $[Cu^{2+}]$ or $[Na_3EDTA]$

2 mL of	Time	Abs.	2mL of	Time	Abs.
_____	_____	_____	_____	_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____
	_____	_____		_____	_____

DATA TREATMENT
Experiment 13B

Make plots (hand-in) of ln Abs of $[Fe(phen)_3^{2+}]$ vs time and 1/Abs of $[Fe(phen)_3^{2+}]$ vs time and determine the order of each reaction in $[Fe(phen)_3^{2+}]$. From these plots, and the data in part B, give the rate expression for each reaction along with the value of its true rate constant (at 40°C). Data manipulation, graphing, and regression analysis (including linear regression) can be easily accomplished using a computer spreadsheet such as QUATTRO.

1. $$\frac{-d\left[\mathrm{Fe(phen)}_3^{2+}\right]}{dt} = k_1 _____$$

k_1 = _____ (units?) for the reaction of ferroin with _____

2.
$$\frac{-d\left[\mathrm{Fe(phen)}_3^{2+}\right]}{dt} = k_2 _____$$

k_2 = _____ (units?) for the reaction of ferroin with _____

Conclusions:

From the rate expression obtained, what conclusions can you draw about the above two reactions? Give what you consider to be a feasible mechanism for each reaction.