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A Study of the Kinetics of a Reaction between VO(HEDTA)-1 and Hydrogen Peroxide

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A Study of the Kinetics of a Reaction between $VO(HEDTA)^{-1}$ and Hydrogen Peroxide.

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Dr. Jeffrey Wardeska, Thesis Mentor Date

Dr. Sharon Campbell, Thesis Mentor Date

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Abstract

Vanadium is commonly used as an agent to make tools rust-resistant. As a transition metal, it can be used as a catalyst due to its ability to change oxidation states. $VO(HEDTA)^{-1}$, a complex of the vanadyl ion, VO^{2+} and HEDTA (N-(2-Hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid) was readily formed. This complex containing vanadium in the +4 oxidation state was reacted with hydrogen peroxide to form a vanadate complex. This vanadate complex was formed as a first step in simulating the vanadate(V)-dependent haloperoxidases in marine algae, a yet uncharacterized reaction. Electron absorption spectroscopy (UV-Vis) was used to observe the oxidation of V(IV) in the complex to V(V) through the color change of the complex from blue to yellow. This color change was observed through the formation of a peak at 450nm. By changing the initial concentrations of $VO(HEDTA)^{-1}$, hydrogen peroxide, and hydronium ion, the change in absorbance at 450nm during the first minutes of the reaction was correlated with time to determine the initial rates for each reactant. Using this method, a rate equation for the reaction was determined. The rate of reaction was determined to be first order with respected to $VO(HEDTA)^{-1}$ and H_2O_2, and 1/2 order with respect to H^+. This half-order indicates that the hydronium ion is engaged in a reversible reaction. The involvement of hydroxyl radicals produced by the reaction, as shown by the effect of free radical scavengers to inhibit the reaction was also studied.

Introduction

Vanadium is most often used industrially for its corrosion and shock resistance. It is added to steel alloys in order to improve them for work in the automotive and aircraft industry.[1] Because of its neutron resistance, it is also useful for applications of nuclear chemistry, used in the creation of tubing for the nuclear power industry.[1] Vanadium, in the form of vanadium(V) oxide (V_2O_5), is used as an industrial catalyst for the formation of sulfuric acid through the conversion of sulfur dioxide to sulfur trioxide.[2] Vanadium chemistry is unique in that it can access all four oxidation states from +2 to +5. A derivative of V_2O_5, NH_4VO_3 can be reduced with zinc and acid to form the vanadyl ion, $VO(H_2O)_5^{2+}$, in aqueous solution.[3] The vanadyl ion, commonly represented as VO^{2+}, can be further reduced to V(III) and V(II).[3] The different oxidation states of vanadium in these reactions produce differently colored solutions (Figure 1). Color changes between oxidation states are visible in the reaction of $VO(HEDTA)^{-1}$ with H_2O_2, the blue solution (V(IV)) becoming yellow (V(V)) over the course of the reaction.

Figure 1. Oxidation states of vanadium from +5 to +2 (left to right).[4]

Vanadium is the second most abundant transition metal in sea water. This is due to the abundance of vanadium in marine algae, which, through their use of vanadate-dependent haloperoxidases (VHPOs), catalyze the oxidation of halide ions by H_2O_2.[5] There are numerous halogenated natural products in marine algae that require oxidation in order to be used as electrophilic intermediates.[6] Hydrogen peroxide is used to convert a halide ion (X^-) to a hypohalite (—OX), such that it is equivalent to an electrophilic X^+.[6] These molecules are necessary for certain biological pathways in marine algae such as chemical defense and signaling.[6] Haloperoxidases are responsible for this halogenation, which often comes without a change in oxidation state for the vanadium center of the enzyme, as would occur with the use of the heme enzyme.[6] This property, along with the high tolerance of VHPOs for organic solvents and high temperatures, ability to halogenate specifically, and oxidation capability in the absence of halides has brought a great amount of attention to VHPOs.[7,8] These abilities have generated interest for pharmaceutical applications as biocatalysts.[9] The kinetics of the formation of peroxycomplexes with vanadium have not been fully studied, with the focus being generally on characterization of the structural properties of these complexes. The aim of this research is to determine the kinetics of the formation of a vanadate(V) complex from the HEDTA complex of vanadyl (IV), $VO(HEDTA)^{-1}$, possibly serving as a model system for understanding the mechanism of VHPOs. Because the oxidation of vanadyl complexes to vanadate is a one electron oxidation and the reduction of hydrogen peroxide is a two electron reduction, it is important to characterize the mechanism of this reaction in order to fully understand the biological pathways in these organisms.

Reactions of transition metals with H_2O_2 often lead to the formation of hydroxy and peroxy free radicals. These reactions are referred to as Fenton reactions, after the man who studied them, Henry John Horstman Fenton.[10] These reactions were characterized based on the reaction of iron(II) and iron(III) and H_2O_2 (Figure 2).

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \text{ ----> } \mathrm{Fe}^{3+} + \cdot\mathrm{OH} + \mathrm{OH}^-$$

$$\mathrm{Fe}^{3+} + \mathrm{H_2O_2} \text{ ----> } \mathrm{Fe}^{2+} + \cdot\mathrm{OOH} + \mathrm{H}^+$$

Figure 2. Fenton reaction of iron and hydrogen peroxide[11]

Fenton reactions are important in biochemical contexts not only because the reduction of iron from Fe(III) to Fe(II) is critical in biological systems, but also due to the creation of reactive oxygen species (ROS). The formation of ROS leads to the damage of many biomolecules and biomolecular systems. These molecules are also the driving force of iron redox cycling, however, and vital to the generation of necessary iron concentration in biological systems.[10] The formation of the V(V) product in this research possibly occurs through a Fenton-like reaction, the H_2O_2 present in the reaction breaking into its free radical constituents and driving the reaction.

Materials and Methods

Preparation of $VO(ClO_4)_2$

Solutions of $VOSO_4$ (0.2500 M, 6.324 g in 100 mL) and $Ba(ClO_4)_2$ (0.2500 M, 9.753g in 100 mL) were combined in a double replacement reaction to form $VO(ClO_4)_2$.

$$VOSO_4\ (aq) + Ba(ClO_4)_2\ (aq) \rightarrow VO(ClO_4)_2\ (aq) + BaSO_4\ (s)$$

The precipitate of $BaSO_4$ was separated through vacuum filtration with a fine glass filter to obtain a solution of $VO(ClO_4)_2$ with a concentration of 0.0825M. UV-Vis spectrometry was used to obtain a spectrum of the solution.

Preparation of $VO(HEDTA)^{-1}$

HEDTA (0.9183g) was added to 40 mL of the 0.0825M solution of $VO(ClO_4)_2$ along with 9.9 mL of 1M NaOH and 5 mL 0.1M KNO_3 for ionic strength to produce a 19.3mM solution of $VO(HEDTA)^{-1}$.

$$VO(ClO_4)_2\ (aq) + HEDTA\ (s) + 3\ NaOH\ (aq) \rightarrow VO(HEDTA)^{-1}\ (aq) + H_2O$$

Perchloric acid was added to adjust the $VO(HEDTA)^{-1}$solution to a pH of ~2.7. UV-Vis spectrometry was used to obtain a spectrum of the solution.

Reaction of H_2O_2 with $VO(HEDTA)^{-1}$

Hydrogen peroxide (0.088M) was prepared by diluting 1 mL of 30% solution (0.88 M) to 10 mL. Aliquots of 0.2 mL of this diluted H_2O_2 were added to 25 mL of the solution of $VO(HEDTA)^{-1}$ and UV-Vis spectrometry was used to obtain spectra of the reaction at various times from 0 to 90 min (0 to 5400 sec).

Determination of Rate Equation through Initial Rate Reactions

The concentrations of H_2O_2 and H^+ (with the use of $HClO_4$) were changed in the reaction of H_2O_2 and $VO(HEDTA)^{-1}$. Concentrations of H_2O_2 in the $VO(HEDTA)^{-1}$ reaction solution were 1.725mM (0.5 mL of 0.088M), 1.386mM (0.4 mL of 0.088M), 1.043mM (0.3 mL of 0.088M), 0.698mM (0.2 mL of 0.088M), and 0.351mM (0.1 mL of 0.088M). Adjusting acid concentration, the reaction was run at varying pH: 3.213, 2.667, 2.5, 1.999, and 1.504. The first 5 minutes of these reactions were monitored at 450 nm with UV-Vis spectrometry.

Addition of Free Radical Scavengers

Ethanol and sodium formate were added to the reaction of H_2O_2 and $VO(HEDTA)^{-1}$ such that their concentrations were 0.2090M (0.5 mL of 20.65M) and 0.1786M (0.306 g, 4.5 mmol in 25 mL), respectively. UV-Vis spectrometry was used to obtain spectra of the reaction at various times from 0 to 90 min (0 to 5400 sec).

Results and Discussion

Preparation of $VO(ClO_4)_2$

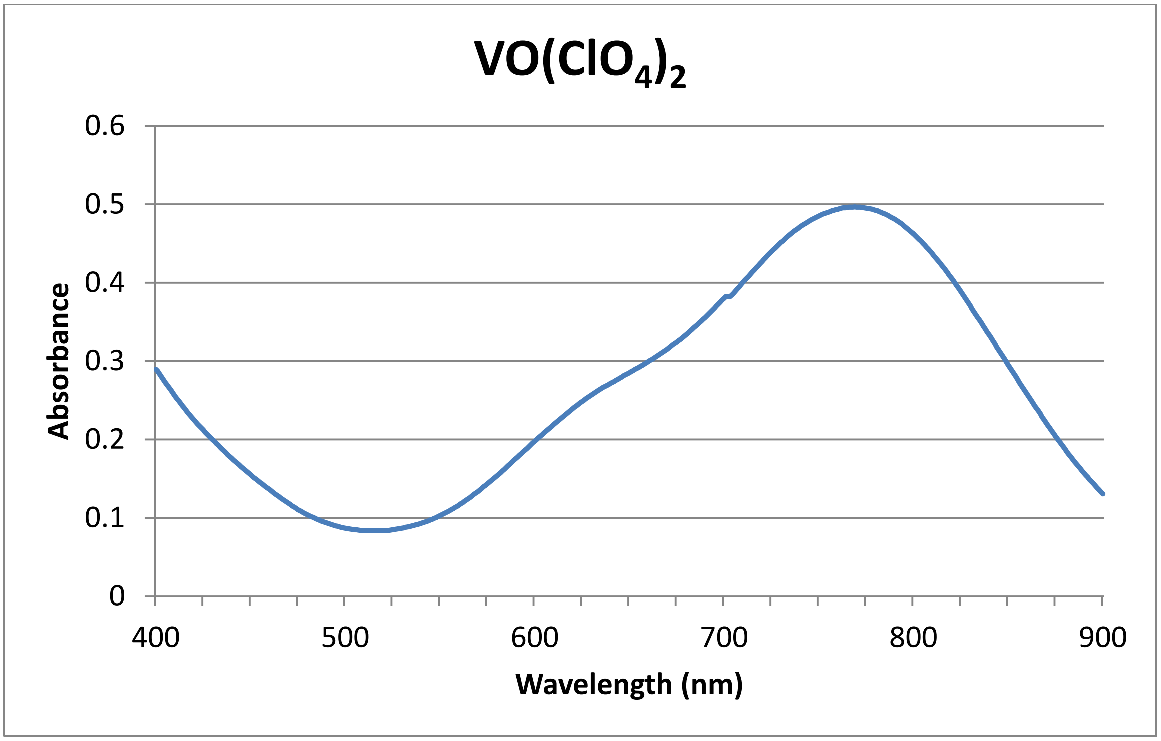

Figure 3. UV-Vis spectrum of $VO(ClO_4)_2$

The absorbance spectrum of $VO(ClO_4)_2$ (Figure 3) showed a peak at 770 nm, indicating the presence of VO(IV). A similar peak, at 775 nm, was also in the spectrum of $VO(HEDTA)^{-1}$ (Figure 4). A secondary peak was also visible in the spectrum of $VO(HEDTA)^{-1}$ at 584 nm. This peak was present in the $VO(ClO_4)_2$ plot as a shoulder at 625 nm. These peaks indicate a d-d transition in the d^1 electron of V(IV). In a perfectly octahedral ion, there would only be one transition with the d electron ($^2T_{2g} \rightarrow {}^2E_g$); the symmetry of this ion is slightly less than octahedral, however, leading to a second transition and causing a second peak, corresponding to the $^2B_{xy} \rightarrow {}^2B_{x2-y2}$ transition. The presence of a shoulder is consistent with the C_{4v} symmetry of the vanadyl ion, which causes splitting of the $^2T_{2g}$ and ^2E_g levels by the lower symmetry.[12,13] The $VO(HEDTA)^{-1}$ spectrum has a fully formed secondary peak because the complex has lower symmetry than that of $VO(ClO_4)_2$, approximately C_{2v}.[12] This symmetry approximation is confirmed by the work of Balhausen and Gray through their work on the $VO(H_2O)_5$ and VO(enta) complexes.[12] The $VO(HEDTA)^{-1}$ solution remains stable over time, but the solution of $VO(ClO_4)_2$ changes color over time, the solution becoming more green and the wavelength of the primary peak lowering. At pH values above 3.5, the $VO(HEDTA)^{-1}$ solution changes in color in a similar manner, the primary spectra peak shifting to a higher energy.

Preparation of $VO(HEDTA)^{-1}$

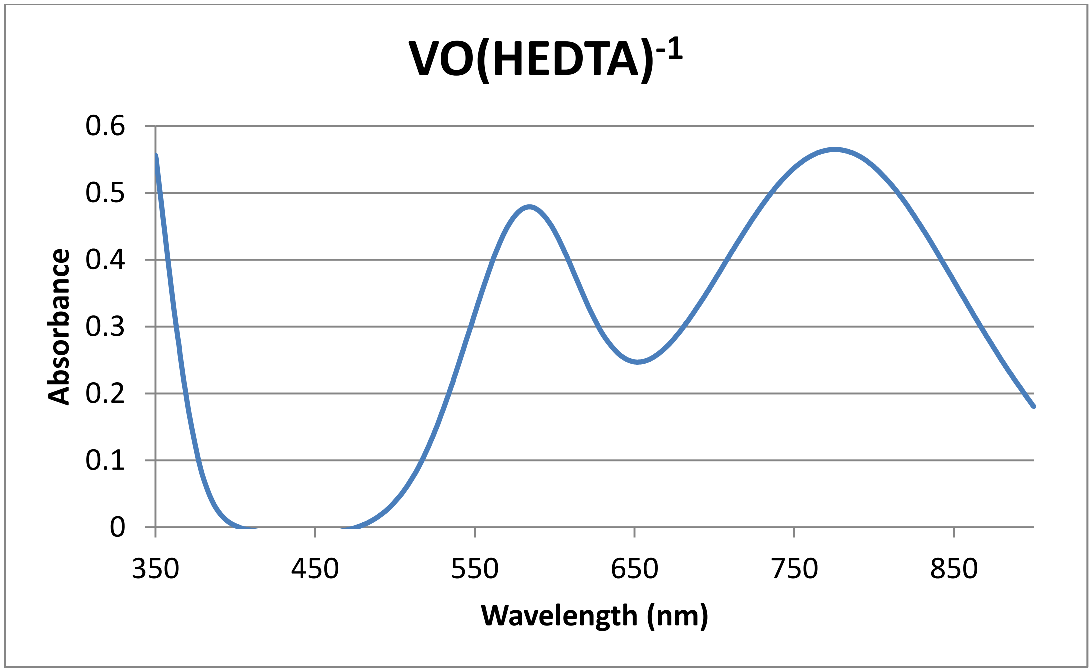

Figure 4. UV-Vis spectrum of $VO(HEDTA)^{-1}$

Reaction of H_2O_2 with $VO(HEDTA)^{-1}$

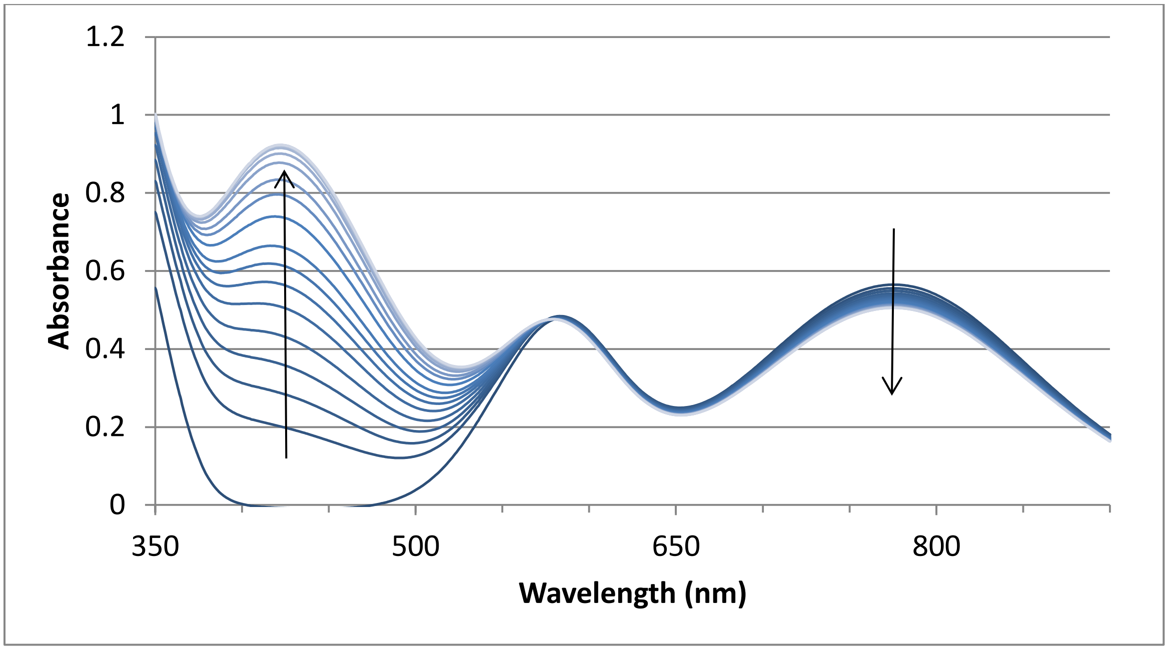

Figure 5. UV-Vis spectra of the reaction between H_2O_2 and $VO(HEDTA)^{-1}$ at: 0, 2, 4, 6, 8, 10, 12, 16, 20, 24, 28, 35, 42, 50, 60, 70, 80, and 90 min.

After adding H_2O_2, a series of spectra (Figure 5) were collected over the 90 minute duration of the reaction, showing a decrease in the intensity of the peak at 770 nm and the formation of a peak at 450 nm. These results indicate the reaction of the V(IV) ion in the reaction solution and the formation of a product with the V(V) ion present. This peak is characteristic of a monoperoxy complex of V(V), and the product is assumed to be such a complex. These spectra also show an isosbestic point at 570 nm, indicating that no side or intermediate reactions were occurring.

Determination of the Rate Equation

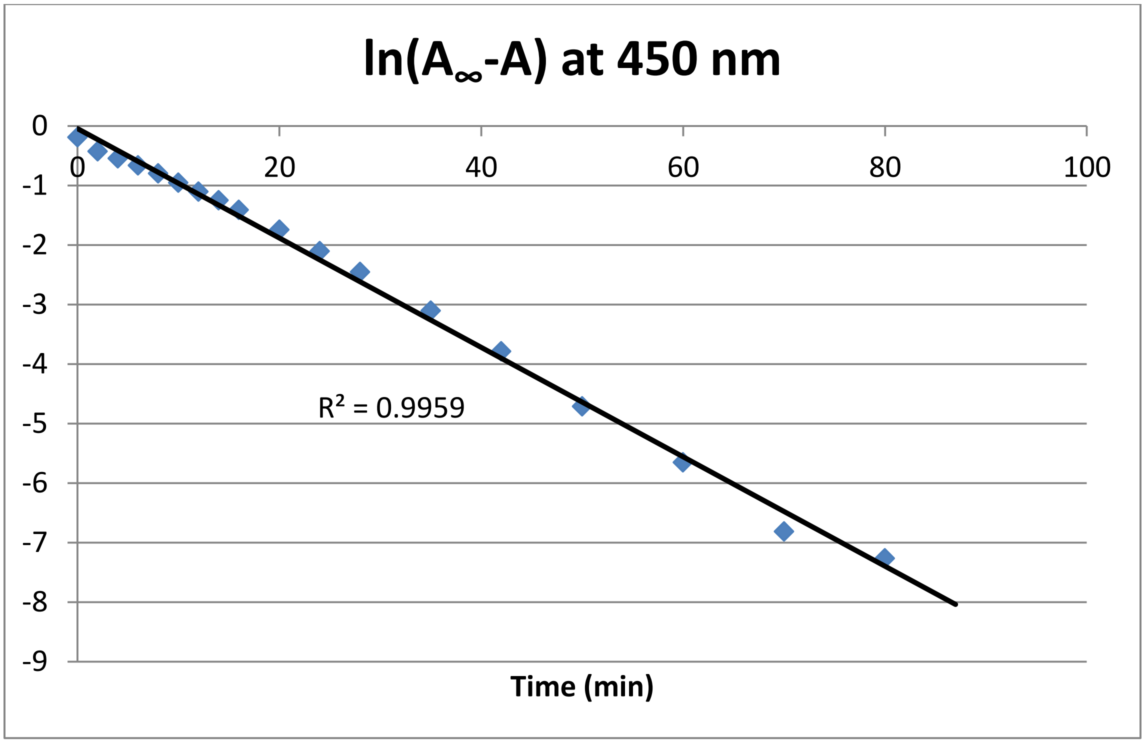

Figure 6. Determination of the order with respect to VO(HEDTA)$^{-1}$

The order of the reaction with respect to VO(HEDTA)$^{-1}$ was calculated from the absorbance data for the complex and H_2O_2. This was performed by taking the natural log of the difference between the absorbance value for 90 min and the absorbance value for each individual time point at 450 nm. The graphical representation of this equation (Figure 6) exhibited a linear correlation, indicating that the order with respect to VO(HEDTA)$^{-1}$ is first order. Because the experiments were all performed with H_2O_2 as the liming reactant and VO(HEDTA)$^{-1}$ in excess, it can be assumed that the order of the reaction does not change during the course of the experiment and that hydrogen peroxide reacted completely.

Having determined that the reaction was first order for VO(HEDTA)$^{-1}$, Beer's Law could be used to determine the maximum molar absorptivity for the V(V) product. Because VO(HEDTA)$^{-1}$ was first order in the rate equation, the change in the concentration of

$VO(HEDTA)^{-1}$ over the course of the reaction was equal to the change of the concentration of the V(V) product. Using the change in absorbance for the V(IV) reactant at 775 nm and its known molar absorptivity of 20.7, the molar extinction coefficient, ε_{450}, of $VO(HEDTA)^{-1}$ was calculated.

$$A = \varepsilon bc$$

$$\Delta[VO(HEDTA)^{-1}] = \Delta[V(V)product] = \frac{\Delta A}{b\varepsilon_{max}}$$

$$\varepsilon_{max} = \frac{\Delta A_{450}}{\Delta C_{VO(HEDTA)^{-1}}} = \frac{0.8188}{0.00286} = 286.30\ L\ mol^{-1}cm^{-1}$$

Initial Rate Experiments

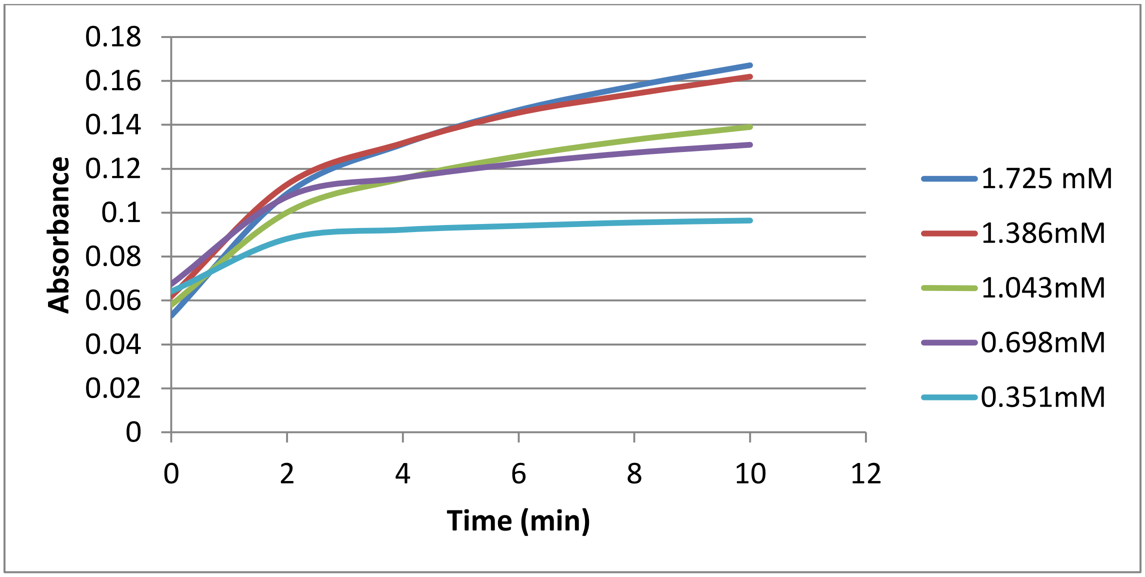

Figure 7. Absorbance at 450 nm for H_2O_2 trials at varying concentrations

In order to determine the order with respect to H_2O_2, initial rates of the reactions were measured by analyzing the first ten minutes of each reaction for the initial linear slope (Figure 7). The changes in absorbance per time unit between 0 and 2 minutes were determined and correlated against the concentration of H_2O_2 for each trial, again obtaining linear correlation

(Figure 8). When other correlations were used, a linear plot was not obtained. These results indicate that the reaction was first order with respect to H_2O_2.

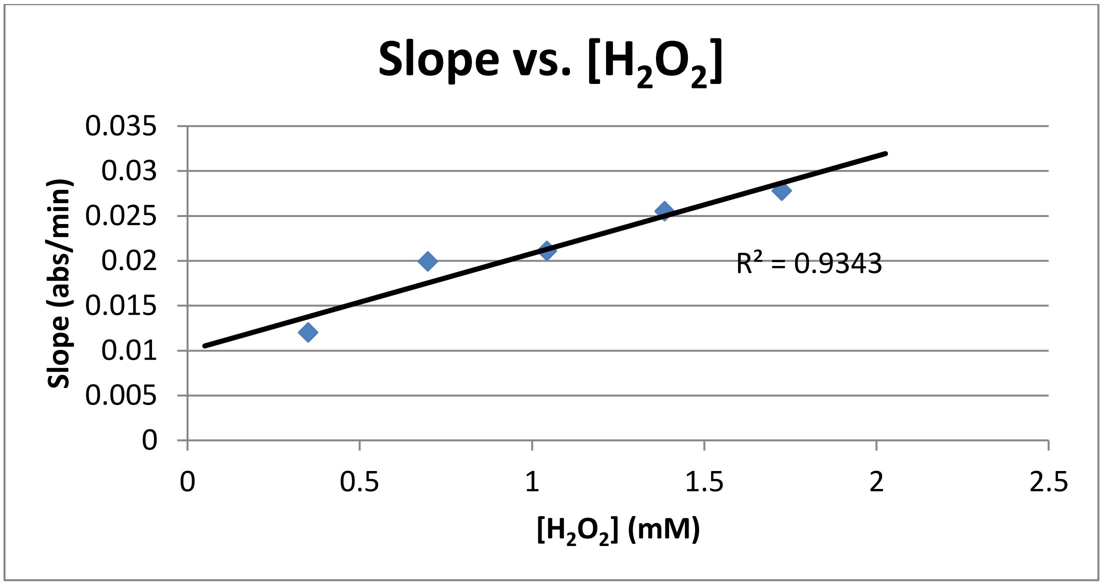

Figure 8. Determination of the order with respect to H_2O_2 by correlating slope of the initial rates for each trial against the concentration of that trial

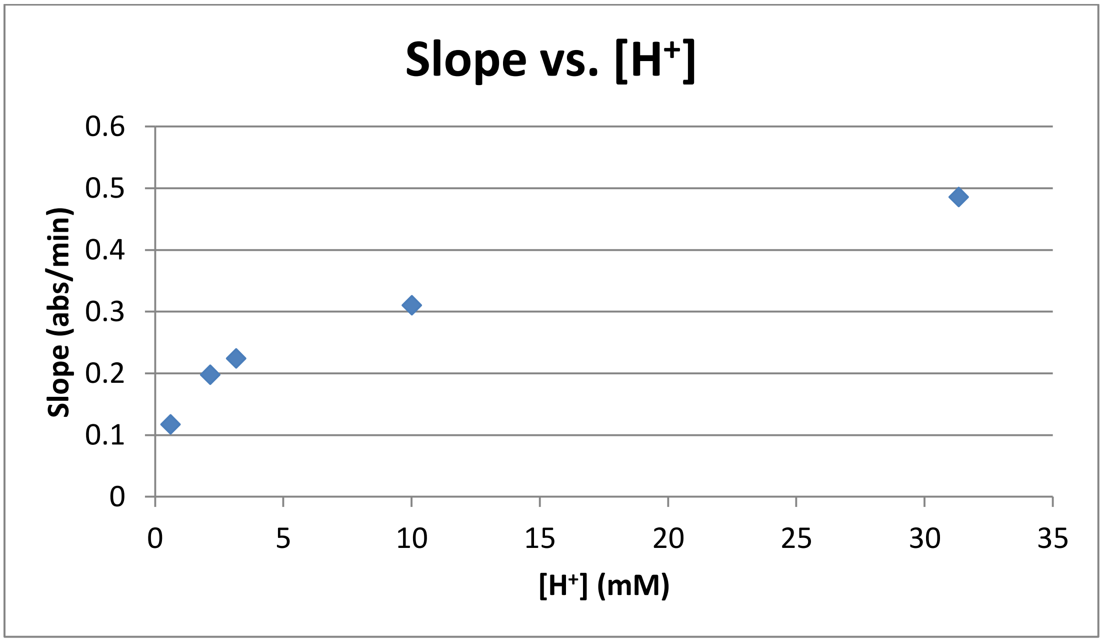

Figure 9. Slope of the initial rates for each acid trial correlated against the concentration of H^+ of that trial

Knowing from Hima Patel's research that pH had an effect on the reaction between $VO(HEDTA)^{-1}$ and H_2O_2, the order with respect to acid concentration must be determined to obtain a full rate equation.[14] This order was determined through the use of initial rate reactions. The correlation for zero and first orders for $[H^+]$ were not linear (Figure 9). A linear correlation was produced only by the graph of the slopes against the square root of the acid concentration indicating half order with respect to H^+ (Figure 10). This indicates the presence of a Fenton-like reaction with vanadium instead of iron.

1. $VO^{(IV)}(HEDTA)^{-1} + H_2O_2 \rightarrow VO^{(V)}(HEDTA) + {}^{\cdot}OH + OH^{-1}$
2. $VO^{(V)}(HEDTA) + H_2O_2 \leftrightarrow VO^{(V)}(O_2)(HEDTA)^{-2} + 2H^+$
3. $VO^{(IV)}(HEDTA)^{-1} + {}^{\cdot}OH \rightarrow VO^{(V)}(HEDTA) + OH^{-1}$
4. $VO^{(V)}(HEDTA) + H_2O_2 \leftrightarrow VO^{(V)}(O_2)(HEDTA)^{-2} + 2H^+$
5. $2H^+ + 2OH^{-1} \rightarrow 2H_2O$

The oxidation of V(IV) to V(V) is a one electron reduction. In order to fully reduce hydrogen peroxide into two hydroxyl ions, two electrons are required. This discrepancy causes a hydroxyl radical to be formed along with a hydroxyl ion. This free radical is necessary to complete the reaction (see below). The production of acid in the second step is reversible, meaning the concentration of acid both pushes the reaction towards the formation of the peroxyvanadium(V) complex as well causing the reaction to revert back to the original $VO^{(IV)}(HEDTA)^{-1}$. The reaction is pushed forward by the acid by pulling the hydroxyl ion produced from H_2O_2 to the product side of the equation, but the addition to acid of the vanadate product in the second step of the mechanism also pushes the reaction toward the formation of $VO^{(V)}HEDTA$. The ultimate effect of acid to reduce the peroxyvanadate product to

VO(HEDTA)$^{-1}$ is confirmed by Tinga Cliford Oyombe Fon's research on the decomposition of the V(V) product.[13]

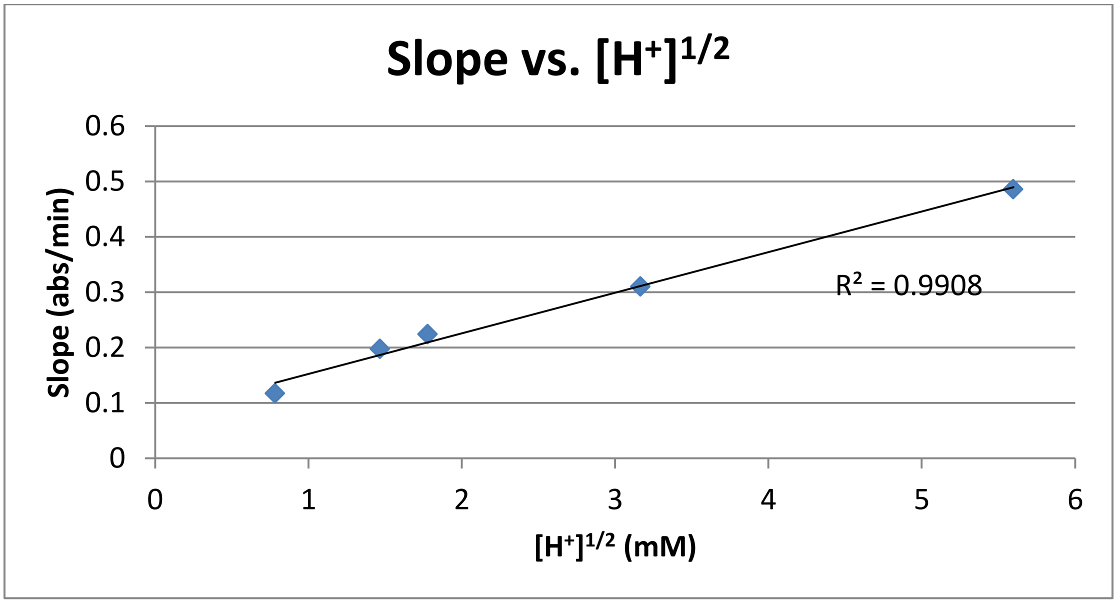

Figure 10. Determination of the order with respect to H$^+$ by correlating slope of the initial rates for each trial against the concentration of that trial

Addition of Free Radical Scavengers

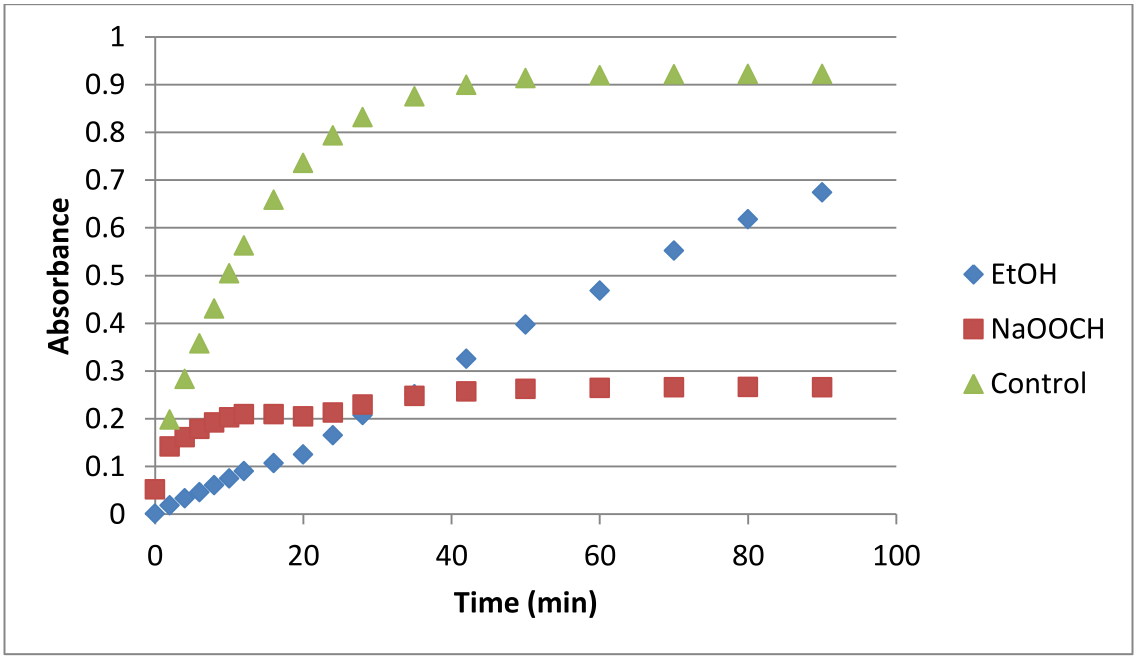

Figure 11. Comparison of absorbance at 450 nm with and without the addition of free radical scavengers

The hydroxyl radical produced in the first step of the Fenton reaction is integral to the progress to the reaction. Free radical scavengers prevent the formation of free radicals in this reaction by preventing the reduction of H_2O_2. Because the formation of the free radical is necessary for the reaction to progress, the addition of a free radical scavenger into the reaction mixture causes the reaction to be slowed or halted. When a weak radical scavenger (ethanol) was used in the reaction, the peak at 450 nm did not begin to form until 20 minutes into the reaction and formed at a much lower rate than without any scavenger. This indicates that ethanol was able to prevent the reduction of H_2O_2, but not permanently. When sodium formate was added, the peak did not form at all, the reaction halted at absorbance 0.3 (Figure 11). The difference in these results indicates that formate is a more effective free radical scavenger than ethanol. This experiment also indicates that the hydroxyl radical is necessary for the reaction to proceed and the V(V) product to be formed due to the lack of the V(V) product peak at 450 nm. These results are confirmed by the results of A. J. Carmichael in reactions with vanadyl ion and H_2O_2.[15]

Conclusions

This research has spectroscopically characterized the $VO(HEDTA)^{-1}$ ion and determined the molar extinction for this species. It has also resulted in the characterization of the rate equation for the reaction of $VO(HEDTA)^{-1}$ by hydrogen peroxide in acidic aqueous solution, and a tentative mechanism for this reaction is suggested.

$$Rate = k[VO(HEDTA)^{-1}][H_2O_2][H^+]^{1/2}$$

The half-order with respect to $[H^+]$ was also confirmed in the results of Hima Patel’s thesis.[14] The peroxyvanadium(V) complex slowly reduces back to the vanadyl ion, as characterized by Tinga Cliford Oyombe Fon.[13]

More research should be conducted on the free radical formation of this reaction, especially with regard to the necessity of radicals to convert the V(IV) reactant into the V(V) product. Kinetic experiments over a wider range of concentrations will be needed to completely determine the rate equations for this reaction. The implications of this reaction with regard to both free radical production and the conversion of halides in the biological processes of marine algae should be considered with more depth. More investigation on the formation and identification of the final peroxyvanadium(V) complex should also be pursued.

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