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The Analysis of the Decomposition of Hydrogen Peroxide Using a Schiff Base Copper Complex By Cyclic Voltammetry

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In partial fulfillment of the Honors-In-Discipline requirements

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Abstract

Copper(II) complexes of Schiff bases can be used in the catalysis of hydrogen peroxide to create water and oxygen. The mechanism and the kinetics of this disproportionation reaction by a dimeric copper(II) complex $[CuSALAD]_2$ have studied in this experiment, where SALAD refers to a Schiff Base ligand formed from salicyaldehyde and 1S,2S-D(+)-1-phenyl-2-amino-1,3-propanediol. The $[CuSALAD]_2$ initially reacted with a base such as imidazole to form the catalytic species, and the ratio of the copper(II) complex to the imidazole was found to be 1:4, consistent with previous electron absorption (UV-Vis) spectroscopy experiments. The reduction and oxidation half waves of the copper(II) catalyst were followed *via* cyclic voltammetry to determine if the copper(II) center undergoes reduction to copper(I) during the hydrogen peroxide catalysis. It has appeared that while the major oxidation and reduction half wave potentials, $E_{1/2}=6.51\times10^{-2}$V, remain unchanged during the decomposition, an additional oxidation wave ($E_{1/2}=1.43\times10^{-1}$V) is observed in the absence of oxygen, suggesting that some portion of the copper is reduced. With this information, a mechanism has been proposed having copper as a catalyst and creating an intermediate that would form the water and the elemental oxygen.

Acknowledgements

I would like to first thank God who, without Him, I would not be here today being able to do anything. With that same accord, I would like to thank my church family who has been faithful and dedicated to my growth as a Christian and as a man. In particular, I would like to thank Mike Mould, who has challenged my entire being, yet has had the good graces to guide me in my walk.

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I would like to also mention my family that has helped me in continuing on in my research even when it got difficult to see the end. My work is finally completed.

I would like to also thank Dr. Zhao and Dr. Roginskaya for both helping me in their own ways. Dr. Zhao was my first chemistry professor at ETSU and made me fall in love with chemistry all over again. Dr. Roginskaya helped, and continues to help, me on my presentation for defending my thesis.

Finally, I would like to thank the Honors College at ETSU for the opportunity that they have provided me with the Honors-In-Discipline Scholarship. Without the HID Scholarship and the staff I have met along the way, I would not have been able to make it through ETSU for the four years to get my Bachelor's Degree.

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Introduction

Copper is one of the many elements that continue to surprise many researchers when they study the properties that it possesses. One area of interest is the ability for copper(II) complexes of Schiff bases, which according to the Compendium of Chemical Technology, is an imine bearing a hydrocarbyl group on the nitrogen atom (i.e. $R_2C{=}NR'$), to act as a catalyst in the decomposition of hydrogen peroxide (H_2O_2) to oxygen and water[1][2].

$$2H_2O_2 \xrightarrow{catalyst} O_2 + 2H_2O \qquad \text{Equation1}$$

but the mystery lies in the mechanism of how this reaction occurs.

The study performed will include the use of copper(II), salicylaldehyde (SA), and (1S,2S)-$(+)_D$-1-phenyl-2-amino-1,3-propanedoiol (LAD)[5]. In order to make this solution, the SALAD portion must be made first as shown in the Figure 1.

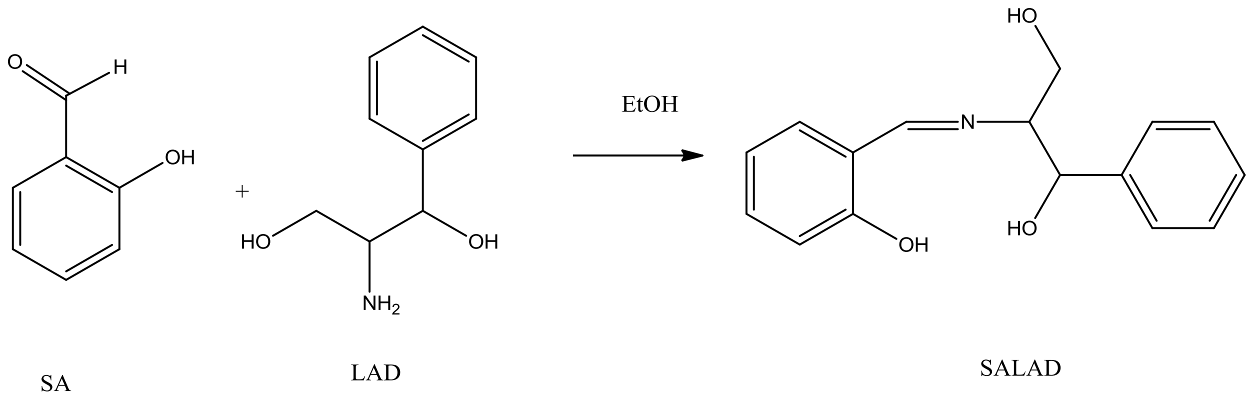


Figure1. A detailed reaction of salicyaldehyde (SA) and (1S,2S)-$(+)_D$ 1-phenyl-2-amino-1,3-propanedoiol (LAD) reacting in ethanol to create the Schiff base, commonly referred, to as SALAD.

When the Schiff base has been formed, copper(II) acetate monohydrate is added to the Schiff base and creates the compound shown in Figure 2 which is known as $[CuSALAD]_2$. There is a subscript two to indicate that the structure creates a dimer of the CuSALAD compound.

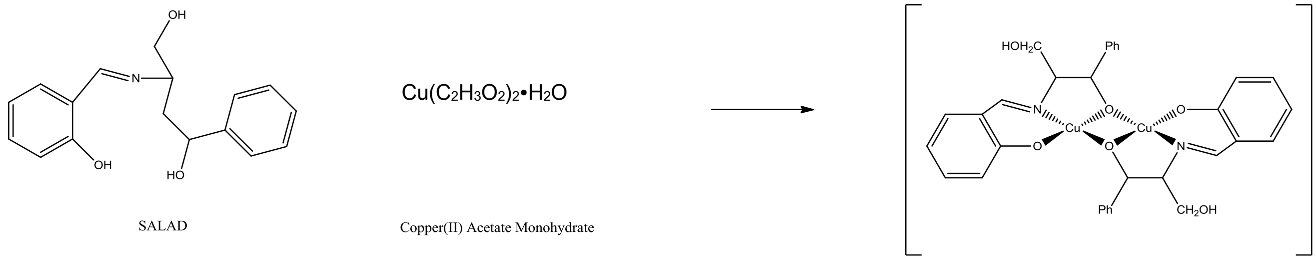


Figure 2. The detailed reaction between SALAD and Copper (II) Acetate Monohydrate to form the $[CuSALAD]_2$ compound.

There are three oxidation states that copper can form; the (I), the (II), and the (III), in extreme conditions. In this compound, the copper is assumed to be in the copper(II) state. In this state, copper complexes often form a four coordinate square planar or a five coordinate square pyramidal structure. With this multi-coordinate ability, the copper site is a very good candidate for binding the hydrogen peroxide and initiating the catalatic reaction. Using the $[CuSALAD]_2$, a base, such as different forms of imidazole (i.e. imidazole, 1-methyl-imidazole, 2-methyl-imidazole, etc.), can be used to split the dimer. The same base can be used at a higher concentration in order to allow the copper to create a five coordinate square pyramidal structure.

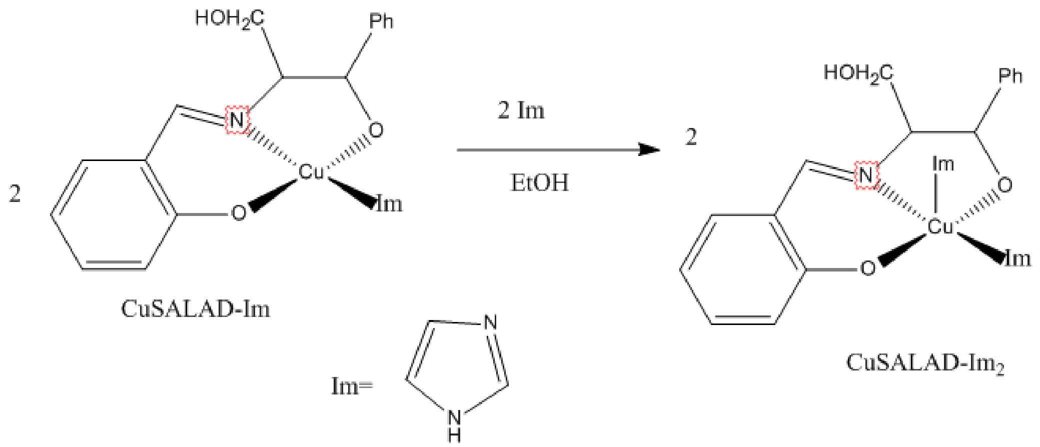


Figure 3. Detailed reaction of CuSALAD-Imidazole reacting with Imidazole to create the CuSALAD-Im_2 complex.

The reaction of $[CuSALAD]_2{\cdot}2Im$ complex with hydrogen peroxide has been investigated using electronic absorption spectroscopy (UV-Vis) to study how the complex decomposes hydrogen peroxide. The proposed intermediate is in Figure 4; it shows a band in the UV-Vis spectrum at about 450 nm [2].

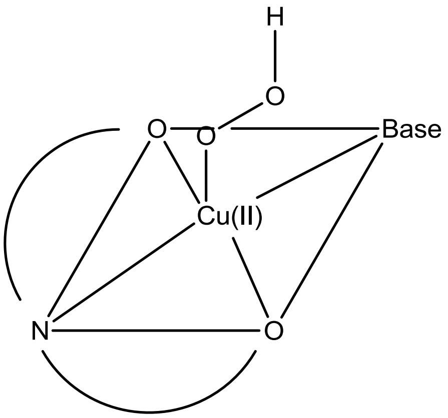
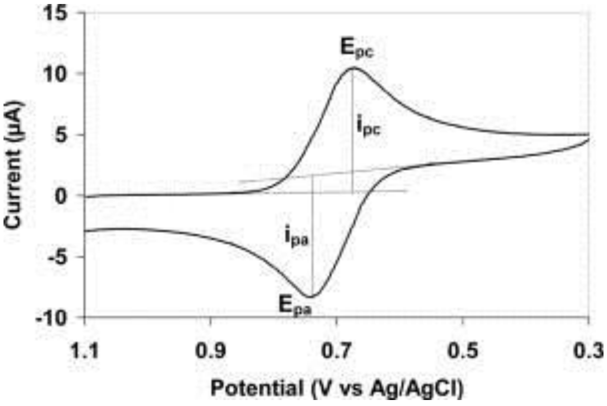


Figure 4. The structure of the copper intermediate used to decompose hydrogen peroxide as proposed in other studies[2].

Knowing that there are various forms of oxidation that copper can take on, the question was raised whether or not the oxidation state of the copper changed throughout the reaction, hence the purpose of this study.



Cyclic voltammetry is very useful since it is able to determine the oxidation and reduction of certain ions. By using three electrodes, cyclic voltammetry will send an electron through the solution and will monitor the rate of oxidation and reduction. The three electrodes are the working electrode that sends the electron through the solution and accepts it (common working electrodes include gold, platinum, and glassy carbon), the reference electrode that shifts the graph to the left or the right depending on the electrode used for easy analysis of the graph (a common reference electrode is a Ag/AgCl electrode), and the counter electrode that is used to measure the current between itself and the working electrode (a common counter electrode is a platinum wire). The peaks that are shown in the y-axis on a cyclic voltammetry graph represent the current that it took for the electron to be accepted for the cathodic state and the anoidic state. The cathodic scan represents the reduction (E_{pc}) and the anodic scan represents the oxidation (E_{pa}). The distance between the two peaks plays a factor in the reaction that occurs. When a reaction is reversible, meaning there is an equilibrium between the two proposed oxidative states, the peaks will be roughly 0.06 V (60mV) from each other for a $1e^-$ transfer based on Nernst Equation addition[6]. The intensity of the peaks is proportional to the concentration of the reaction.

There are many variables that can factor into the readings of cyclic voltammetry. With a higher scan rate, more intense peaks are made, but with slower scan rates, more precise and more reversible readings are given with smaller peaks. The common scan rate is 50 mV/s because it provides intense peaks and gives the electrode time to absorb the electron in a qualitative method. The scan range can affect a reading as well because the scan being ran will have a "start-up" and a "slow-down" peaks that do not represent the compound in question. The "start-up" and "slow-down" peaks may show skewed results because the electronic potential starts and when it is turning off. There is no clear way to measure if the machine turns the current on/off immediately, therefore we assume that there is a period of time when the current is beginning or ending. Most of the time, an 800 mv scan range (-400 mV to 400 mV) is suitable. In the experiment performed, a 650 mV range is used instead to ensure that the reduction and oxidation of oxygen did not affect the readings. The number of scans must be 4 or more because the first scan gets an initial current that makes the curve have a steep decline that does not fit the expected curve. The last scan must be taken out as well because the current will suddenly stop making the curve have a steep incline to zero potential. The final variable is the scan range that will limit the view of the graph to a certain area. Scan range is helpful focusing in on a small portion of the cyclic voltammetry graph or widening the view to see larger peaks.

With the use of cyclic voltammetry, it is possible to determine whether a compound changes the oxidation state with a test run. By using the peak intensity and positions of the peaks, the oxidation/reduction state of a reaction can be easily determined. With this technique, it can be determined whether this reaction uses an oxidation/reduction mechanism or a catalytic mechanism.

Beng [1] proposed a mechanism for the decomposition of hydrogen peroxide using [CuSALAD-B_2] with the [H_2O_2] being in excess:

$$CuB_2 + H_2O_2 \leftrightarrow CuBOOH^- + BH^+ \qquad (1)$$

$$CuBOOH^- \rightarrow CuBOH^- + 1/2O_2 \qquad (2)$$

$$CuBOH^- + BH^+ \rightarrow CuB_2 + H_2O_2 \qquad (3)$$

Cu= $[CuSALAD]_2$ B=Imidazole (i.e. CuB_2= [CuSALAD]·2Im)

Finnochio [2] then stated that Beng's theory shows limited aspects of the catalytic process and proposed a new mechanism for the decomposition of H_2O_2:

$$CuB_2 + H_2O_2 \leftrightarrow CuBOOH^- + BH^+ \qquad (4)$$

$$CuBOOH^- + H_2O_2 \rightarrow (Cu(OOH)_2)^{2-} + BH^+ \qquad (5)$$

$$(Cu(OOH)_2)^{2-} + 2BH^+ \rightarrow {}^*CuB_2 + 2H_2O + O_2 \qquad (6)$$

Cu= $[CuSALAD]_2$ B=Imidazole (i.e. CuB_2= [CuSALAD]·2Im)

With this mechanism, Finnochio proposed that both the water and the elemental oxygen detached from the intermediate that was formed. Finnochio's proposed mechanism also has the assumption that the Cu will have to be reduced to the Cu(I) state during the reaction, as shown by the asterisk.

In this study, cyclic voltammetry was used to test whether or not the Cu(I) is ever formed in the reaction and, if it is, about how long it takes in order to form the oxidation state. There are certain aspects of cyclic voltammetry that need to be made in the lab. A supporting electrolyte is repured, the electrolyte can be something as simple as KNO_3, but for this experiment tetrabutyl ammonium perchlorate (TBAPC) will be used as the electrolyte and thus must be made. TBAPC is a good electrolyte in organic solvents such as the solution used in the experiment, ethanol. The temperature and pH of this reaction was not changed such as those of Finnochio and Beng's experiments. This experiment includes the use of argon to saturate the system with a gas other than oxygen to ensure that the system does not depend on natural oxygen to push the reaction to completion. The instrument being used to study the complex's oxidation state with cyclic voltammetry will be the BASi EC Epsilon. BASi EC Epsilon has been used to study the complex's ability to oxidize and reduce.

Materials and Methods

Preliminary Potassium Ferrocyanide Experiments

To make the potassium ferrocyanide solution, about 1.0 g of KNO_3 was mixed in 100 mL of deionized water. Potassium ferrocyanide, 0.440 g (1.19×10^{-3} mol), was added to the solution to make a 0.0119 M solution. The scan rate was set at 5 mV/s, the potential was set between -100 mV and 700 mV, and the full scale (y-axis) was set at 10 μA. The electrode was polished using powdered Al_2O_3 and deionized water. The electrode was then checked under a microscope to ensure that there were no scratches or blemishes. The full scale was changed to 100 μA at times to see if the graph fits better on the setting. The scan rate was also varied to 50 mV/s and 100 mV/s to see the effects on the graph.

Polishing the Working Electrode

A base with polishing paper on top was obtained. A spatula full of Al_2O_3 was placed on the base, and a plastic pipet was used to apply distilled water to the Al_2O_3, making sure that the mixture was not watery, but also did not have chunks in it. The glassy carbon electrode was then lightly rubbed on the felt part of the polishing paper and the Al_2O_3 suspension. The electrode should feel as though "it were skating on ice," as claimed by Dr. Peng Sun. If the electrode is forced too hard onto the polishing paper, divots will show up in the electrode, but if the electrode is not pushed onto the felt hard enough the indentions on the electrode would persist. There was constant changing of directions with the electrode to ensure that, if pressed too hard, there would not be lines left on the electrode. The electrode was then checked under a microscope using multiple lenses to ensure that there were not any indentions.

Synthesizing and Purifying Tetrabutylammonium Perchlorate (TBAPC)

54.414 g of tetrabutylammonium bromide (TBABr) was added to 500 mL deionized water in a 1000mL beaker. A mixture was made with 15 mL of water and 15 mL of 70% $HClO_4$ that was poured into the TBABr slowly to create a white precipitate. The product, tetrabutylammonium perchlorate (TBAPC), was suction filtered and dried on the filter in a large watch glass to ensure the absence of contaminants. The product was weighed after a week of drying. A percent yield of 93.1% (50.656 g) TBAPC was recovered.

To recrystallize TBAPC, a 100 mL beaker was filled with 25 mL of DI water and 4.9995 g of the TBAPC was added. The mixture was heated until near boiling and DI water was added in 1.0 mL increments until the TBAPC completely dissolved. The total amount of volume that was used was 135 mL of water in the first trial and 112 mL of water in the second trial. The process yielded 3.1428g of TBAPC or 62.862% recovered.

Preliminary Voltammetry tests of $[CuSALAD]_2$

0.353 g of TBAPC was placed in a 100mL flask. Ethanol was then added until the lower meniscus was touching the 100 mL line. Two glassy carbon electrodes, one as the working and one as the reference, were used to scan the mixture. The scan rate was set at 10 mV/s, the potentials were set at -100 mV and 700 mV, and the full scale was set at 100 μA. There was a flat base line when the scan was taken. Both of the glassy carbon electrodes were polished with Al_2O_3 powder and deionized water. An arbitrary amount of $[CuSALAD]_2$ was added to the ethanol/TBAPC mixture and a cyclic voltammogram was taken. An arbitrary amount of imidazole was crushed up and added it to the $[CuSALAD]_2$. There was a color change observed and another cyclic voltammogram was taken with the same parameters that were used for the observation of the $[CuSALAD]_2$ complex by itself.

Determination of the Mole ratio of $[CuSALAD]_2$ to Imidazole

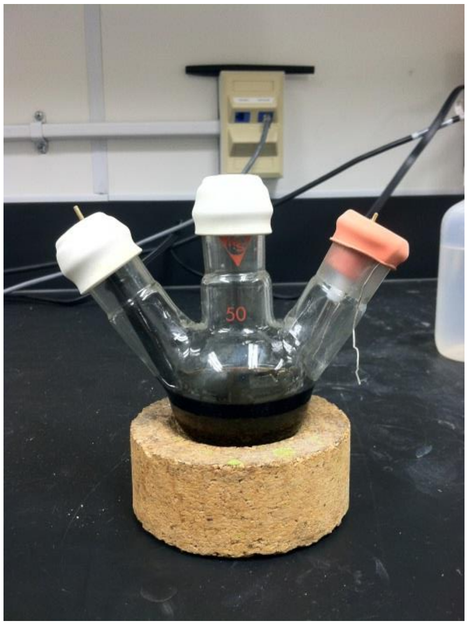
10mL of a 0.01 M $[CuSALAD]_2$ solution was made in ethanol with 0.0683 g ($1.0x10^{-4}$ mol) $[CuSALAD]_2$ until 10 mL was obtained and 0.3419 g TBAPC was added to the solution. A 1.0 M imidazole solution was made in ethanol using 1.7019 g ($2.5x10^{-2}$ mol) imidazole and adding 0.854775 g TBAPC to make the 25 mL of solution. The solution was sealed with Parafilm and argon gas was allowed to bubble through the solution for 10 minutes. A CV scan of the $[CuSALAD]_2$ solution was obtained at the scan rate of 50 mV/s and with the scan range of -250 mV to 400 mV and both cathodic and anodic peaks were recorded. The range was condensed due to a peak that formed on the right side of the graph that was assumed to be oxygen reducing. The glassy carbon was used as the working electrode, the Ag/AgCl electrode was the reference electrode, and platinum was used as the counter electrode. Once that run was performed, 25 μL of the imidazole solution was added to the $[CuSALAD]_2$ solution, the CV scan recorded. Scans were performed with increments of 50, 75, 100, 200, 300, 400, 500, 600, 700,800, 900, 1000, 1200, 1500, and 2000 μL of imidazole. The results were all recorded.

The Reaction of Hydorgen Peroxide in $[CuSALAD]_2$·Imidazole complex

Using the solution that was used to test the mole ratio of $[CuSALAD]_2$ to imidazole, 50 μL ($1.5x10^{-6}$ mol) of 3% hydrogen peroxide was added to the solution and a cyclic voltammetry scan was performed. The results were recorded over the span of an hour, running a cyclic voltammetry scan once every 5 minutes.

In a second experiment, a new solution was made up of 0.002 g (2.36×10^{-6} mol) of Imidazole, 0.1089 g (1.59×10^{-4} mol) of CuSALAD, and 1.059 g of TBAPC. The new mixture was reacted with 50 µL of 3% hydrogen peroxide that was diluted from 30% hydrogen peroxide.

The Reaction of Hydrogen Peroxide in $[\mathrm{CuSALAD}]_2\cdot$Imidazole complex in the prescence of Argon

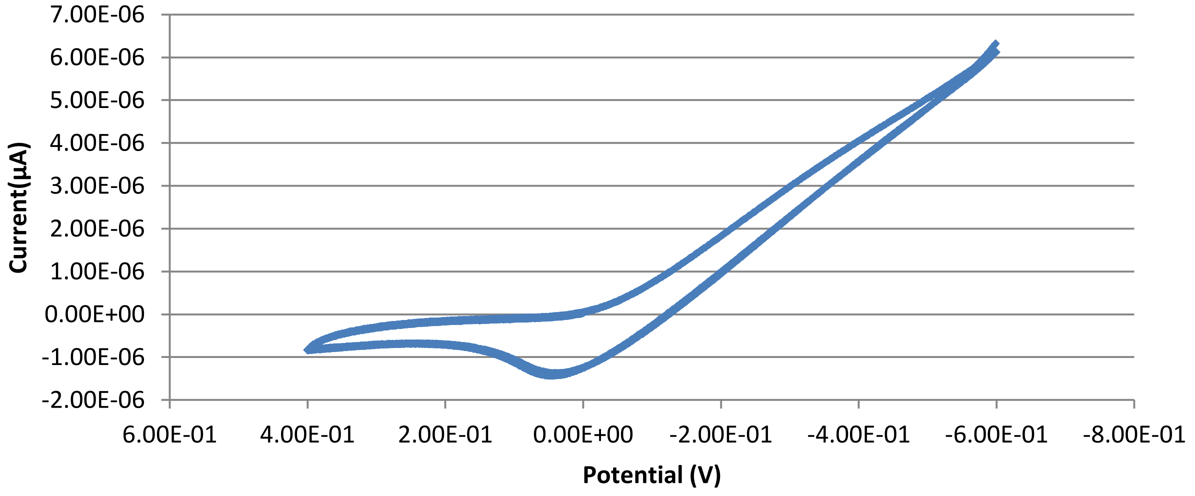


An air tight cell from three rubber septa and a three neck flask was prepared as pictured. For the working electrode and reference electrode, holes that fit around the tip of the electrodes were made in the septum to allow for no air to escape. The counter electrode went underneath the rubber septum on the same side as the reference electrode. A long needle that could submerge in the solution was placed through the middle septum. Argon was then allowed to bubble through for 10 minutes. The cyclic voltammograms with this system were taken as those in a normal cell.

Results

In making the TBAPC, about 50.656 g crude compound was obtained. When put into the hot water (around 80˚C), it took nearly 135 mL to dissolve the 1.0 g TBAPC. When the experiment was run a second time, the water was between 90˚ and 100˚C and only took 112 mL of water. When allowed to cool, the second solution gave closer to 1.0g with a percent yield of about 95% (0.95 g) than that of the first solution (0.648 g). This ratio of TBAPC to water was used in succeeding recrystallizations.

Figure 4. Scan of [CuSALAD]2 at 0.05M with a Scan Rate of 50



In Figure 4 [CuSALAD]$_2$ is scanned without any imidazole or hydrogen peroxide. There is an E_{pa} around 0.025V and a sharp peak up toward -6.0x10^{-1} V and a slower incline toward 4.0x10^{-1} V. The graph is a baseline for the [CuSALAD]$_2$.

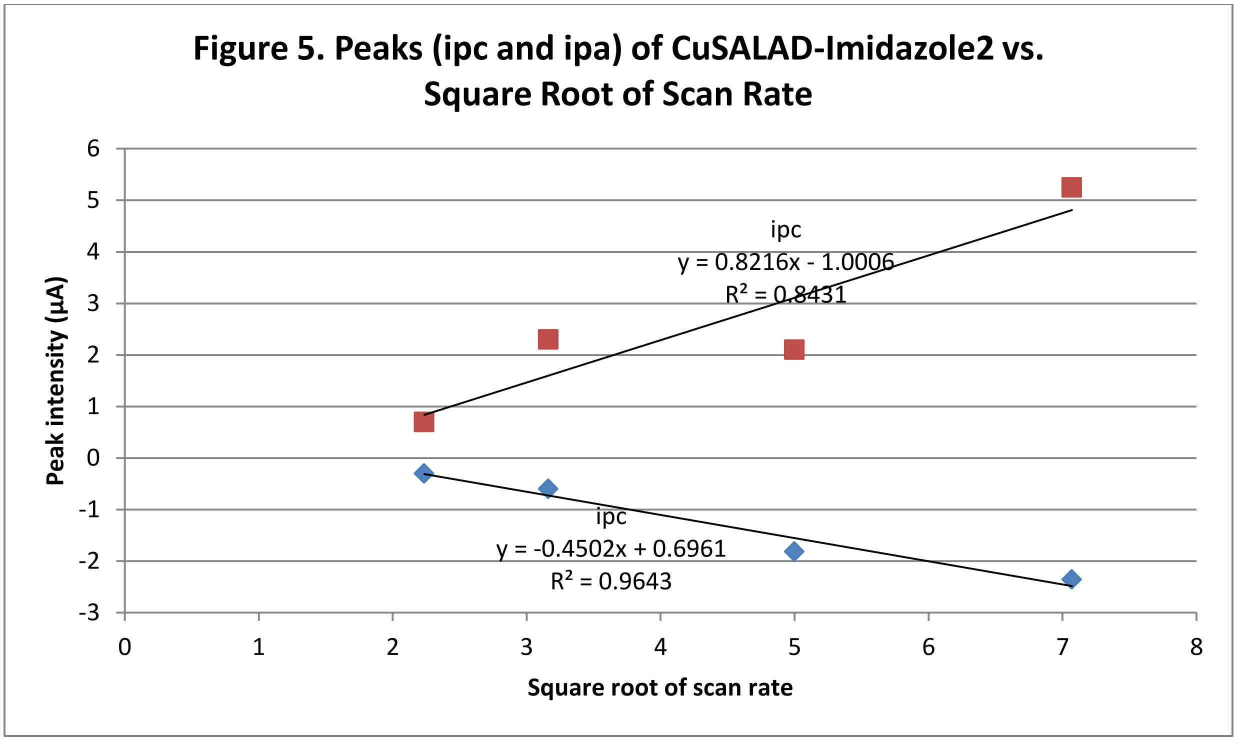
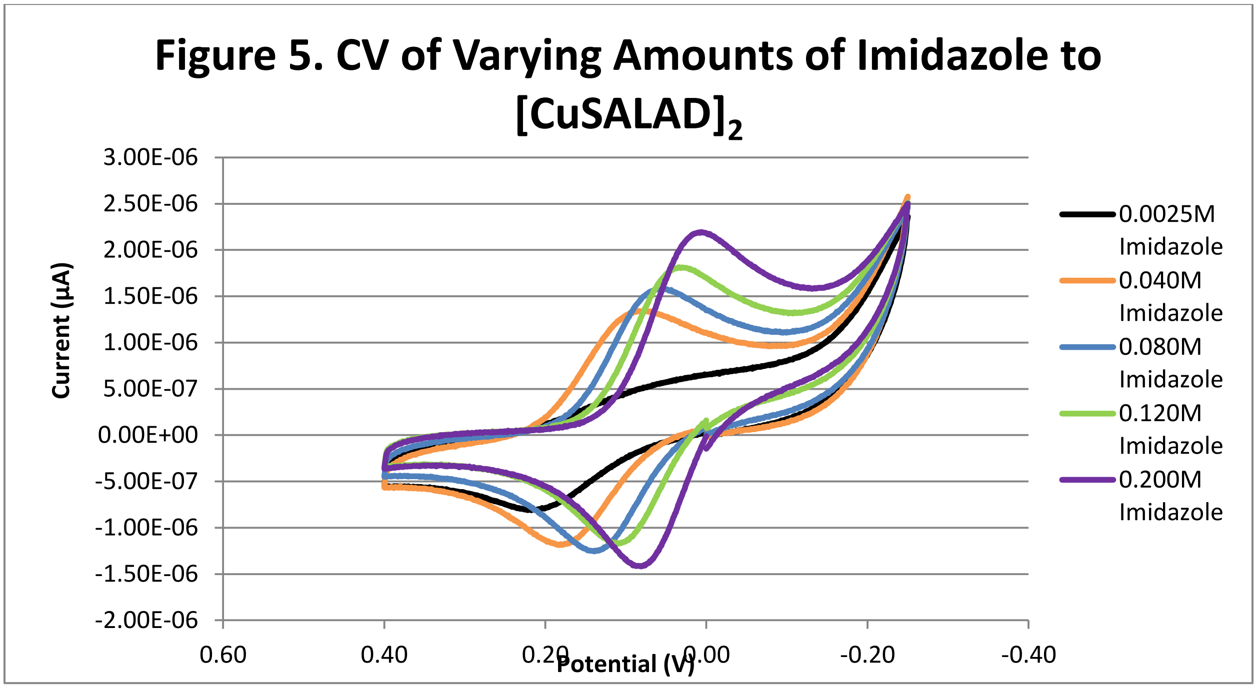


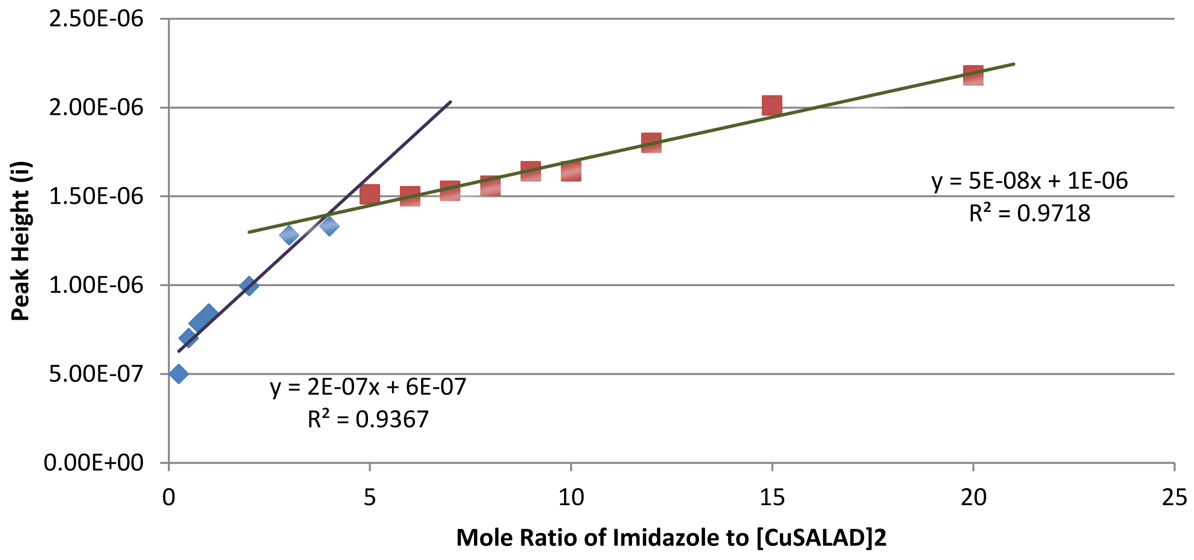
Figure 5. Peaks (ipc and ipa) of CuSALAD-Imidazole2 vs. Square Root of Scan Rate

In Figure 5, the square root of the scan rate against the peak intensity shows the reversibility of the reaction. As seen by in Figure 5, both sets of peaks versus their squared scan rate have linear equations. The i_{pa} peaks have a very high proportionality to the squared scan rate.



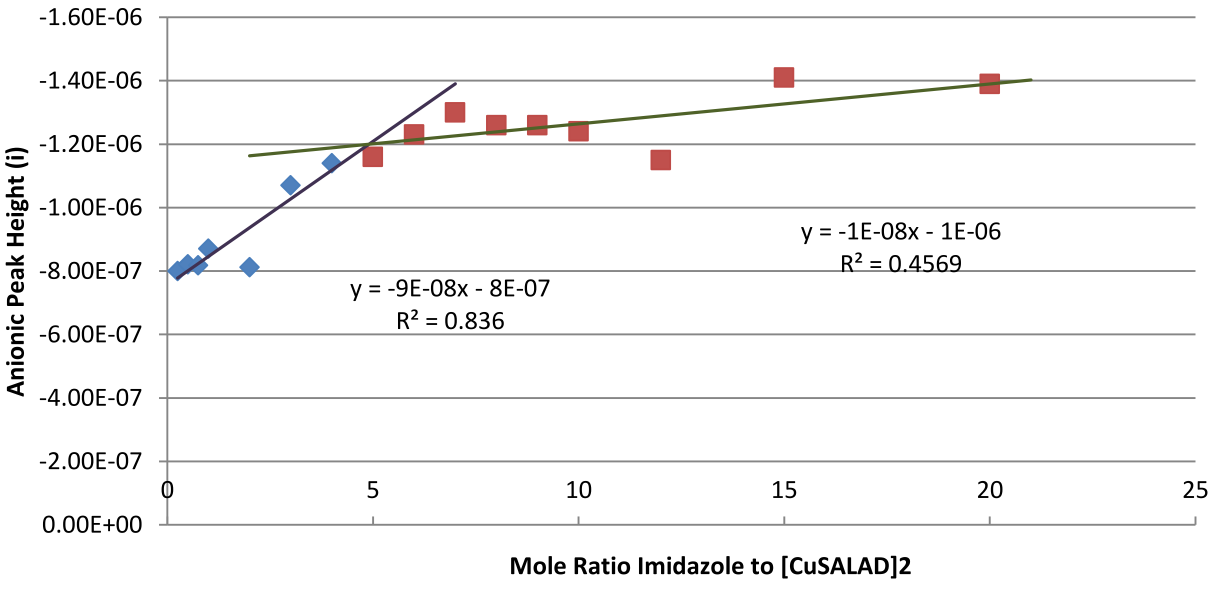
To determine the stoichiometric mole ratio of the imidazole to $[CuSALAD]_{2,}$ a plot of intensities of cathodic and anodic peaks *vs*. imidazole to $[CuSALAD]_2$ mole ratio graph was made and proved that a 4:1 stoichiometric ratio is obtained. Figure 6 shows the cyclic voltammograms demonstrating the changes from adding imidazole. As more imidazole is added, the $E_{1/2}$ moves to the right, the peaks grow in intensity and become more reversible; i.e. the peak separation gets closer to 60 mV, as more imidazole is added to the reaction.

Figure 7. Mole Ratio vs. Cathodic Peak Intensity



As seen in Figure 7, the cathodic peak intensity, i_{pc}, proved to have some strong relation to the mole ratio. There is a steady rise in i_{pc} from the 0.0025 M to 0.040 M of imidazole, but plateaus it after 0.05 M. The lines cross around the 4:1 ratio.

Figure 8. Mole Ratio vs. Anodic Peak Intensity



The data in the Figure 8, shows a weaker relationship in the set of data. The data rise and fall in no particular order, making the R-squared values weak. The lines cross at around the 5:1 ratio.

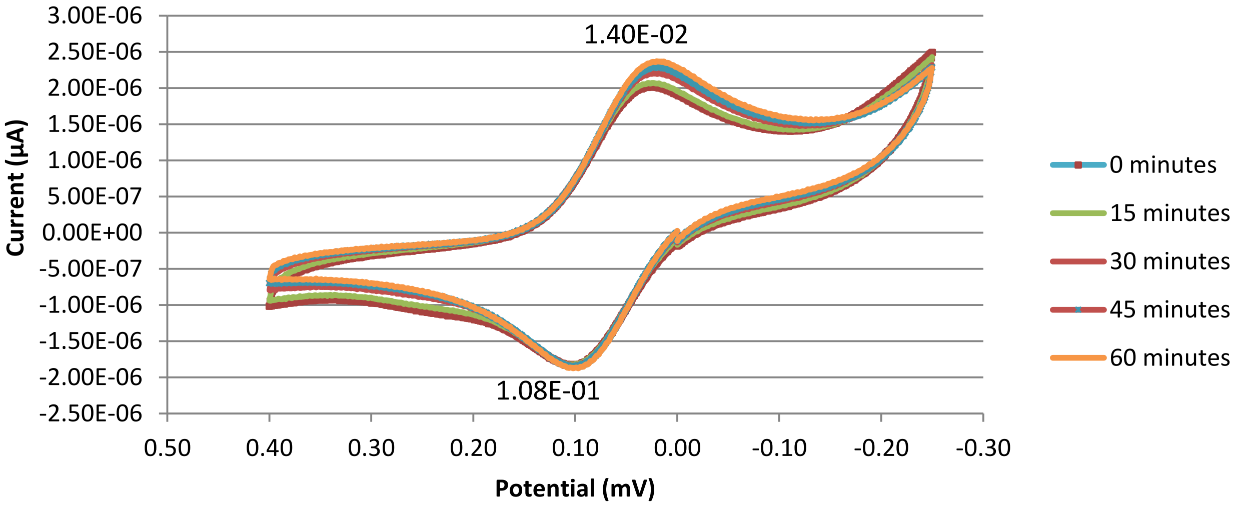


Figure 9. CuSALAD-Imidazole2/H2O2 Cyclic Voltammetry Runs

In the next set of results, the graph Figure 9 displays the effect of H_2O_2 on the CV of the CuSALAD-Imidazole$_2$ complex. The cyclic voltammograms were taken every five minutes and, as in the graph Figure 9, the overlaying cycles represent a separate scan at a set time (see data in Appendix, Table 4). It is apparent that there is not much variance between the scans at different times.

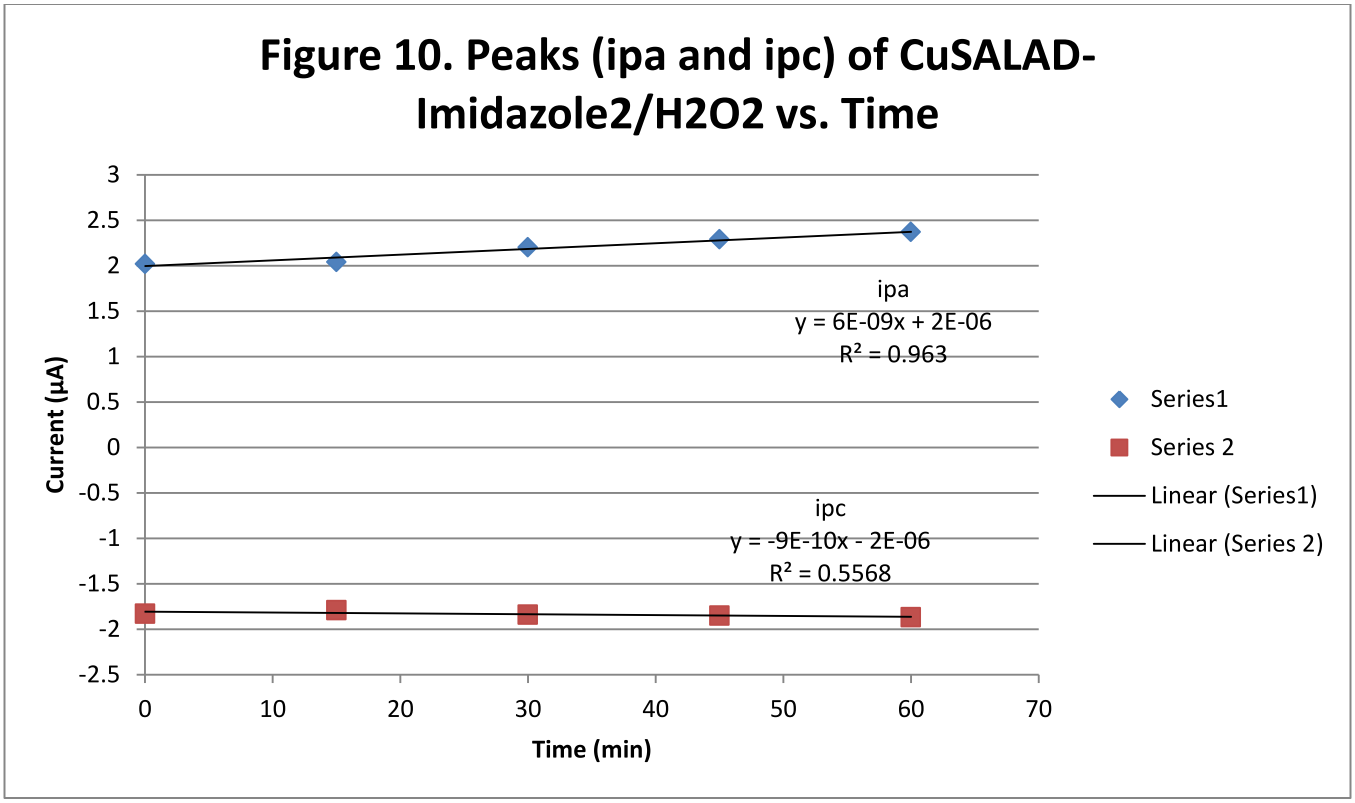


Figure 10. Peaks (ipa and ipc) of CuSALAD-Imidazole2/H2O2 vs. Time

In Figure 10, the times of the CuSALAD-Imidazole adducts are time course. The i_{pa} has a definitive incline, but the i_{pc} starts its decline after 15 minutes.

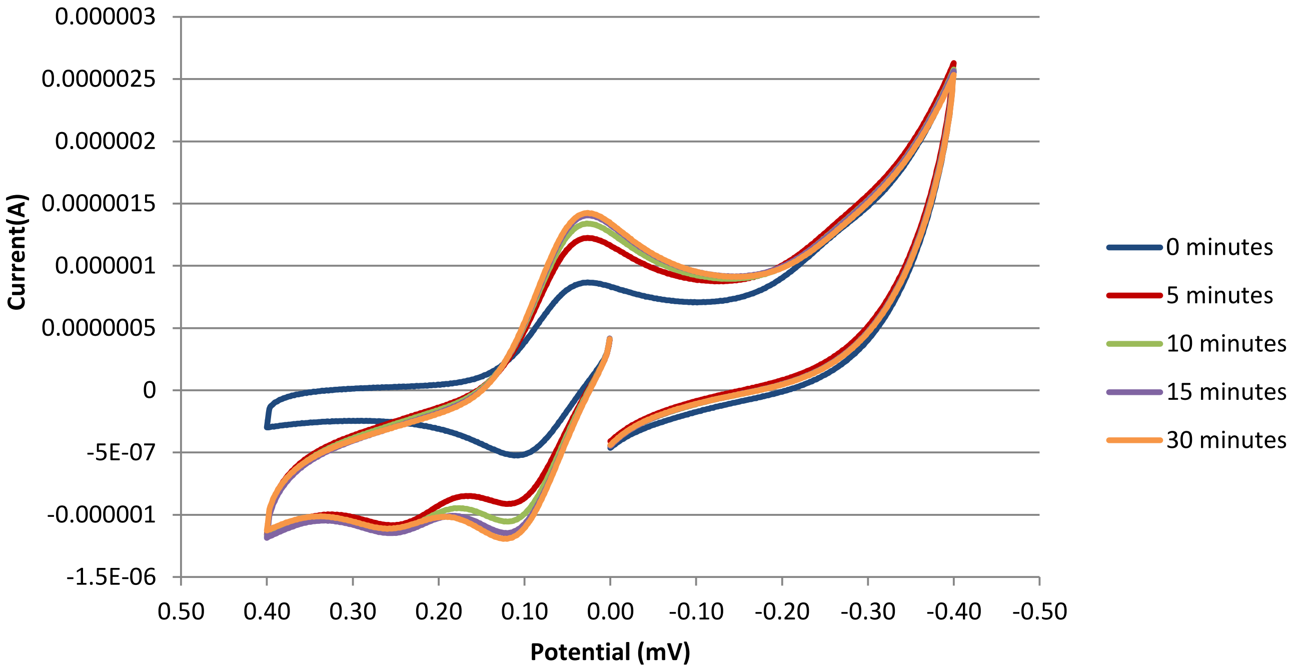


Figure 11. CuSALAD-Imidazole2/H2O2 Cyclic Voltammetry Runs; system saturated with Argon

As seen by Figure 11, the system was placed in an argon rich environment. The curve has a normal curvature to it, but there are three peaks at the anodoic peak. There is not much change from that of Figure 9, but there seems to have been a new peak formed at the oxidation region around $2x10^{-1}$ mV.

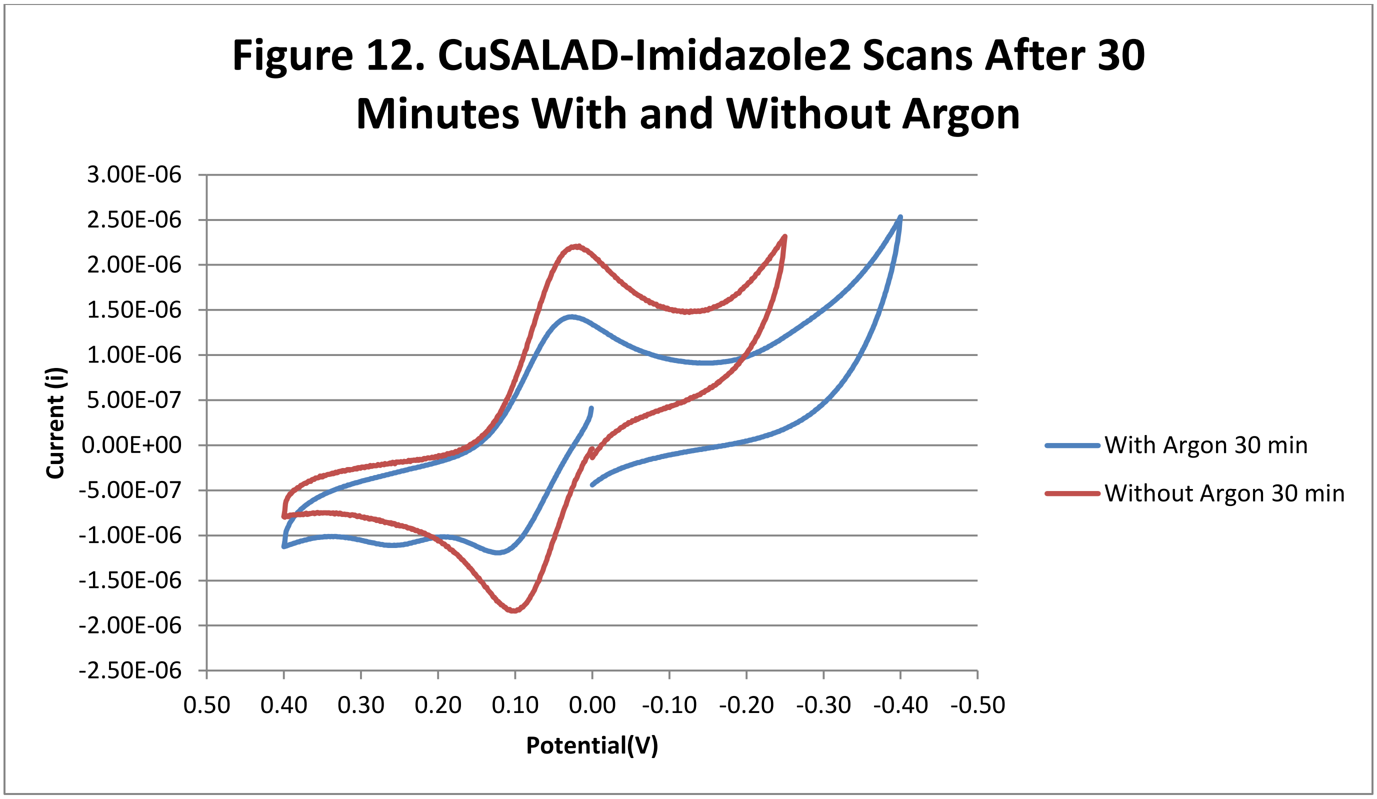


Figure 12 is a representation of the experiments that were seen in Figure 9 and 11. The graph shows that the air exposed complex has a wider spread between the peaks, as opposed to the peaks between the argon enriched complex. The peaks of the scan in the air are 38 mV for the E_{pc} and 101 mV for the E_{pa} making the $\Delta E_{1/2}$ =69.5 mV and $E_{1/2}$=73 mV. The peaks of the argon scan are 28 mV for the E_{pc} and 122 mV for the E_{pa} making the $\Delta E_{1/2}$= 75 mV and $\Delta E_{1/2}$=75mv.

Discussion

Mole Ratio Imidazole to [CuSALAD]$_2$

In the mole ratio experiment for imidazole and [CuSALAD]$_2$, the E_{pc} peak intensities rose steadily for the cathodic peaks, but not as definite for the anodic peaks as imidazole is added. The peaks leading up to 0.040M showed little to no intensity difference. As seen in the graph (Figure 7.), the 0.0025 M imidazole (1:4 imidazole to [CuSALAD]$_2$ ratio) showed a very small anonic peak and no cathodic peak. Once the mole ratio increased above 0.040M imidazole (4:1 imidazole to [CuSALAD]$_2$ ratio) the peak was distinct. The peaks did continue to rise, but the slope of the line flattened out after the 4:1 imidazole to [CuSALAD]$_2$ ratio, as seen in the graph (Graph 4 and 5.). With this data, it is evident that the [CuSALAD]$_2$ complex uses 4 imidazoles in order to establish an equilibrium shown in Figure 2 ; previous studies[2] utilizing UV-Vis have also found this same stoichiometery. Thus we are confident we are studying the same equilibrium as in the previous work.

The equations ((7) and (8)) represent the proposed formation of the [CuSALAD-Imidazole$_2$] adduct using Im to represent imidazole and Cu to represent [CuSALAD]$_2$.

$$Cu_2 + 2Im \leftrightarrow 2Cu\text{-}Im \qquad (7)$$

$$2Cu\text{-}Im + 2Im \leftrightarrow Cu\text{-}Im_2 \qquad (8)$$

The imidazole in subsequent studies was added in a large excess in order to push the reaction to the right. By supplying a 5 time higher quantity of imidazole, according to Le Chatelier’s principle, all of the [CuSALAD]$_2$ complex should have been completely forced into [CuSALAD-Imidazole$_2$].

Effects of [H_2O_2] on Peak Intensity

Using the final solution of the above experiment with the $[CuSALAD]_2$ complex, [H_2O_2] was added to the complex that was completely converted into the [CuSALAD-Imidazole$_2$] complex. The graph (Figure 7) shows decrease of peak intensity with time. With very little change in the peaks, it is safe to say that there is no change in the oxidation state of the Cu(II) complex as opposed to the previous thoughts of other studies[2]. The results provided show more of a catalytic reaction occurring rather than any form of oxidation-reduction reaction.

Reaction of [CuSALAD-Imidazole$_2$] with H_2O_2 in Argon

When it came to the reaction [CuSALAD-Imidazole$_2$] catalyzing H_2O_2 decomposition in argon, the reaction was the same as the reaction without the argon. The main difference was that there was a second i_{pa} peak at 241mV. The second peak is indicative of some molecule being oxidized a second time. It is believed that the second oxidation is an oxidation of the copper intermediate (Figure 4) so that the intermediate would make the copper a neutral molecule for the time that the hydrogen peroxide was using the copper complex as a catalyst. The reaction was also a bit more irreversible which leads to the assumption that the reaction uses the ambient oxygen to help the reaction progress. With the knowledge that the reaction uses the oxygen from the air, the broad peak could be absorbing the second peak that is seen in the argon peaks.

Reaction Mechanism for [H_2O_2]>>[CuSALAD-Imidazole$_2$]

With the knowledge of previous studies [1][2], and the findings of this experiment the proposed mechanism is as follows for [H_2O_2] in great excess ((9), (10), and (11)) and the overall equation (12):

$CuIm_2 + H_2O_2 \leftrightarrow CuImOOH^- + ImH^+$ (9)

$CuImOOH^- + H_2O_2 \leftrightarrow (Cu(OOH)_2{}^{2-} + ImH^+$ (10)

$(Cu(OOH)_2) + 2ImH^+ \leftrightarrow CuIm_2 + 2H_2O + O_2$ (11)

Overall; $2H_2O_2 \leftrightarrow 2H_2O + O_2$ (12)

The proposed mechanism is consistent with Finnochio's proposed mechanism [2] and provides evidence that the proposed copper (II) intermediate, $(Cu(OOH)_2{}^{2-}$ undergoes reduction, presumably to a copper(I) species, during the decomposition of the hydrogen peroxide. Under atmospheric conditions, there is sufficient oxygen in the system to re-oxidize this copper back to copper(II). However, under argon atmosphere, there is not sufficient oxygen present to accomplish this re-oxidation and we see the anodic peak from the electrochemical re-oxidation of this species.

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Appendix

Table 1. The E_{pc} and E_{pa} of Graph 1. The final column also shows the difference in distance to show whether the reaction is reversible or not.

M	i_{pc}	i_{pa}	E_{pc}	E_{pa}	ΔE
0.025	2.19E-6	-1.42E-6	6.0E-3	7.0E-2	
0.040	1.82E-6	-1.2E-6	4.2E-2	1.1E-1	
0.080	1.55E-6	-1.25E-6	6.0E-2	1.29E-1	
0.120	1.33E-6	-1.1E-6	1.0E-1	1.65E-1	
0.200	3.51E-6	-7.84E-7	1.19E-1	2.7E-1	

Table 2. The points in Graph 2.

Mol ratio to $[CuSALAD]_2$	Cathodic peak (i_{pc})
0.25	5.00E-7
0.5	7.00E-7
0.75	7.84E-7
1	8.39E-7
2	9.95E-7
3	1.28E-6
4	1.33E-6
5	1.51E-6
6	1.5E-6
7	1.53E-6
8	1.56E-6
9	1.64E-6
10	1.64E-6
12	1.8E-6
15	2.01E-6
20	2.18E-6

Table 3. The points in Graph 4.

Mol ratio to $[CuSALAD]_2$	Anodic peak (i_{pa})
0.25	-8E-7
0.5	-8.21E-7
0.75	-8.18E-7
1	-8.7E-7
2	-8.12E-7
3	-1.07E-6
4	-1.14E-6
5	-1.16E-6
6	-1.23E-6
7	-1.30E-6
8	-1.26E-6
9	-1.26E-6
10	-1.24E-6
12	-1.15E-6
15	-1.41E-6
20	-1.39E-6

Table 4. The peaks of Graph 5.

Time (minutes)	i_{pc}	i_{pa}
Baseline	1.73E-6	-1.83E-6
0	2.27E-6	-1.83E-6
15	2.05E-6	-1.83E-6
30	2.03E-6	-1.83E-6
45	2.24E-6	-1.83E-6
60	2.3E-6	-1.70E-6

Table 5. The peaks of Graph 6.

Time (minutes)	E_{pc}	E_{pa}
0	8.47E-7	-1.17E-6
5	1.21E-6	-1.13E-6
10	1.38E-6	-1.03E-6
15	1.40E-6	-8.8E-7
30	1.40E-6	-5.04E-7