

5-2010

A Proposal for The Mechanism of The Iron-Ascorbate, Fenton, and Hydroxyl Radical-Quenching Series

Jonathan Velasco
University of Texas-Pan American

Follow this and additional works at: https://scholarworks.utrgv.edu/leg_etd

 Part of the [Chemistry Commons](#)

Recommended Citation

Velasco, Jonathan, "A Proposal for The Mechanism of The Iron-Ascorbate, Fenton, and Hydroxyl Radical-Quenching Series" (2010). *Theses and Dissertations - UTB/UTPA*. 499.
https://scholarworks.utrgv.edu/leg_etd/499

This Thesis is brought to you for free and open access by ScholarWorks @ UTRGV. It has been accepted for inclusion in Theses and Dissertations - UTB/UTPA by an authorized administrator of ScholarWorks @ UTRGV. For more information, please contact justin.white@utrgv.edu, william.flores01@utrgv.edu.

A PROPOSAL FOR THE MECHANISM OF THE IRON-ASCORBATE,
FENTON, AND HYDROXYL RADICAL-QUENCHING SERIES

A Thesis

by

JONATHAN VELASCO

Submitted to the Graduate School of the
University of Texas-Pan American
In partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2010

Major Subject: Chemistry

A PROPOSAL FOR THE MECHANISM OF THE IRON-ASCORBATE,
FENTON, AND HYDROXYL RADICAL-QUENCHING SERIES

A Thesis
by
JONATHAN VELASCO

COMMITTEE MEMBERS

Dr. Philip Delassus
Chair of Committee

Dr. Elamin Ibrahim
Committee Member

Dr. Narayan Bhat
Committee Member

Dr. Jason Parsons
Committee Member

May 2010

Copyright 2010 Jonathan Velasco
All Rights Reserved

ABSTRACT

Velasco, Jonathan. A Proposal for the Mechanism of the Iron-Ascorbate, Fenton, and Hydroxyl Radical-Quenching Reaction Series. Master of Science (MS), May, 2010, 26 pages, 2 tables, 15 figures, 4 titles.

The Fenton reaction between [Fe(II)] and [HOOH] is observed in the presence of ascorbic acid, [AscH⁻], during [Fe(III)] and HO• reduction; this is done as part of consecutive redox reactions between [Fe(III)] and [Fe(II)]. As a result, the rate orders with respect to [Fe(III)], ascorbic acid, and [HOOH] are of (approximately) 2nd, 1st, and 4th order, respectively. However, the rate constants for each reaction in this study show patterns when measured against solution pH; empirically, reactions proceed faster at smaller pH and vice versa.

DEDICATION

I would like to thank my mother and father, Nenette and Alejandro Velasco, and my sister, Nicole Velasco for their support during my studies during my college education. I would also like to thank my wife, Jasel Cantu-Velasco, for her love, motivation, and encouragement to continue my pursuit of higher education.

ACKNOWLEDGEMENTS

I would like to thank Dr. Philip Delassus, the chair of my committee, for encouraging me through his mentoring and advice for continuing my studies and my research toward its completion. I would also like to thank Dr. Elamin Ibrahim and Dr. Jason Parsons for their comments regarding my thesis to ensure the quality of both my methods and my thesis. I would also like to thank Dr. Narayan Bhat and Dr. Banglin Chen for their advice during the course of my research.

TABLE OF CONTENTS

	Page
ABSTRACT.....	iii
DEDICATION.....	iv
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii
CHAPTER I. INTRODUCTION.....	1
CHAPTER II. EXPERIMENTAL.....	8
Fe(III)-AA Reaction.....	8
Fenton Reaction.....	8
Statistical Analysis.....	9
CHAPTER III. RESULTS AND DISCUSSION.....	10
Fe(III)-AA Reactions.....	10
Fenton Reactions.....	16
CHAPTER IV. CONCLUSION.....	22
LITERATURE CITED.....	24
BIOGRAPHICAL SKETCH.....	26

LIST OF TABLES

	Page
Table 1: Previous studies	2
Table 2: Reagent setup.....	9

LIST OF FIGURES

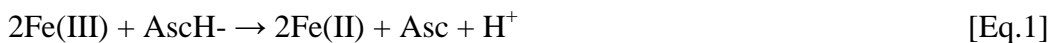
	Page
Figure 1: Calibration curve	11
Figure 2: 10:1 [Fe(III)] vs. time	12
Figure 3: 10:1 double-log vs. time	12
Figure 4: $1/[\text{Fe(III)}]^{1.176}$ vs. time	13
Figure 5: 1:1 [Fe(III)] vs. time	13
Figure 6: 1:1 double-log vs. time	14
Figure 7: $1/[\text{Fe(III)}]^{2.167}$ vs. time	15
Figure 8: $[\text{H}^+]_0$ vs. k , non-Fenton	16
Figure 9: 10:1:1 [Fe(III)] vs. time	17
Figure 10: 10:1:1 double-log vs. time	17
Figure 11: 1:1:1 [Fe(III)] vs. time	18
Figure 12: 1:1:10 [Fe(III)] vs. time	18
Figure 13: 1:1:1 double-log vs. time	19
Figure 14: $1/[\text{Fe(III)}]^{6.472}$ vs. time	19
Figure 15: $[\text{H}^+]$ vs k_{obs} , $k_{3,4}$	20

CHAPTER I

INTRODUCTION

The oxidation-reduction reaction between iron (as Fe(III)) and ascorbic acid has been studied due to its biofunction and availability. As a biofunction, the reduction of Fe(III) to Fe(II) allows a pathway for Fe(III) to be used in the body as Fe(II), which is more readily absorbed as it is a cofactor and a component of hemoglobin (Ryan and Aust, 1992, Miller et. al., 1990). Also, it is known for its antioxidant activity, as demonstrated by its ability to readily quench species such as hydroxyl radical, HO• (Buettner and Schaeffer, 2004). As for its availability, iron and ascorbic acid (as vitamin C) are readily available as parts of a supplement or as their own supplements. They are also found as additives in food products to augment their nutritional values. However, studies beyond this reaction have been carried out as one of the products, Fe(II), is a reactant of the hydrogen peroxide-induced Fenton reaction, which produces the hydroxyl radical, HO•, a free radical believed to cause DNA damage. Ascorbic acid may still be present, which can readily quench the radical (Buettner and Schaeffer, 2004). Hydroxyl radical can still be quenched, but some of the ascorbic acid is “wasted”, in terms of Fe(III) reduction, since some of the ascorbic acid is used for radical quenching but will still proceed as long as there is enough of the acid present (Velasco and Ibrahim, 2005).

Previous studies have shown that the reaction of Fe(III) with ascorbic acid is as follows (Zhu and Frei, 2002, Hsieh and Hsieh, 2000):



The reaction is carried out in aqueous medium and yields a reaction that is kinetically dependent on the initial amount of ascorbic acid, which acts as an electron donor through an unclear mechanism (Banhegyi and Loewus, 2004). It is a radical-producing reaction; one of its products is the ascorbyl radical, which can be further oxidized into dehydroascorbate and decomposed into other products. Since neither the radical nor dehydroascorbate show any significant antioxidant/reductive ability (May and Asard, 2004), they will not influence in the kinetics of the reaction; the radical can still donate an electron, but is not likely to be competing with ascorbate anion. Rate laws for this reaction have been proposed as exhibiting near 2nd-order kinetics:

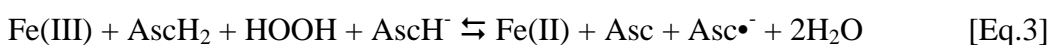
$$\text{rate} = k[\text{Fe(III)}]^m[\text{AscH}_2]^n \quad [\text{Eq.2}]$$

Study	<i>k</i>	<i>m</i>	<i>n</i>
1	Varied	1.811±0.309	Near-zero
2	1.6814x10 ⁻³ (±8.2737x10 ⁻⁵) mM ^{-0.8809} sec ⁻¹	1.8782±0.0615	0.3344

Table 1: Previous studies. Values of the rate orders *a*, *b*, and rate constant *k* of two previous studies. 1) Hsieh and Hsieh, 2000; 2) Velasco and Ibrahim, 2005.

If the reaction was of apparent zero-order kinetics (*b*) with respect to ascorbic acid, then *k* should not change despite the change in concentration of ascorbic acid. In both studies, however, there was a correlation in *k* and pH; as the initial concentration of ascorbic acid was increased, *k* also increased.

A proposed overall reaction of iron, ascorbic acid, and hydrogen peroxide is as follows (Velasco and Ibrahim, 2005):



The reaction between ascorbate and the hydroxyl radical works similar to the iron-ascorbate reaction in that reduction takes place through electron donation by ascorbate. As opposed to the iron-ascorbate reaction, which only uses 1 mol of ascorbic acid to reduce 2 moles of Fe(III), the Fenton reaction requires 2 moles of ascorbic acid (as ascorbate in physiological pH) to reduce 1 mol of Fe(III). The same study showed that there was some slowing down of the overall kinetic of the iron-ascorbic acid reaction as described in Equation 2; this could be indicative of a non-zero order reaction with respect to ascorbic acid.

The focus of this study is to propose a mechanism for the overall reaction between the iron-ascorbate, Fenton, and radical quenching reactions of iron, ascorbate, and hydrogen peroxide. This kind of reaction could conceivably happen within the body since all three reactants occur in the body in some way. To reach this mechanism, there is a

need to refine the steps used in our previous study (Velasco and Ibrahim, 2005). One reason for refinement comes from the variation in results of the rate constant; ideally, rate constants of the iron-ascorbate reaction, from individual processes in different concentrations of ascorbate, should have little variation between them regardless of reactant concentration. Another reason comes from the lack of data provided by the Fenton reaction in regards to kinetics. Hydrogen peroxide is used up very quickly in the reaction, and although it was able to slow down the reaction while it was present, the exact kinetic was not found as after the first 30 seconds of reaction, the rate of Fe(III) reduction ($d[\text{Fe(III)}]/dt$) during the Fenton reaction was the same as the iron-ascorbate reaction. From this it can be assumed that all of the hydrogen peroxide was used up during that window of time. Also, it must be noted that this is an oxidation-reduction reaction involving components that are sensitive to oxygen attack, ascorbate and Fe(II) in particular. Since ascorbic acid is a scavenger of ROS (reactive oxygen species) (Zhu and Frei, 2002), and oxygen may undergo radical reactions with Fe(II), some amount of ascorbic acid may be used up to quench any ROS that may have evolved as a result of contact with oxygen. Also, steps in finding the rate law will have to be expanded as pH could be influencing the rate of reaction. There have been studies of ascorbic acid kinetics where rates and constants are influenced by the pH of solution (Song et. al., 2002, Hsieh and Hsieh, 2000, Velasco and Ibrahim, 2005); these studies have found that ascorbic acid can achieve higher rates and/or constants at lower pH, $[\text{H}^+]$ could be tied into the overall rate kinetics.

For the overall reaction series, however, the rate law includes the terms for [HOOH], which produces the following rate equation:

$$\text{rate} = k[\text{Fe(III)}]^m[\text{AscH}_2]^n[\text{HOOH}]^p \quad [\text{Eq. 4}]$$

Where k is the rate constant for the overall reaction series. To find the rate orders, two separate experiments must be carried out. The first set of experiments focus on the Fe(III)-ascorbic acid reaction similar to that done by Hsieh and Hsieh (2000). To find the rate order m , it is carried out as a pseudo- m th order reaction with excess ascorbic acid in that:

$$\text{rate} = k_1[\text{Fe(III)}]^m \quad [\text{Eq. 5a}]$$

As the rate constant $k_1 = k[\text{AscH}_2]^n$, of which the term is near constant. The constant k_1 could be attributed with Equation 3b because at excess $[\text{AscH}_2]$, Fe(III) is more likely to undergo one-electron transfers with AscH^- than $\text{Asc}\cdot^-$. The rate order m can be found as the slope of the following equation:

$$\log \text{rate} = \log k_1 + m \cdot \log[\text{Fe(III)}] \quad [\text{Eq. 5b}]$$

In the same set of experiments, n can be found with equivalent amounts of iron and ascorbic acid so that:

$$\text{rate} = k'_{1,2}[\text{Fe(III)}]^{m+n} \quad [\text{Eq. 6a}]$$

Where $k'_{1,2} = k_{1,2}(0.5)^n$, and $k_{1,2}$ corresponds to the two-stage reduction of [Fe(III)] as described in Eq. 3b and 3c, such as $k_{1,2} = k_1k_2$. To find n , a logarithm plot is also made which has n as the slope of the equation:

$$\log \text{rate} = \log k'_{1,2} + (m+n) \cdot \log[\text{Fe(III)}] \quad [\text{Eq. 6b}]$$

And the rate order n will be the difference between the slopes of Equation 6b and 5b.

The rate constant for the iron-ascorbate (non-excess) $m+n$ th order reaction, $k'_{1,2}$, can be found by integrating Equation 6b as such:

$$[\text{Fe(III)}]^{-(m+n-1)} = [\text{Fe(III)}]_0^{-(m+n-1)} + (m+n-1)k' t \quad [\text{Eq. 7}]$$

The slope of the graph generated by Equation 7 is substituted into $k'_{1,2} = k_{1,2}(0.5)^n$ to get $k_{1,2}$, the constant for the $m+n$ th-order reaction.

Completion of the first reaction set allows for the second set of experiments, which focuses on the Fenton reaction. Excess [AscH₂] produces a similar equation to Equation 5b:

$$\log \text{rate} = \log k'_{obs} + m \cdot \log[\text{Fe(III)}] \quad [\text{Eq. 9a}]$$

Except there is a new rate constant, k'_{obs} , and $k'_{obs} = k_{obs}[\text{AscH}_2]^m[\text{HOOH}]^p$. Equivalent $[\text{AscH}_2]$ reactions, however, are treated differently. According to Equation 3, 1 mol of ascorbic acid will reduce 1 mol of HOOH and 1 mol of Fe(III), so a logarithm plot similar to Equation 6b can be used:

$$\log \text{rate} = \log k_{obs} + (m+n+p) \cdot \log[\text{Fe(III)}] \quad [\text{Eq.9b}]$$

The slope of the plot gives $m+n+p$, which gives the rate order p after subtracting the slope of Equation 6b.

To find k_{obs} , results of this section are treated similar to Equation 7, substituting $(m+n+p-1)$ for $(m+n-1)$.

CHAPTER II

EXPERIMENTAL

Ascorbic acid (Sigma-Aldrich, Inc.) does not have a significant aging effect on its concentration (Hsieh and Hsieh, 2000), but fresh 1M and/or 0.1M solutions are made every day. The source of iron will be a 0.1M solution of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, Inc.). 0.1M and 1.0M hydrogen peroxide is made from a 30% solution (Sigma-Aldrich, Inc.). The above reagents will be added to a 0.1M solution of potassium hydrogen phthalate, buffered to pH 4, 4.5, 5, and 5.5 by using NaOH and HCl to make adjustments to pH.

Fe(III)-AA Reaction

The reaction and analysis vessel will be a quartz cuvette (10mm) containing 3mL KHP buffer, 36 μL FeCl_3 , and 36 μL 1.0M ascorbic acid for the excess-[Fe(III)] reaction or 0.1M for the equivalent-[Fe(III)] reaction. A microstirrer is placed on a UV/Visible spectrophotometer scanning at 375nm with constant stirring for 30 seconds.

Fenton Reaction

The reagent setup is the same as that of the Fe(III)-AA reaction, but with the addition of 36 μL of HOOH , 36 μL ascorbic acid, and using 0.1M FeCl_3 . It is also placed in UV/Visible analysis. Table 2 summarizes the reagent setup for both types of reactions.

Reaction Name	Fe(III)	AscH ₂	HOOH
10:1	0.1M, 36μL	1.0M, 36μL	
1:1	0.1M, 36μL	0.1M, 36μL	
10:1:1	0.1M, 36μL	1.0M, 36μL	0.1M, 36μL
1:1:1	0.1M, 36μL	0.1M, 36μL	0.1M, 36μL
1:1:10	0.1M, 36μL	0.1M, 36μL	1.0M, 36μL

Table 2: Reagent setup. Reagent setup for all reactions in this study. The 10:1 (excess [AscH₂]) and 1:1 (equivalent [AscH₂]) reactions are for the iron(III)-ascorbate reactions; the 10:1:1 (excess [AscH₂], equivalent [HOOH]), 1:1:1 (equivalent [AscH₂] and [HOOH]), and 1:1:10 (equivalent [AscH₂], excess HOOH)] Fenton reactions.

Statistical Analysis

Curve-fits were analyzed and created using LoggerPro 3 (Vernier Software & Technology). Resulting data was exported to Microsoft Excel for representing graphs and curve-fitted equations (wherever possible).

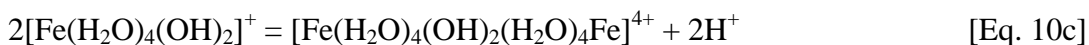
CHAPTER III

RESULTS AND DISCUSSION

(Author's note: all references to [H+] or pH in the text or on graphs refer to starting [H+], or [H+]₀)

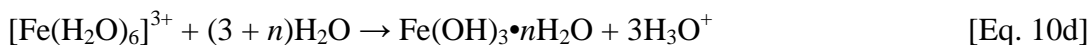
Fe(III)-AA Reactions

Fe(III) coordinates with water to become the acidic species hexaaquairon(III), which hydrolyzes as such:



Each equation has an equilibrium constant K of $10^{-3.05}$, $10^{-3.26}$, and $10^{-2.91}$, respectively (Cotton et al. 1995). The hexaaqua species has a pale purplish color that cannot be seen at the pH range of the experiment due to the strong orange color of the pentaqua species. A hydroxo dimer species as described in Equation 8c is likely to appear within the pH range of the experiment [Spiro and Saltman, 1969]. A point of interest is that the calibration curves for each pH are different, their slopes approaching 1 as pH increases.

What is possibly happening is equilibrium shifting to the left as pH is decreasing due to increase in $[H^+]$ and less of the optically-strong pentaqua species is appearing. Another point of interest is the presence of a hydrous oxide that precipitates above $pH > 4$ (Shriver and Atkins, 1990);



This precipitate may be a factor in the linearity of the calibration curve with increasing pH. However, Fe(III) can still be read at 375nm with a roughly 1:1 concentration to absorbance ratio (Figure 1). It should also be noted that because of the KHP buffer, changes in pH were limited to ± 0.08 units as the reaction proceeded.

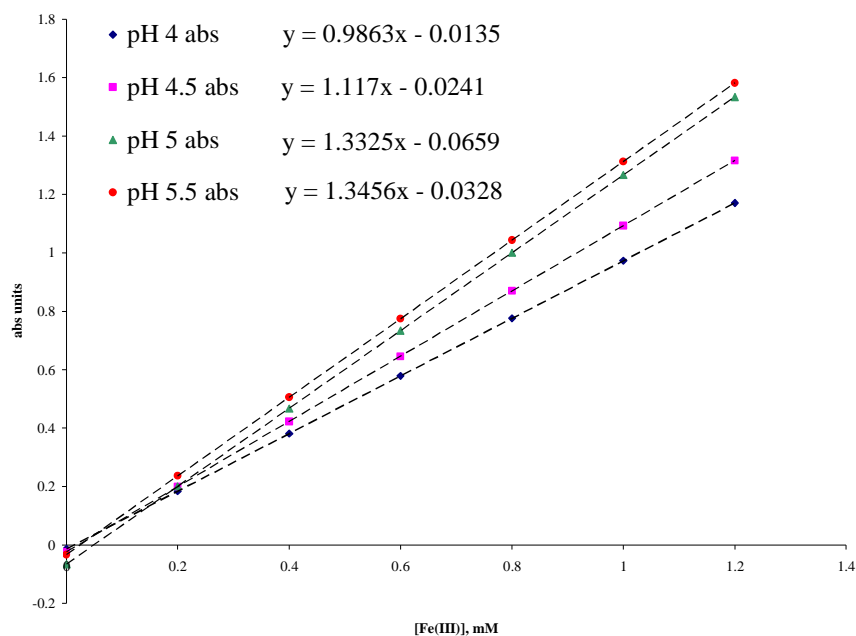


Figure 1. Calibration curve used for all experiments.

Plotting $\log[\text{Fe(III)}]$ vs. $\log \text{rate}$ for the 10:1 reaction gives the slope with the value m as shown in Figure 3.

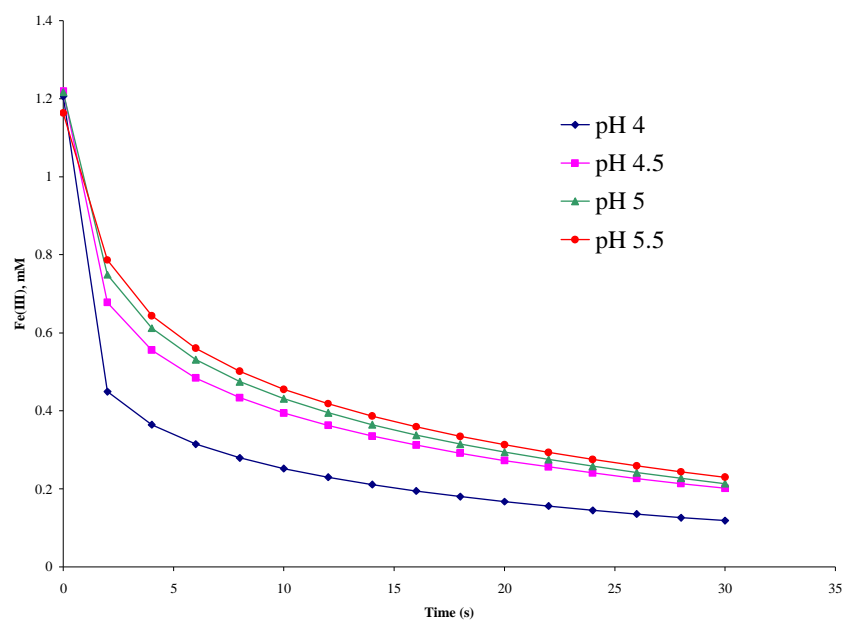


Figure 2. $[\text{Fe(III)}]$ vs. time graph of the $\text{Fe(III)}\text{-AscH}^-$ reactions (concentrations 10:1).

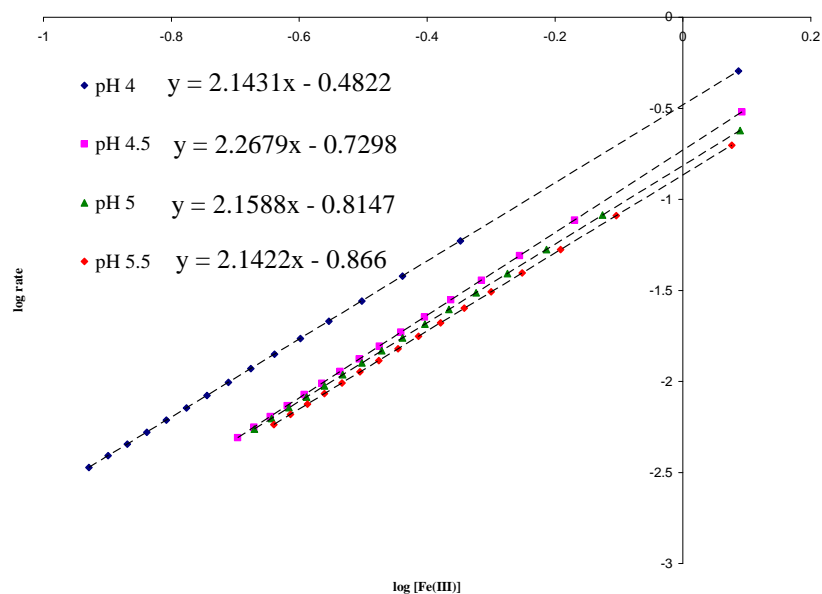


Figure 3. Double-log graph of reactions from Figure 2. Slopes correspond to the rate order m .

Taking the average of the slopes of Figure 2-2, $m = 2.178 \pm 0.06$. This means that if the rate $= k'_1[\text{Fe(III)}]^m$, the differences between reaction behaviors shown in Figure 2 must be affected by k_1 , as shown on Figure 4. As the starting pH increases, k_1 decreases, which shows that acidity of the solution affects the kinetics of this reaction, even at excess $[\text{AscH}^-]$.

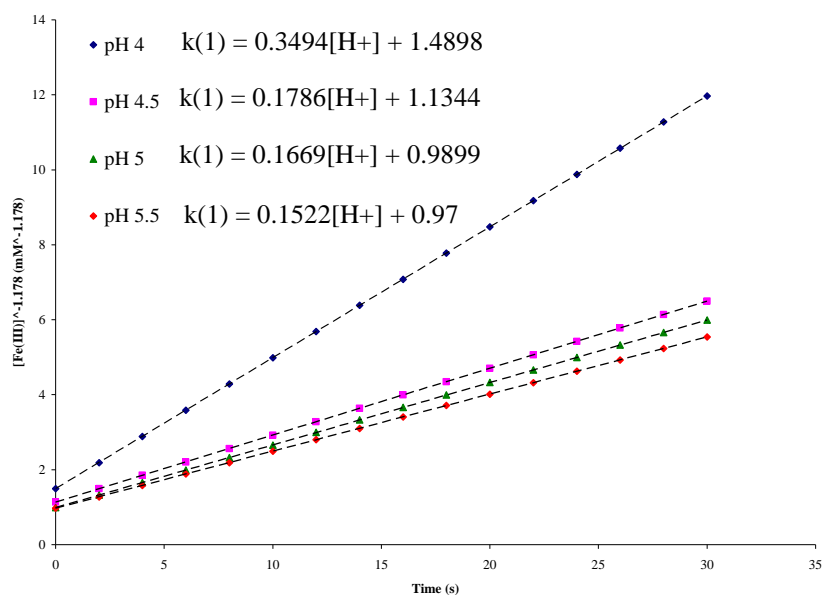


Figure 4. Plot of $1/[\text{Fe(III)}]^{1.176}$ vs. time. Slopes were curve-fitted for use in Figure 4.

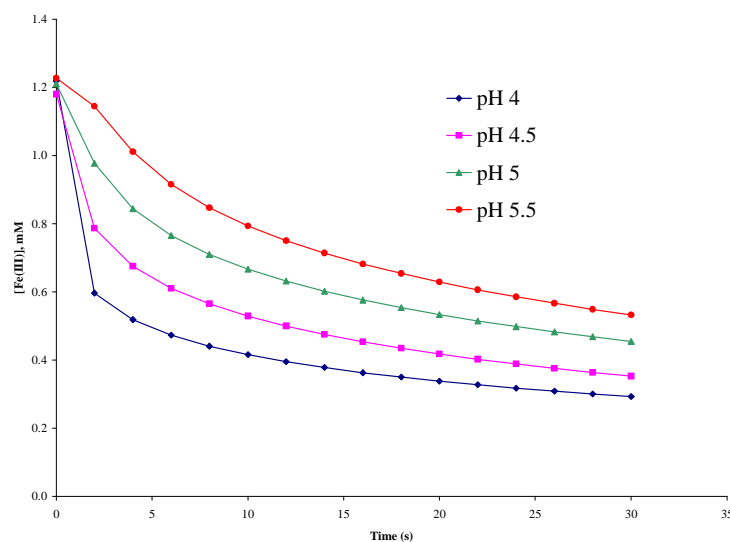


Figure 5. $[\text{Fe(III)}]$ vs. time graphs for the $\text{Fe(III)}\text{-AscH}^-$ reactions (1:1 concentration).

However, when $[\text{Fe(III)}] = [\text{AscH}]$, the double-log graph (Figure 6) shows that $m + n = 3.167 \pm 0.084$. Subtracting the known value of m from this sum gives $n = 0.9893$. There is another correlation between $k'_{1,2}$ and $[\text{H}^+]$, as shown on Figure 7.

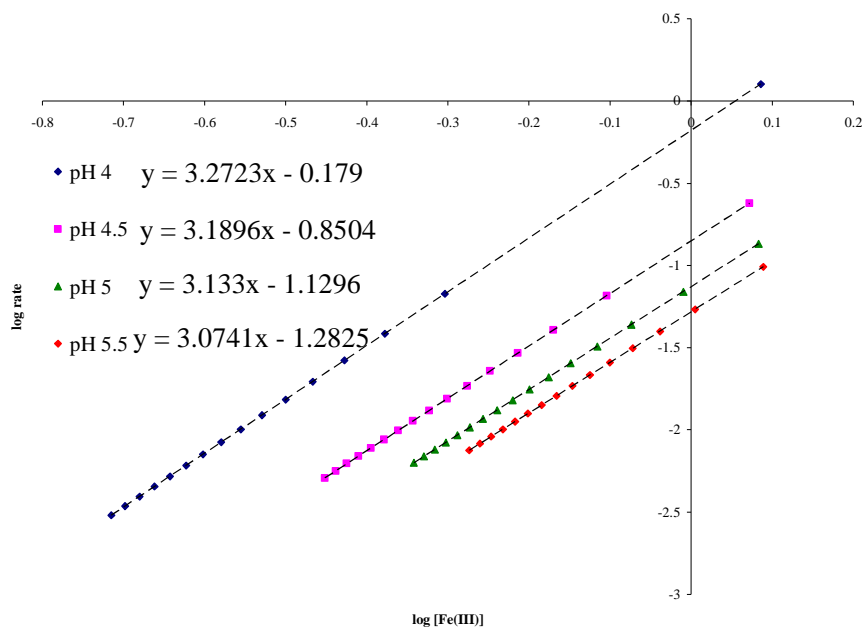


Figure 6. Double-log graph of reactions from Figure 5. Slopes correspond to the sum of the rate orders m and n .

Moreover, because $k'_{1,2} = k_{1,2}(0.5)^n$, the values of $k_{1,2} = 1.0914, 0.28, 0.1572,$ and $0.1108 \text{ mM}^{-2.167} \text{ s}^{-1}$ for pH 4, 4.5, 5, and 5.5 respectively. Plotting these points against $[\text{H}^+]_0$ on Figure 4 show another relationship between $[\text{H}^+]_0$ and rate constant, indicating that the rate constant may have $[\text{H}^+]_0$ as a factor in it, in the same manner as k_1 . The rate constants for the excess-AscH reaction, k_1 , when plotted (Figure 4), have values of 0.3494, 0.1786, 0.1669, and 0.1552 $\text{mM}^{-1.178} \text{ s}^{-1}$ pH 4, 4.5, 5, and 5.5 respectively; these values can be described by the equation $k_1 = 2057.5[\text{H}^+]_0 + 0.1373 \text{ mM}^{-1.178} \text{ s}^{-1}$. Since $k_{1,2} = k_1 k_2$, dividing these values at each $[\text{H}^+]_0$ gives values of k_2 that can be described by the equation $k_2 = 400.82[\text{H}^+]_0^{0.5266} \text{ mM}^{0.011} \text{ s}^{-1}$.

It can be empirically said that higher $[H^+]$ (or lower pH) makes the reaction proceed faster, which is supported by a study by Hsieh and Hsieh (1997). One interpretation of this is that ascorbate is better able to form complexes with hexaaquairon(III) than with pentaquairon(III), which indicates some competition between hydroxide and ascorbate for complexation (Hsieh and Hsieh 2000). This kind of correlation is shown in Equation 10a and 10b; as more $[H^+]$ is present (lower pH), equilibrium favors the creation of non-hydroxo species. It is also possible that the creation of hydroxo dimers, as illustrated by Equation 10c, may also be reducing the reaction rate due to its correlation with pH, and the likelihood of dimerization at higher pH. The reaction rate may also be affected by the precipitated hydrous oxide described in Equation 10d; this could mean a preference of ascorbate anion to form coordinated complexes with aqueous iron.

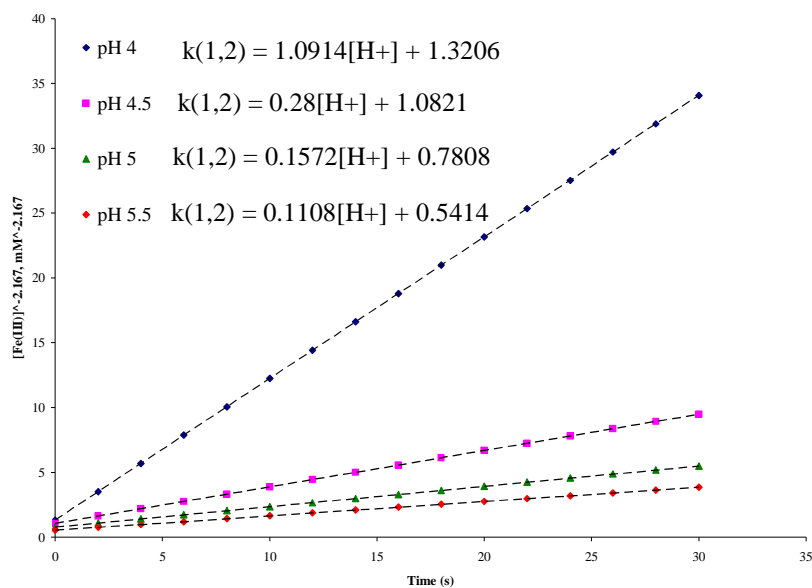


Figure 7. Plot of $1/[Fe(III)]^{2.167}$ vs. time. Slopes represent $k_{1,2}$.

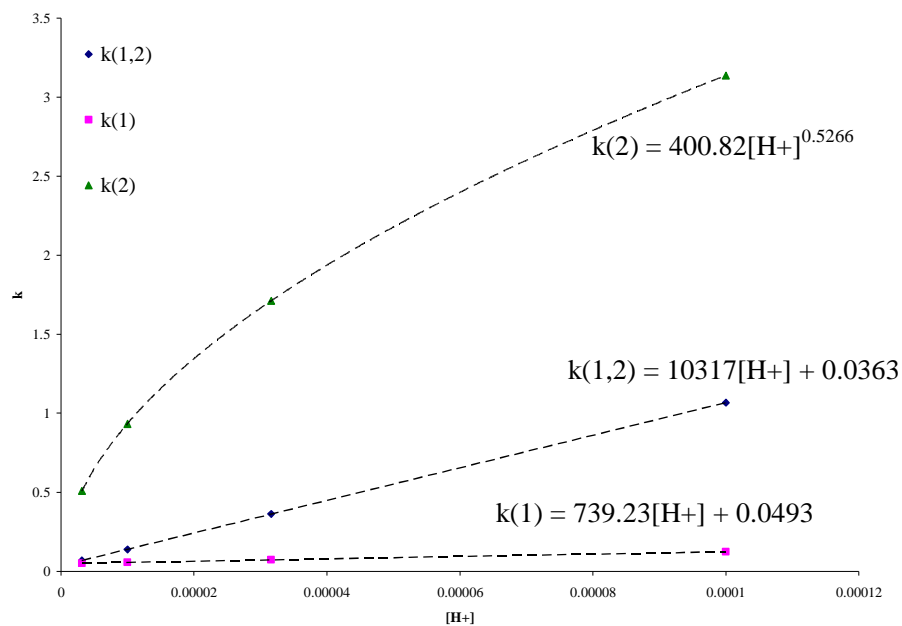


Figure 8. Plot of $[H^+]_0$ vs. rate constant values.

Fenton Reactions

If HOOH is added to the reaction (10:1:1), causing the Fenton reaction to take place, $m = 2.367 \pm 0.05$ (Figure 10), which is not significantly different from $m = 2.178$. However, when the concentration ratios of all reactants are equal (1:1:1 reactions), the reaction profile changes significantly (Figure 11). The addition of [HOOH] causes the Fe(III)-AscH⁻ reaction to not only slow down but also to level out at higher [Fe(III)]. This means that some Fe(II) is autoxidizing back to Fe(III) as AscH⁻ is being consumed for both reduction and Fenton reactions; this is illustrated in Figure 12, where [Fe(III)] does not decrease as the reaction progresses.

It should be noted that the value of $m+n+p$ is irrational (7.472 ± 0.655 order, Figure 13). This means that the value of p , the rate order with respect to [HOOH], is 4.305.

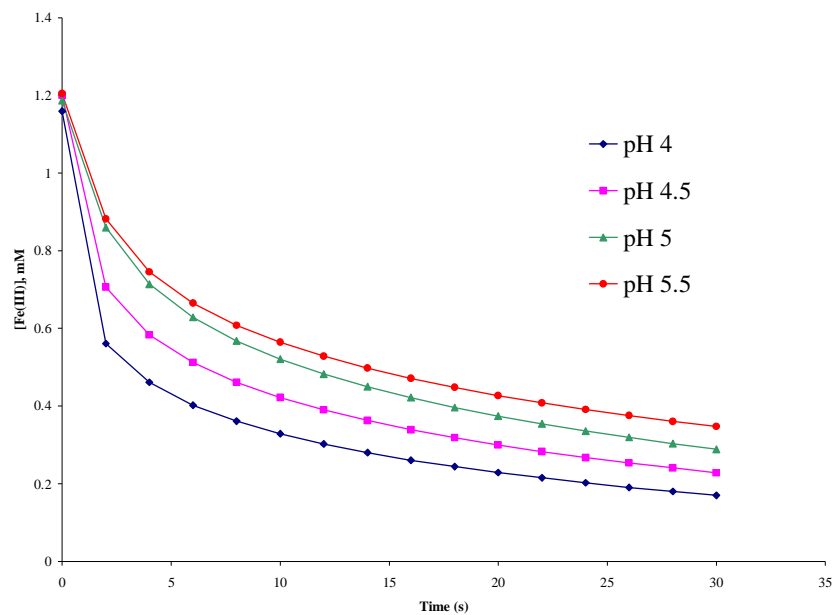


Figure 9. Plot of [Fe(III)] vs. time for all [AscH-]-[Fe(III)]-[HOOH] reactions (concentration ratio 10:1:1).

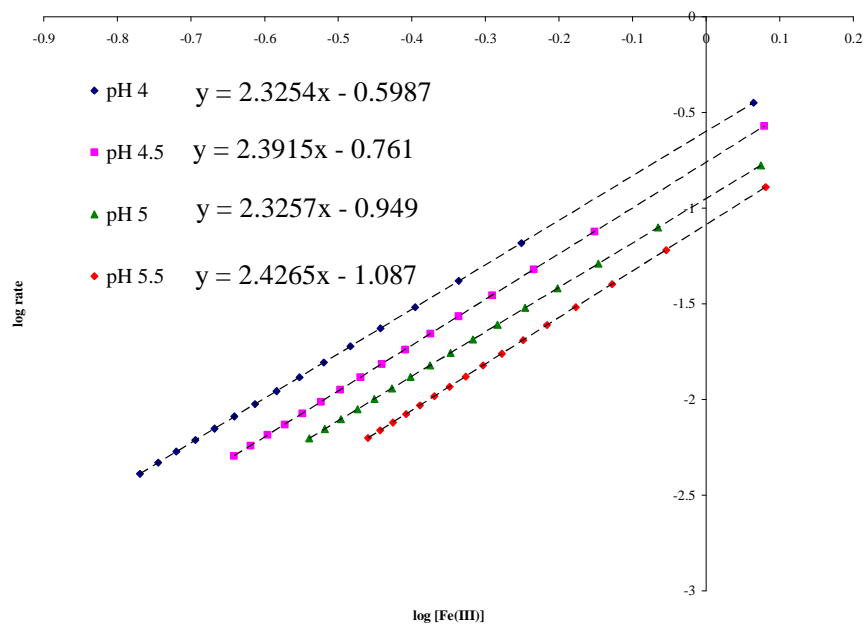


Figure 10. Double-log plot of 10:1:1 reactions. Slope equations represent rate order m .

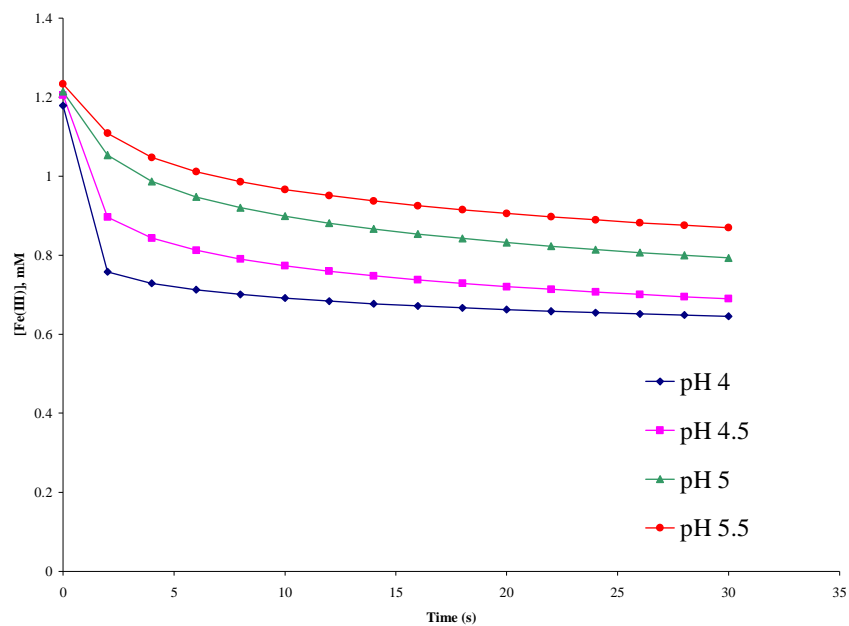


Figure 11. [Fe(III)] vs. time plot when [Fe(III)] = [AscH⁻] = [HOOH] (concentration ratio 1:1:1).

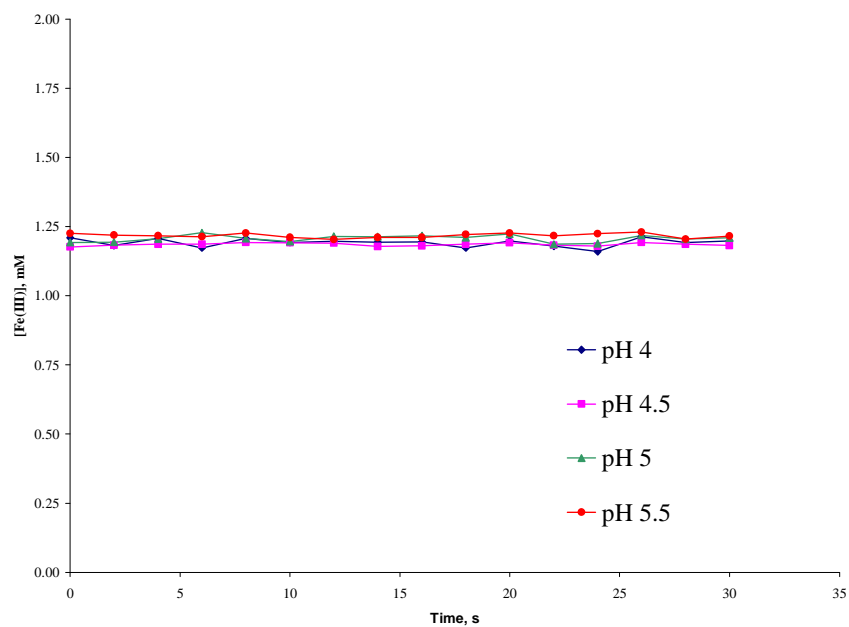


Figure 12. [Fe(III)] vs. time plot, (concentration ratio 1:1:10). The erratic readings average at ~1.2 mM, and there is no evident negative trend that signifies decreasing [Fe(III)] as the reaction progresses.

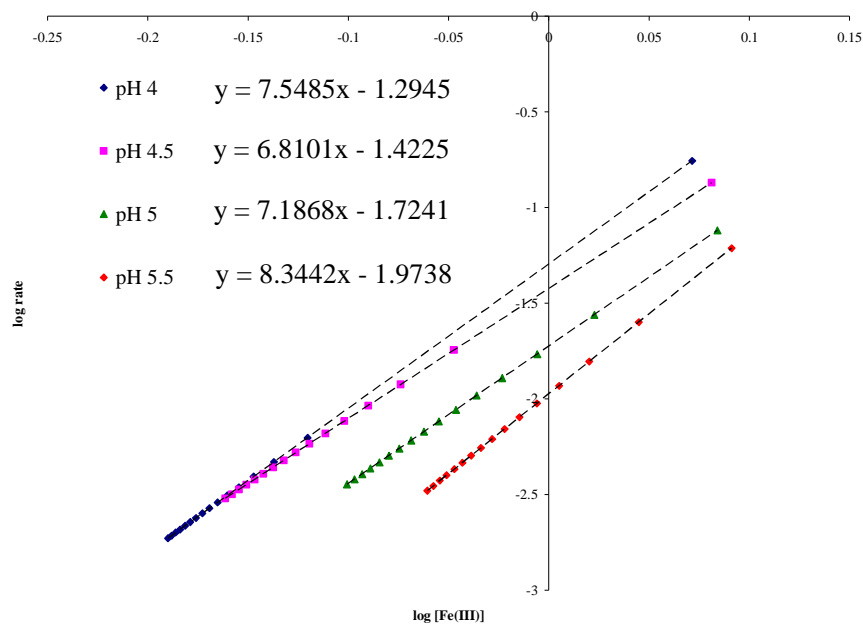


Figure 13. Double-log plot of the 1:1:1 Fenton reaction.

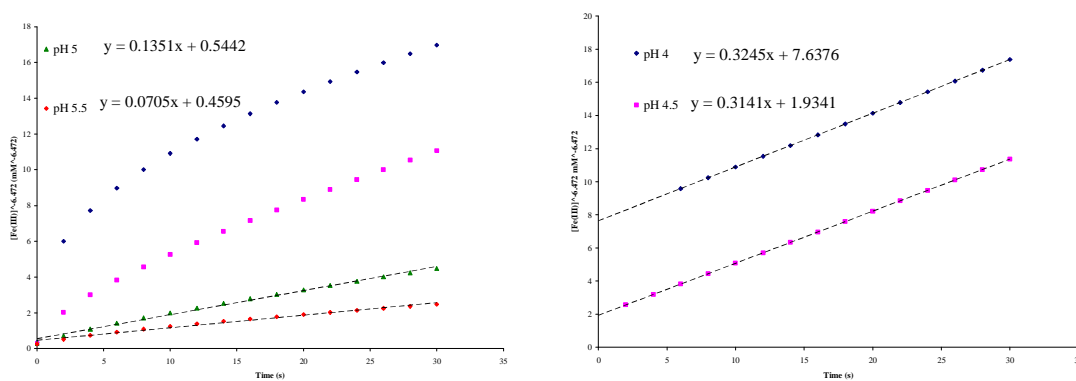


Figure 14. $1/[\text{Fe(III)}]^{6.472}$ vs. time plot. Slopes of each graph are values of k_{obs} , and values were later curve-fitted into Figure 7. Plots on the right-hand graph were done to correct for outlying results.

A plot of $1/[\text{Fe(III)}]^{6.472}$ against time is made (Figure 14) to find k_{obs} in such a way that the slope gives the constant:

$$[\text{Fe(III)}]^{-(m+n+p-1)} = [\text{Fe(III)}]_0^{-(m+n+p-1)} + (m+n+p-1)k_{\text{obs}}t \quad [\text{Eq. 11}]$$

These slopes are plotted against $[H^+]_0$ on Figure 15, which shows another correlation between k_{obs} , the rate constant for all equations involved (Equations 3a-e), and $[H^+]_0$ through the equation $k_{obs} = 0.1882 \cdot \log(7.431 \times 10^5 [H^+]_0 \text{ mM}^{-6.472} \text{ s}^{-1})$.

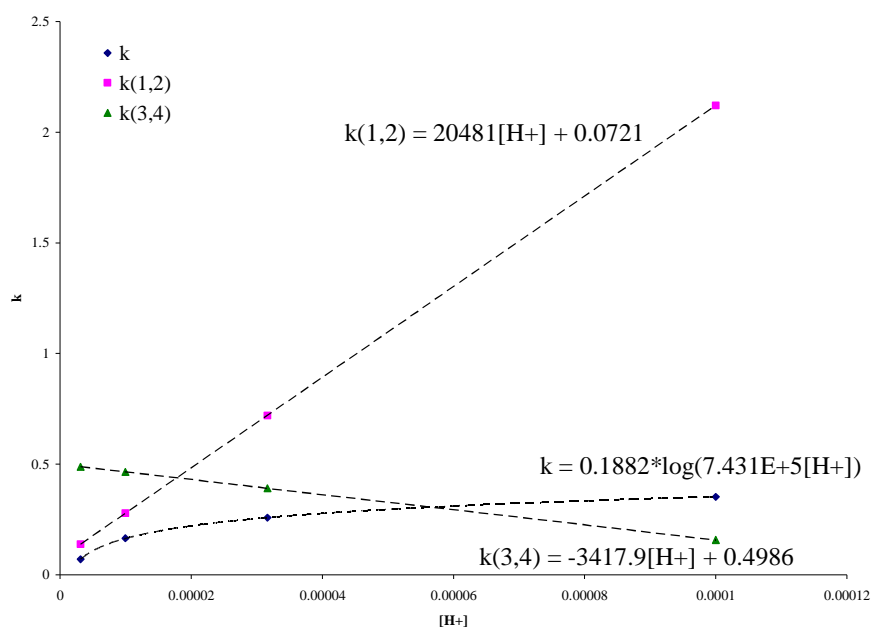


Figure 15. Plot of $[H^+]$ vs k_{obs} and of $k_{3,4}$.

The rate constants for the Fe(II) oxidation step (Eq. 3d) and the hydroxyl radical quenching step (Eq. 3e) are given the labels k_3 and k_4 , respectively, for this study. The rate constant k_3 oxidizes Fe(II) to Fe(III); although k_3 is not actually the reverse reaction of k_1 and/or k_2 (therefore k_{-1} or k_{-2}), it could be considered as such because it regenerates reactant. Because k_3 is not actually a reverse reaction, and adding HOOH decreases the rate of Fe(III) reduction, this means that k_3 could be a much smaller value than k_1 , k_2 , and possibly k_4 . The rate constant k_4 may actually play a role in lowering the rate of Fe(III) reduction due to consuming $AscH^+$, which is the more favored reducing agent; this forces

Fe(III) reduction to undergo k_2 instead of k_1 . Because of this, k_4 must be less than k_1 and k_2 .

It should also be noted on Figure 15 that as $[H^+]$ increases, $k_{3,4}$ is decreasing, showing that at higher pH, $[HOOH]$ plays a larger role in $[Fe(II)]$ reoxidation. This may be another factor that causes the shape of the $[Fe(III)]$ vs. time plots in Figure 11. However, the same separation of plots could be seen in other $[Fe(III)]$ vs. time plots, so the $k_{3,4}$ in the reaction may indeed be small.

CHAPTER IV

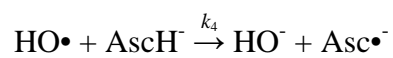
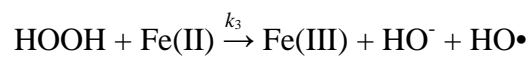
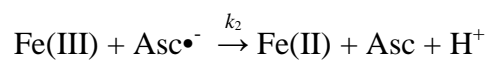
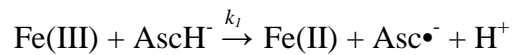
CONCLUSION

An overall pH-dependent mechanism for the Fenton reaction cannot be found through the methods described in this study. However, some reaction behaviors can be seen from the proposed rate law in Equation 2, substituting for all values of m , n , and p :

$$\text{rate} = k_{obs}[\text{Fe(III)}]^{2.2}[\text{AscH}_2][\text{HOOH}]^{4.3} \quad [\text{Eq. 12}]$$

With $k_{obs} = 0.1882 \cdot \log(7.431 \times 10^5 [\text{H}^+]_0 \text{ mM}^{-6.472} \text{ s}^{-1})$ as the overall rate constant of the reaction series. $[\text{H}^+]$ is included in rate constants due to the apparent dependence of $[\text{H}^+]$ to the overall rate. The positive correlation between $[\text{H}^+]$ and rate (or inverse correlation between pH and rate) could be attributed to the appearance of hexaaquairon(III) species and possible competition between hydroxide and ascorbate anions for complexation with Fe(III). Although the contribution of $[\text{HOOH}]$ to the overall Fenton reaction is high, it should be noted that the overall rate constant of the reaction series is small because the rate constant of the Fenton reaction.

Empirically, a mechanism of what is occurring in the Fenton reaction based on the rate equation from Equation 12 can be seen as such:



As $k_1 = 2057.5[\text{H}^+]_0 + 0.1373 \text{ mM}^{-1.178} \text{ s}^{-1}$ and $k_2 = 400.82[\text{H}^+]_0^{0.5266} \text{ mM}^{0.011} \text{ s}^{-1}$.

Though the values of k_3 and k_4 were not found with these methods, empirically, $k_3k_4 = k_{\text{obs}}/(k_1k_2) = -3417.9[\text{H}^+] + 0.4986$ if $k_{\text{obs}} = k_1k_2k_3k_4$, $k_3 \ll k_{1,2}$, and $k_4 < k_{1,2}$.

LITERATURE CITED

- Banhegyi, G; Loewus, FA. "Ascorbic acid catabolism: breakdown pathways in animals and plants." Vitamin C: Function and biochemistry in plants and animals. BIOS Scientific Publishers, 2004.
- Buettner, GR and Schafer, FQ. "Ascorbate as an antioxidant." Vitamin C: Function and biochemistry in plants and animals. BIOS Scientific Publishers, 2004.
- Cotton, FA; Wilkinson, G; Gaus, PL. Basic Inorganic Chemistry (3rd ed.) John Wiley & Sons, 1995, 566-67.
- Hsieh, YHP; Hsieh, YP. Valence State of Iron in the Presence of Ascorbic Acid and Ethylenediaminetetraacetic Acid. *J. Agric. Food Chem.* 1997, 45, 1126-1129.
- Hsieh, YHP; Hsieh, YP. Kinetics of Fe(III) Reduction by Ascorbic Acid in Aqueous Solutions. *J. Agric. Food Chem.* 2000, 48, 1569-1573. May, JM; Asard, H. "Ascorbate recycling." Vitamin C: Function and biochemistry in plants and animals. BIOS Scientific Publishers, 2004.
- Miller, DM; Buettner, GR; Aust, SD. Transition Metals as Catalysts of "Autoxidation" Reactions, *Free Radic. Biol. Med.* 1990. 8, 98-108
- Ryan, TP; Aust, SD. The Role of Iron in Oxygen-Mediated Toxicities, *Crit. Rev. Toxicol.* 1992, 22, 119-141.
- Shriver, DF; Atkins, PW. Inorganic Chemistry (3rd ed.) Oxford University Press, 1990, 155-156.
- Song, B; Aebischer, N; Orvig, C. Reduction of $[\text{VO}_2(\text{ma})_2]^-$ and $[\text{VO}_2(\text{ema})_2]^-$ by Ascorbic Acid and Glutathione: Kinetic Studies of Pro-Drugs for the Enhancement of Insulin Action. *Inorg. Chem.* 2002, 41, 1358-364.
- Spiro, TG; Saltman, P. Polynuclear complexes of iron and their biological implications. *Struct. Bonding* 1969, 6, 116-156.
- Velasco, J; Ibrahim, E. Determination of the Reductive Performance of Ascorbic Acid on Fe(III) Against the Fe(II)-catalyzed Fenton Reaction. 2005, *Unpublished*.

Zhu, B.; Frei, B. "Interactions of Vitamin C and Iron." The Antioxidant Vitamins C and E. AOCS Press, 2002.

BIOGRAPHICAL SKETCH

Jonathan Velasco graduated with from the University of Texas – Pan American in 2005 with a Bachelor of Science degree in Chemistry, designated an honor student per the requirements of the University Honors Program, minoring in Biology and English. He received his Master of Science degree, also in Chemistry, with University of Texas – Pan American in 2010. Professionally, he is a science teacher for South Texas High School for Health Professions (‘Med High’, Mercedes, TX) of South Texas Independent School District.

He currently lives in 2501 N. McColl Road, Apartment 825, McAllen, Texas, 78501.