

AN ABSTRACT OF THE THESIS OF

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Title: Kinetics of Oxidation of Cu(II) in Basic Solutions

of Dimethylglyoxime by Persulfate Ion

Abstract Approved: W. G. Davies

This thesis describes investigations into the kinetics of the color reaction which occurs when Cu(II) in unbuffered basic solutions of dimethylglyoxime is oxidized by persulfate solution.

The color change accompanying the reaction was monitored by a dipping-probe colorimeter at wavelength of 520 nm. A double-injection technique was developed in order to improve the reproducibility of experimental results. The concentration of Cu(II) was kept in the vicinity of 5×10^{-5} mol/L while those of Na_2dmg and $\text{K}_2\text{S}_2\text{O}_8$ were usually around 5×10^{-4} mol/L.

The production of the pink color was found to be half order with respect to $\text{K}_2\text{S}_2\text{O}_8$ for concentrations below about 5×10^{-4} mol/L and first order with respect to Cu(II) for concentrations up to about 8×10^{-4} mol/L (i.e. $\text{Na}_2\text{dmg}/\text{Cu(II)}$ ratio in excess of 5:1). The dependence of the reaction rate on the hydrogen ion concentration could not be established with certainty.

These results suggest that the rate determining step of the reaction is a one-electron transfer reaction between the SO_4^- radical and the $\text{Cu}^{\text{II}}(\text{Hdmg})_2$ complex.

Kinetics of Oxidation of Cu(II) in Basic Solutions of Dimethylglyoxime by Persulfate Ion

**A Thesis
presented to
the Division of Physical Sciences
EMPORIA STATE UNIVERSITY**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

by

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Introduction

1.1 Historical

When dilute basic solutions of copper(II) salts containing dimethylglyoxime are oxidized by persulfate ion, a transient pink color develops. This color is presumably due to copper in a higher oxidation state, and is perhaps a copper(III)dimethylglyoxime complex isoelectronic with the well-known nickel(II) complex shown in Figure 1.

This reaction was first described in 1929 by Clarke and Jones¹, and shortly afterwards by Kolthoff² who were interested in it as a method for the detection of copper at very low concentrations. They showed that a color could be developed using either the persulfate ion $S_2O_8^{2-}$ or the periodate ion IO_4^- in buffer solutions. For over 35 years, this reaction remained uninvestigated. However, in 1977, Mopurgo and Tomlinson³ published an article on this system. They concentrated mainly on the copper(II) species present before oxidation. They concluded that when the ratio of dimethylglyoxime (H_2dmg) to copper is kept at 2:1 and the pH lies between 2.5 and 11.0, the only species present in solution is $[Cu(Hdmg)_2]$. However, if the ratio of H_2dmg to Cu is kept at 1 : 1,

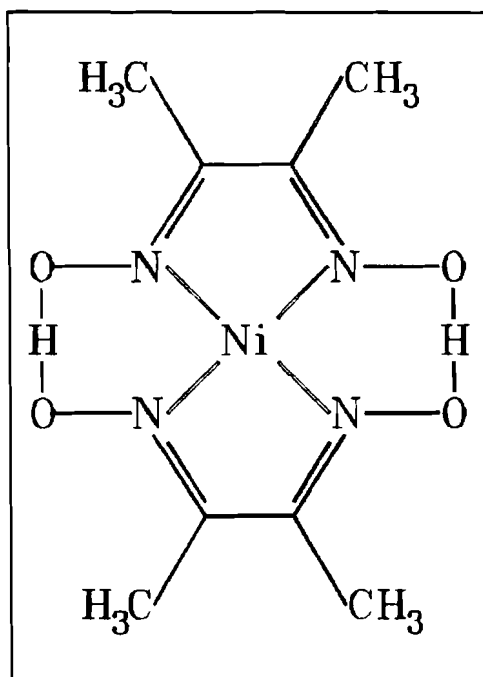


Figure 1: Structure of $Ni(Hdmg)_2$

there is evidence that the predominant species at pH values above 5 is a 1:1 complex. They suggest that this is a hydroxo-bridged tetramer $[\{\text{Cu}(\text{Hdmg})(\text{OH})\}_4]$. Mopurgo and Tomlinson also investigated the kinetics of the oxidation of this tetramer by $\text{S}_2\text{O}_8^{2-}$ and claimed that the interaction of the tetramer with $\text{S}_2\text{O}_8^{2-}$ forms two molecules of a dimer having mixed oxidation states of +2 and +3 for copper.

Over the period 1985–1986, this reaction was studied at Texas Wesleyan College by several undergraduates under the guidance of Dr. W. G. Davies and Dr. A.N. Starks^{4,5,6,7,8}. The reaction was accidentally rediscovered by a student there⁴ who initially thought that it was an original discovery. This work was done mainly in dilute basic solutions using persulfate as an oxidant. One outcome of this research was the discovery that the reaction produces hydrogen ions. It was also discovered that the color changes accompanying this reaction depended not only on the pH but also on the buffer used. Different buffers at the same nominal pH often gave significantly different results.

During 1988–1989 further work on this system was pursued at Emporia State University by Li-Ching Tseng⁹ under the direction of Dr. W. G. Davies. Their investigations started with an attempt to unravel the stoichiometry of the reaction. This work was done on unbuffered solutions which were initially basic. Under these conditions, it was found that the dimethylglyoxime is hydrolyzed and oxidized and that the copper eventually returns to an oxidation state of +2. Furthermore, two hydrogen ions are produced for every persulfate ion reduced. In the second half of these investigations, attention was focused on a colorimetric survey of the reaction using a dipping probe

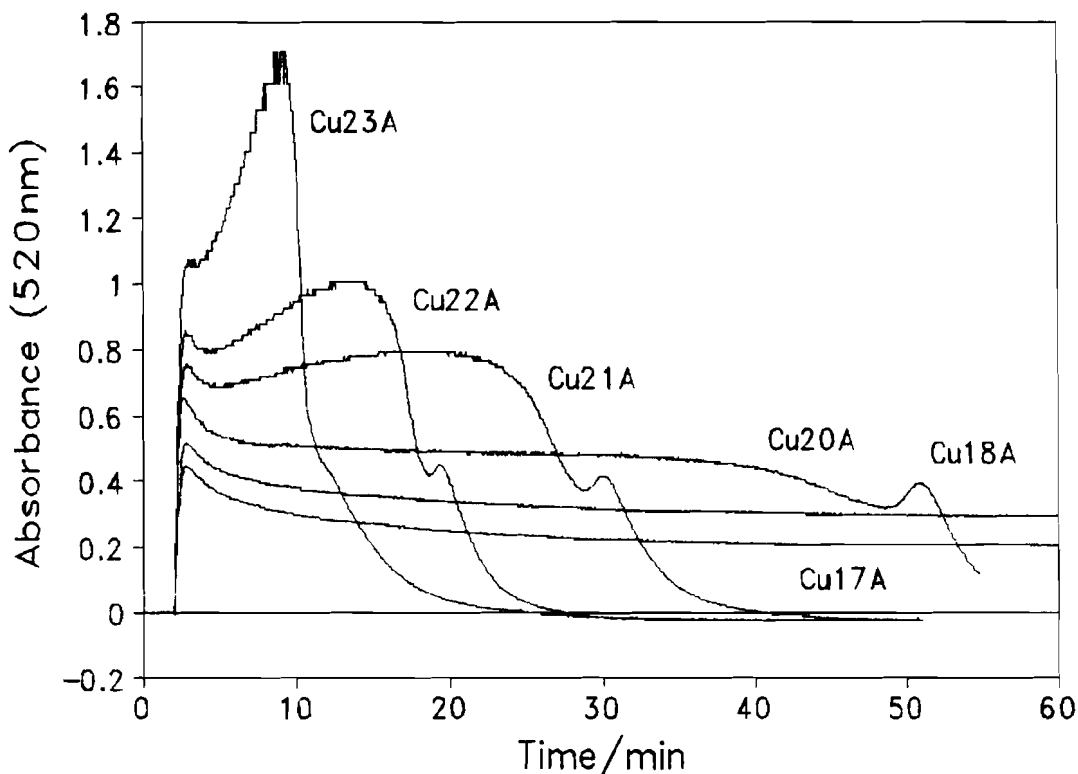


Figure 2: Variation of Absorbance at Various Copper Concentrations

colorimeter. The apparatus used in this part of the investigations was quite similar to that used in the present research described later in this thesis and illustrated in Figure 4.

Figure 2 shows the absorbance results obtained by Tseng using a 520nm interference filter for six different runs. The only variable in the initial composition of these six solutions is the concentration of Cu(II) which varies from 6.8×10^{-5} mol/L for run Cu17A up to 9.2×10^{-5} mol/L for run Cu23A. The other three reagents were held constant, H_2dmg at 4×10^{-4} mol/L, OH^- at 8×10^{-4} mol/L and $\text{K}_2\text{S}_2\text{O}_8$ at 2×10^{-3} mol/L.

The four most concentrated solutions in this series exhibit the most complex behavior while the two least concentrated solutions behave somewhat

differently. In the former case, three absorbance maxima can be seen (suggesting that at least three colored species are produced in succession) followed by a return to an absorbance value slightly below the initial value. At the same time the pH shows a slow initial decline followed by a sudden drop which coincides with the final disappearance of the red color. This behavior can be seen in Figure 3 where the results for run Cu22A are plotted.

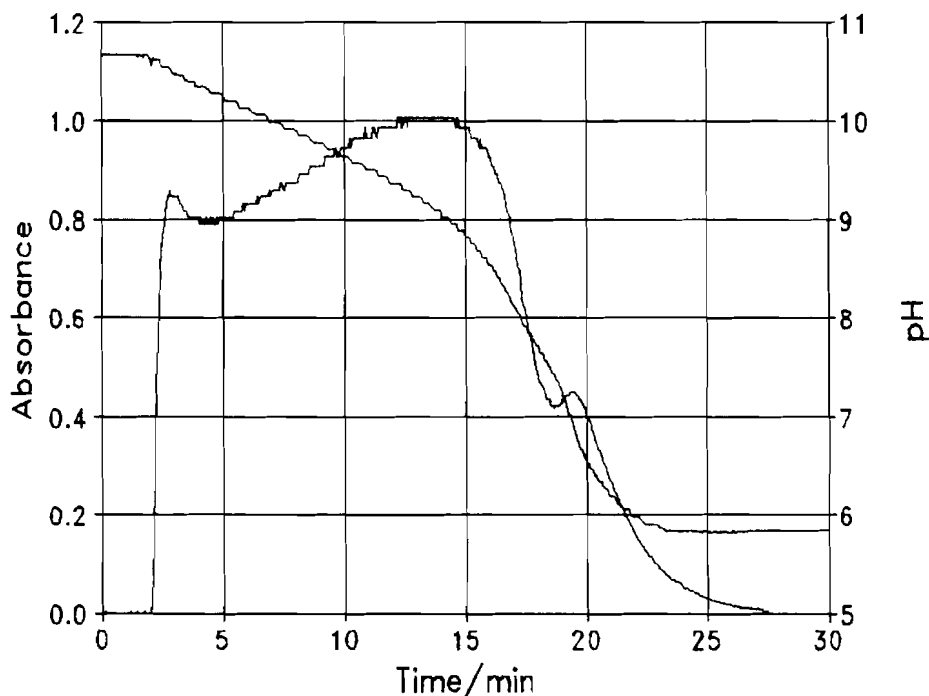


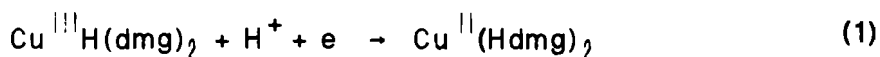
Figure 3: pH and Absorbance Behavior for Run Cu22A

In runs CU17A and Cu18A, by contrast, after the usual initial jump, the absorbance decays to a constant value while the pH change is both slow and small (from 10.5 down to 9.5). The decay in this case is strictly first order. Plots of $\log(A-A^\infty)$ against t for the latter part of these two runs, each involving over 600 points, yield two straight lines each with an R^2 value of 0.99, both having essentially the same slope.

All six runs shown in Figure 2 exhibit an initial sharp jump in

absorbance at the start of each run. As plotted, all six curves appear to have the same initial slope but this is purely a matter of scale. A plot of the log of these six initial slopes against the log of the initial copper concentrations yields a straight line with an R^2 value of 0.87 and a slope of 2.20. These results suggest the initial reaction is second order with respect to Cu(II), and therefore that the rate determining step involves two copper atoms.

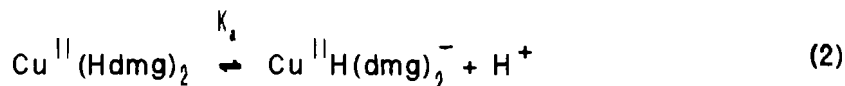
Shortly after this work was completed, Sulfab¹⁰ published a paper concerning the oxidation of bis(dimethylglyoxime) copper (II) (i.e. $\text{Cu}^{\text{II}}(\text{Hdmg})_2$). This paper has two parts. In the first part, the cyclic voltammetry of $\text{Cu}(\text{Hdmg})_2$ is described. The species exhibits quasi-reversible one electron transfer behavior with a peak to peak separation of about 80 mV and an $E_{1/2}$ varying linearly with pH and a slope of -59 mV consistent with an electrode reaction of the form:



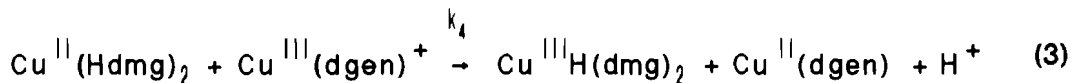
In the second part of this paper, Sulfab followed the kinetics of the oxidation of $\text{Cu}^{\text{II}}(\text{Hdmg})_2$ by the copper (III) complex of diglycylethylenediamine (i.e. H_2dgen). This reaction was shown to be first order with respect to both oxidant and reductant and also to vary with the hydrogen ion according to the equation:

$$k_2 = k_1 + \frac{k_5 K_a}{[\text{H}^+]}$$

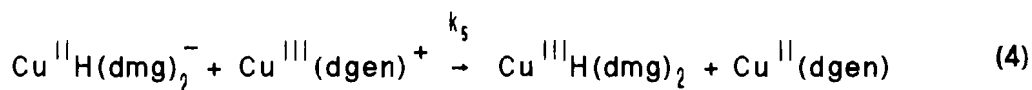
where k_2 is the second order rate constant. This behavior is easily explained in terms of an initial acid-base equilibrium:



followed by the simultaneous oxidation of both of these copper (II) species by $\text{Cu}^{\text{III}}(\text{dgen})^+$, each at a different rate, i.e. the reaction:



alongside the reaction:



1.2 Proposed Investigation

In the work described in this thesis, it was hoped that the investigation begun by Tseng could be extended in two ways:

- i) by further development of the apparatus used; and
- ii) by investigating the initial rate of the reaction.

Apparatus

The apparatus used by Tseng had two major disadvantages. In the first place, it was attached to an 8-bit A/D converter, enabling the transmittance to be read only to 1 part in 256. This lack of resolution accounts for the stair-step behavior at high absorbances of the curves shown in Figure 2.

In the second place, readings were taken every three seconds. This was mainly because the program reading the A/D converter was written in BASIC. This program could easily be rewritten in machine language so as to enable readings to be taken every second. Though a much faster rate of data-acquisition is possible with this combination of software and hardware, it was considered unnecessary to exceed one reading per second. The solutions could not possibly be mixed in less time than one second without the use of a special (and expensive) mixing apparatus.

Measurement of the Initial Rate

The results obtained by Tseng shown in Figure 2 demonstrate that the color reaction to be studied could be quite complex. Under some conditions as many as three light-absorbing species were produced in succession. Because of this, the decision was made to investigate the reaction under those conditions where it appeared most simple. Attention was therefore centered on the initial rate of change of absorbance. Hopefully, this initial slope would correspond to the occurrence of a single reaction step producing a single colored species without the occurrence of subsequent reactions removing it.

The decision was also made to confine investigations to basic solutions. Earlier work⁶ indicated that when buffers were used, the results often changed when the conjugate acid-base pair was changed even though the pH was held constant. If the solutions used were sufficiently basic on their own, the pH would be kept fairly constant without the need for buffers. There was another important reason for using basic solutions. Of the curves shown in Figure 2 those with lowest copper(II) concentration, namely runs Cu17A and Cu18A, were also those with the simplest behavior. These solutions were also the solutions which remained basic for the longest time.

Accordingly, it was decided to investigate the initial rate of the reaction in solutions which were not very different in composition from runs Cu17A and Cu18A. The change of absorbance with time would be measured at the same time as various parameters were altered. Attention would be concentrated on determining how the initial rate depended on the concentration of Cu(II), of persulfate ion, and of hydrogen ion in an attempt to find the order of the reaction with respect to these components.

Experimental

2.1 Apparatus

The absorbance measurements of solutions were made using a Brinkmann Model PC700 dipping probe colorimeter (Figure 4) interfaced to a Commodore 64 computer through a 12-bit analog-to-digital interface (Figure 5).

As shown in Figure 4, light from a tungsten lamp in the main housing enters the probe through a fiber-optic cable, traverses a fixed length of solution, and then is reflected by a mirror firmly attached to the end of the probe. The reflected beam then passes through solution again, this time in the reverse direction, and returns to the main housing through a second fiber-optic cable. The beam is then made monochromatic by

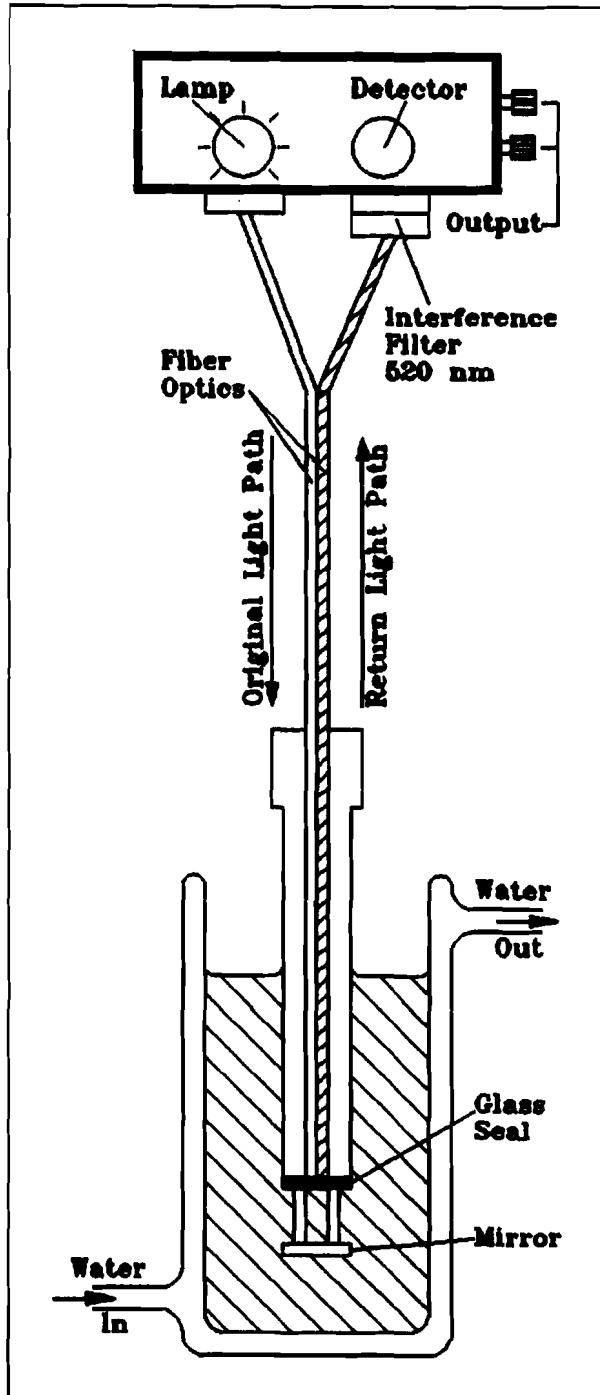


Figure 4: Experimental Setup

passing through an interference filter and is detected with a solid state detector. The light is chopped electronically at a fixed frequency and the detecting circuit is tuned to this frequency so that ambient light not at this frequency does not interfere with results. The spectrophotometer has a pair of outlet terminals intended for connection to a pen recorder. These terminals are connected to the A/D interface board of Figure 5. This allows the output voltage of the colorimeter to be converted to a 12-bit binary number which is then sent to the parallel port of a Commodore computer through a ribbon cable.

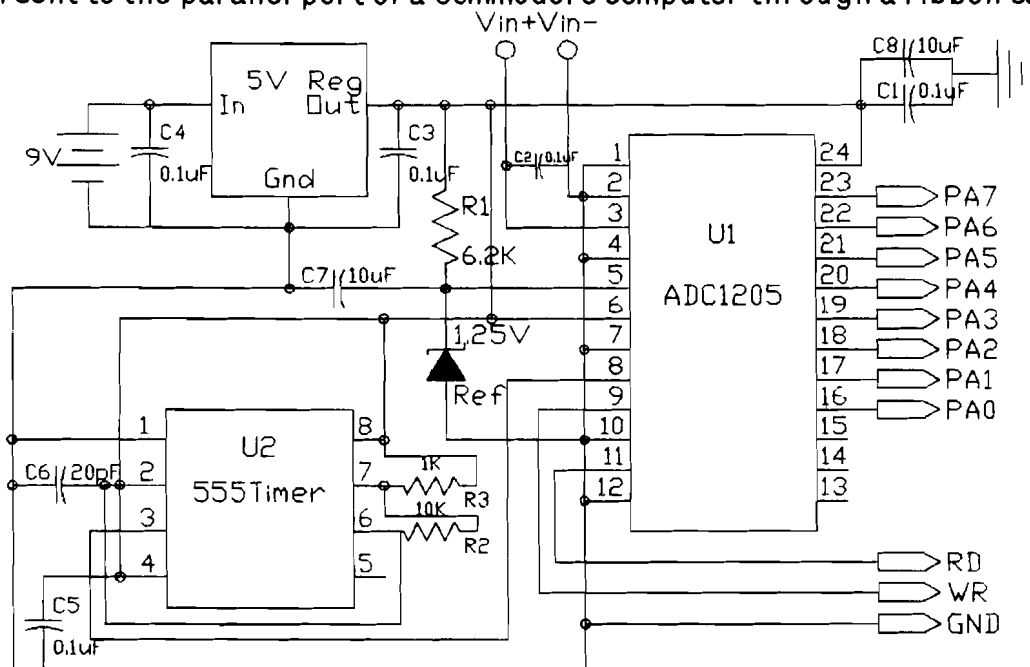


Figure 5: Analog to Digital Interface

All measurements were carried out at 25⁰C in a double-walled Pyrex beaker fitted with a star magnetic stirrer. The total volume of mixed solutions in the beaker was always well inside the limits 200 ± 0.1 mL. The solution temperature was kept constant by circulating water from a constant temperature bath through the outer jacket. The constant temperature bath

was a Haake Model FS. The temperature was kept at $25^{\circ}\text{C} \pm 0.02^{\circ}\text{C}$ in this bath. Almost all runs were made using a 520 nm filter with a band width of ± 10 nm. Absorbance measurements were taken at a rate of one per second.

Data obtained in the course of a run were stored directly on floppy disk. These data were later converted from Commodore-readable form to IBM-readable form using the program "Big Blue Reader" and a Commodore 1571 disk drive. All data manipulation was performed on IBM-compatible computers, mainly with the use of the Quattro Pro spreadsheet program.

2.2 Reagents

The following reagents were used in this work:

1. Copper (II) sulphate pentahydrate $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$: ACS reagent grade; Baker & Adamson Chemical Company
2. Potassium persulfate $[\text{K}_2\text{S}_2\text{O}_8]$: analytical reagent grade, 99.9%; J.T.Baker Chemical Corporation
3. Dimethylglyoxime sodium salt octahydrate $[\text{Na}_2\text{dmg}, 8\text{H}_2\text{O}]$: Sigma Chemical Company
4. Dimethylglyoxime $[(\text{CH}_3)_2\text{C}_2(\text{NOH})_2]$: analytical reagent grade, 99.9%; Mallinckrodt Chemical Works
5. Sodium hydroxide (diluted from ampoule to exactly 1N): SS267-100, Fisher Chemical Company

All solutions were prepared from these reagents using distilled water.

All persulfate solutions used were freshly prepared for each set of runs.

Experimental Results

3.1 Reproducibility of the Interface

Immediately after its construction, the A/D Interface shown in Figure 5 was tested for reproducibility. A Leeds and Northrup potentiometer was used as a constant potential source. Repeated measurements of the same potential as a 12-bit number initially gave a standard deviation of about 4 digits (i.e. a relative deviation of 4 in 4096). This reproducibility was somewhat improved by adding more by-pass capacitors and better grounding. A much larger improvement was obtained by not using the +5V power supply from the Commodore computer. Instead, a 9-volt battery attached to a 7805 5V regulator was used as an independent power source for the interface. As a result, the standard deviation was reduced to a low of 0.7 digits, with occasional fluctuations as high as 1.3 digits. This behavior was regarded as satisfactory.

3.2 Reproducibility of Mixing

Initially, mixing was accomplished by dumping 50 mL of persulfate solution from a 100 mL beaker as quickly as possible into 150 mL of basic solution containing both CuSO_4 and Na_2dmg placed in the reaction vessel. Throughout this process the mixture was stirred as rapidly as possible with the magnetic 'star' stirrer. The absorbance of the solution was monitored every second by the computer before, during and after mixing. A typical run is shown in Figure 6 where the absorbance of the solution is plotted against time. The sudden change in absorbance corresponds to the instant of mixing.

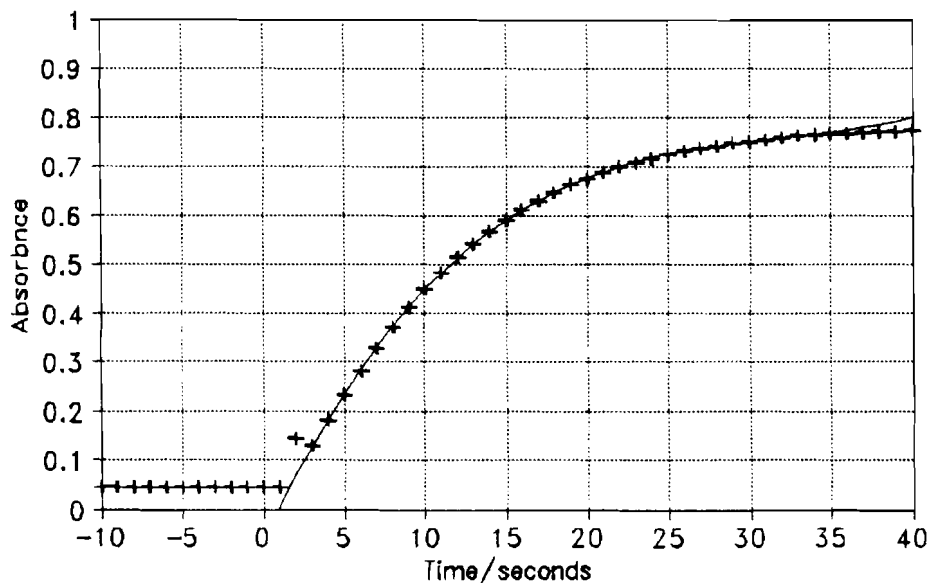


Figure 6: Variation of Absorbance with time for run ELEVENA

The smooth curve passing through most of the points in Figure 6 was obtained by finding the best cubic fit using the regression program built into the Quattro Pro spreadsheet. A total of 20 points was used for this purpose. The first reading after mixing was always ignored, because, as shown in Figure 6, it was sometimes inconsistent with the subsequent readings. This inconsistency, which was not always evident, was due to the finite time taken for mixing.

In Figure 7, the deviations of the actual readings from the best cubic fit are shown for run ELEVEN A. There is excellent internal consistency. The standard deviation for the twenty points used (i.e. excluding the first point) is 0.0017 absorbance. In most runs, the standard deviation was somewhat better than in this run.

In order to ensure good reproducibility for the volume of persulfate solution added, the following technique was used. A 100 mL beaker was first

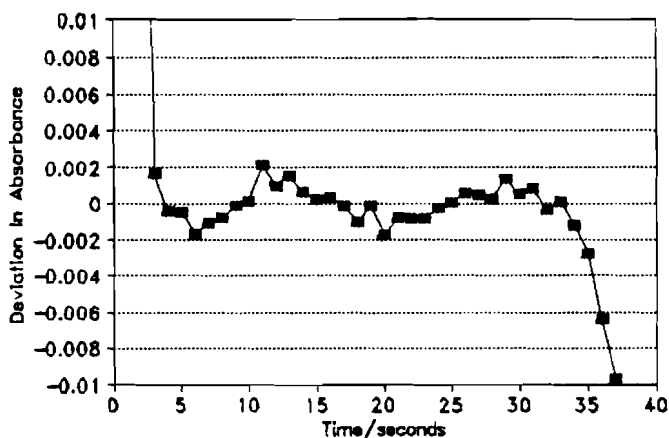


Figure 7: Deviations of Measured Absorbance from Best Cubic Fit

filled with about 50 mL of the solution in order to wet it, after which this volume was quickly dumped into the sink. Next, 50 mL of the solution was pipetted into this wet 100 mL beaker. The contents of this beaker was now added as quickly as possible (i.e. dumped) into the reaction vessel. This technique was tested by weighing the beaker before and after dumping. A relative standard deviation of less than 0.2% (0.1 mL absolute) was obtained.

Although the initial consistency of the points in each run was very good, when the same run was repeated several times, the agreement between successive runs was very unsatisfactory. The agreement between runs was judged in terms of the initial slope of the absorbance versus time curve like that shown in Figure 6. This initial slope was calculated from the best cubic fit equation. A typical result is shown in Table I. Seven repetitions of the same run involving the same initial concentrations were performed. As can be seen from the table, the lowest value of the seven initial slopes is almost a third of the highest value. The mean and standard deviation for the set is $0.044 \pm 0.012\text{s}^{-1}$. This is a relative standard deviation of 27%!

Table I. Initial Slopes for Seven Repetitions of the Same Run

Run	19A	19B	19C	19D	19E	19F	19G
Initial slope/s ⁻¹	0.023	0.038	0.042	0.060	0.045	0.056	0.045

In order to try to improve on this reproducibility, a different method for adding the persulfate was adopted. Instead of dumping a large volume, a volume of 1 mL was injected into the vigorously stirred solution in the reaction vessel. The reproducibility of the delivery of a 1 mL syringe was first tested. Ten successive deliveries were weighed. A relative standard deviation of 0.5% was obtained. This was considered acceptable for the purpose of this experiment.

Next, this injection method was tested by repeating the same run five times. In each run, identical solutions and volumes for each reactant were used. As usual, readings were taken every second and the initial slope of the absorbance curve was deduced from a cubic fit. Values for these initial slopes are shown in Table II. The mean and standard deviation of these data is $0.029 \pm 0.004 \text{ s}^{-1}$. This constitutes a relative standard deviation of 14%, half as much as before, but still not entirely satisfactory.

Table II. Reproducibility of Initial Slope Using Single-injection Technique

Run	C10S1MX1	C10S1MX2	C10S1MX3	C10S1MX4	C10S1MX5
Initial slope/s ⁻¹	0.026	0.031	0.034	0.027	0.025

3.3 Reproducibility of the Chemical Species

During the investigation just described, the observation was made that the mixing history of the solution into which the persulfate solution was injected was also important. If neither the CuSO_4 solution nor the Na_2DMG solution was diluted before being mixed, no pink color reaction was observed at all when oxidized with fresh persulfate solution. A structured investigation of this phenomenon was accordingly undertaken. Results are given in Table III. In this

Table III Effect of Methods of Mixing

Run	History of Mixing	Results
SLN1	0.5 mL 0.1M CuSO_4 + 5.0 mL 0.1M Na_2DMG + 1000 mL H_2O	No Color with $\text{K}_2\text{S}_2\text{O}_8$
SLN2	5.0 mL 0.1M Na_2DMG + 0.5 mL 0.1M CuSO_4 + 1000 mL H_2O	No Color with $\text{K}_2\text{S}_2\text{O}_8$
SLN3	0.5 mL 0.1M CuSO_4 + 500 mL H_2O + 5.0 mL 0.1M Na_2DMG + 500 mL H_2O	Pink Color with $\text{K}_2\text{S}_2\text{O}_8$
SLN4	5.0 mL 0.1M Na_2DMG + 500 mL H_2O + 0.5 mL 0.1M CuSO_4 + 500 mL H_2O	Pink Color with $\text{K}_2\text{S}_2\text{O}_8$

table, the order in which the solutions are listed is the order in which they were added to the reaction vessel. In addition to the behavior observed in this table, it was also observed that allowing any solution to stand overnight resulted in a distinct reduction in its reactivity towards persulfate, usually destroying it altogether. The ultraviolet spectrum of all four solutions was

also measured, before and after aging. No significant differences were found.

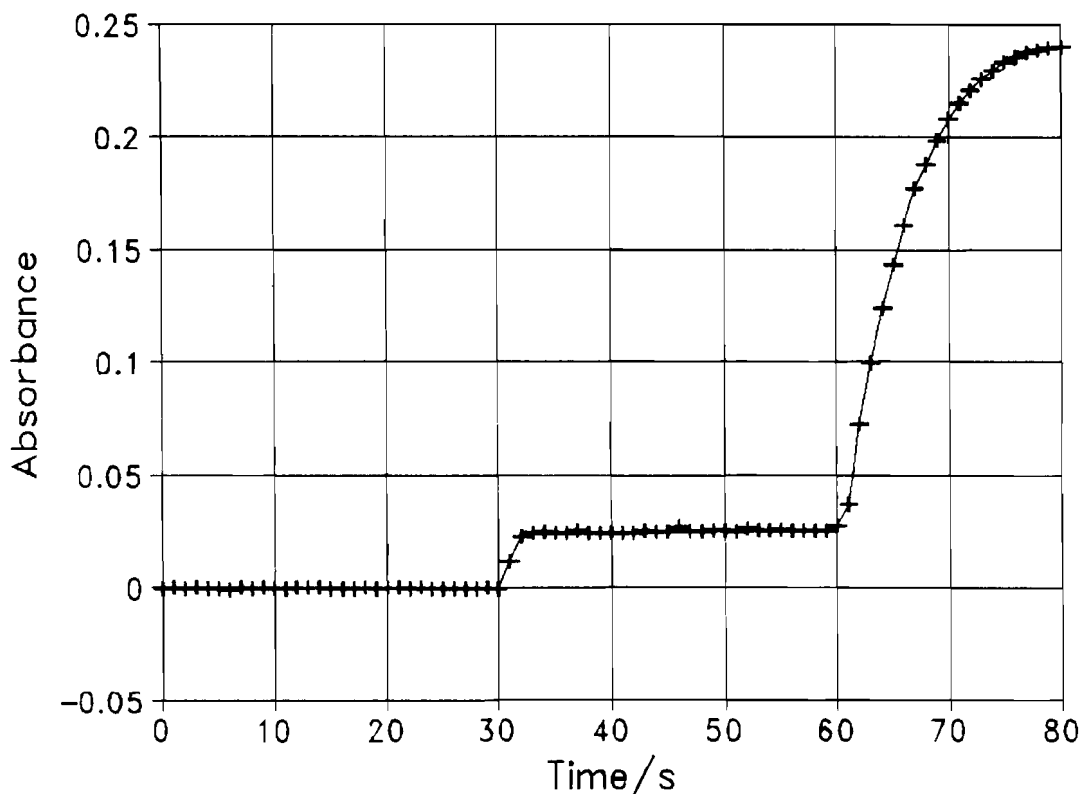


Figure 8: Behavior of Absorbance with Double-injection Technique

In order to eliminate the effects just described, a further technique was developed. The initial solution in the reaction vessel contained only Na_2dmg and base. The required amount of CuSO_4 was then injected from a syringe at a signal from the computer. At a second signal, half a minute later, the persulfate was injected. Figure 8 shows the initial stages of a typical run. The initial level region corresponds to the Na_2dmg solution. The upward step in absorbance to a new plateau corresponds to the addition of the copper sulfate. The final larger jump in absorbance corresponds to the addition of

$K_2S_2O_8$ and the production of the red color.

Table IV shows the results for four repetitions of the same run by using this double injection technique. All concentrations in one run were the same as in all the others. The mean and standard deviation for the initial slope of the absorbance was $0.0336 \pm 0.0015 \text{ s}^{-1}$. This corresponds to a relative standard deviation of 4%. This reproducibility was considered to be satisfactory.

Table IV. Reproducibility of Initial Slope Using Double-injection Technique

Run	BD50S1LA	BD50S1LB	BD50S1SA	BD50S1SB
Initial slope/ s^{-1}	0.0342	0.0333	0.0351	0.0317

Kinetic Study of the Reaction

4.1 Introduction

All the kinetic investigations described below involve measuring the initial rate of change of the absorbance with time, i.e. dA/dt . If only one light-absorbing species is involved and this species is a product, then, by the Beer-Lambert Law:

$$A = \epsilon b c$$

where b is the thickness of the solution in the light path, c is the molar concentration of the absorbing product and ϵ is its molar absorption coefficient. Differentiating the absorbance with respect to time gives the result

$$\frac{dA}{dt} = \epsilon b \frac{dc}{dt} = K \frac{dc}{dt} \quad (5)$$

i.e. the slope of the absorbance curve is proportional to the rate of the reaction, even though K , the constant of proportionality, is unknown.

This result is true even if there is more than one absorbing species, provided only that no simultaneous side reactions occur. Suppose that the reaction being studied is



where $\nu_A, \nu_B, \nu_M, \nu_N$, etc. are the stoichiometric coefficients (products positive, reactants negative). Suppose also that each species X absorbs light with a

molar absorption coefficient ϵ_X . Then, the following equation holds:

$$A = b (\epsilon_A C_A + \epsilon_B C_B + \epsilon_H C_H + \epsilon_N C_N + \dots)$$

where C_X denotes the concentration of species X. If no side reactions occur, all concentration changes are simply related to each other by the relationship:

$$d\xi = \frac{dc_A}{\nu_A} = \frac{dc_B}{\nu_B} = \frac{dc_H}{\nu_H} = \frac{dc_N}{\nu_N} = \dots$$

where $d\xi$ is the change in the extent of the reaction. Thus,

$$\frac{dA}{dt} = b (\nu_A \epsilon_A + \nu_B \epsilon_B + \nu_H \epsilon_H + \nu_N \epsilon_N + \dots) \frac{d\xi}{dt} \quad (6)$$

Since all terms inside the parentheses are constant, it is concluded that:

$$\frac{dA}{dt} = K \frac{d\xi}{dt} \quad (7)$$

Again the rate of change of absorbance dA/dt is proportional to the rate of the reaction whether one or several of the species involved absorbs light.

This proportionality means that even though it may not be possible to measure the actual rate of the reaction, it will still be possible to determine the order of the reaction with respect to the various reactants. For example, if it is found that the initial slope is first order with respect to the initial copper(II) concentration, then it follows that the rate of the initial reaction is first order with respect to copper(II).

Obviously the situation would be improved if the value of K in Equation 7 could be determined. The actual rate of the reaction at any time could then

be measured and hopefully fitted to a theoretical model. However, this is only possible if the reaction goes virtually to completion. The reason why this is so is best seen by assuming that only one species, a product, absorbs light. If the reaction goes to completion, the final concentration of the product, c_{∞} , will be known from the initial composition of the solution. The final absorbance, A_{∞} , can be measured. In consequence K , the proportionality constant connecting A and c , can be found.

Under the experimental conditions used here, it was never possible to obtain a solution in which the reaction had virtually gone to completion. The main absorbing species, the pink complex, was too reactive. No sooner was it formed than it reacted further. In all runs the absorbance first increased, and then decreased. In no case did it approach a maximum value asymptotically and then remain there, the behavior needed to find the final value of the absorbance A_{∞} .

Because of this difficulty, attention was restricted to investigating only the initial rate of change of absorbance with time.

4.2 Dependence on Persulfate Ion Concentration

Experiments to investigate the dependence of the initial rate of this reaction on persulfate ion were started after the single-injection technique described above was developed, but before the development of the double-injection technique. All solutions used in these experiments had the same initial concentrations of Na_2dmg and CuSO_4 , but varied in the concentration of $\text{K}_2\text{S}_2\text{O}_8$ involved. Volumes used were always 50 mL of 2.0×10^{-3} mol/L Na_2dmg solution and 10 mL of 1.0×10^{-3} mol/L CuSO_4 solution and the final volume was

always 200 ± 0.1 mL. Thus, the concentrations of Na_2dmg and CuSO_4 in the reaction vessel were always kept at 5.0×10^{-4} mol/L and 5.0×10^{-5} mol/L respectively. The variation of persulfate concentration was realized by injecting different volumes of 0.10 mol/L persulfate solution. Slightly different volumes of water were used in each run so as to keep the total volume constant. The initial pH of all solutions was in the range 10.3 to 10.4.

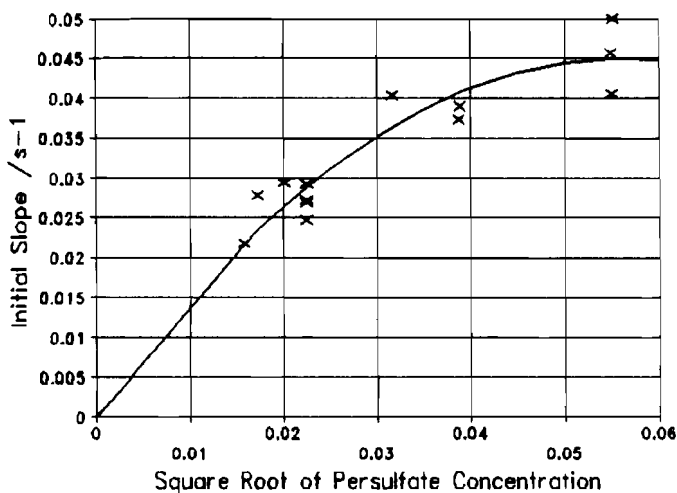


Figure 9: Variation of Initial Rate with Persulfate Concentration

Figure 9 and Figure 10 show the results of two different sets of runs. The y-axis values correspond to the initial slopes of absorbance versus time curves, while the x-axis values correspond to the square roots of the persulfate concentration in the initial reaction mixture. In the first set (i.e. Figure 9), points start to deviate from the linear relationship above a persulfate concentration of about 9×10^{-4} mol/L $\{0.03 \text{ mol}^{1/2} \text{L}^{-1/2}$ in the figure}. In the second set, Figure 10, somewhat lower persulfate concentrations were used. Here a reasonably straight line was obtained with an R^2 value of 0.81.

After the double injection technique had been developed, the

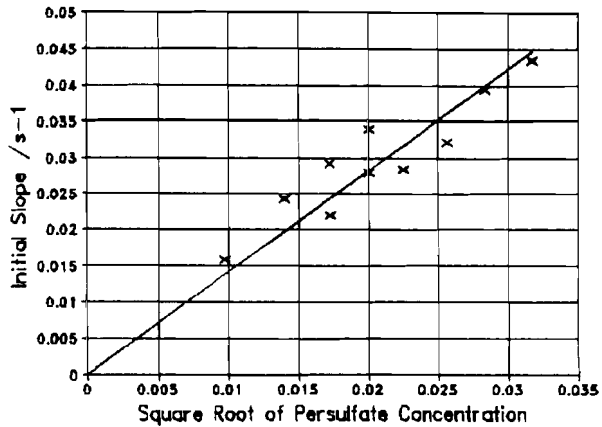


Figure 10: Variation of Initial Slope with Square Root of Persulfate Concentration (Low Concentrations)

dependence of the initial rate of the reaction on persulfate concentration was reinvestigated. Results are shown in Figure 11. Three different runs were performed, each indicated with a different symbol. The range of persulfate concentration used was about the same as that in Figure 10. This time, however, the curvature is more marked. Nevertheless, the data are consistent with a linear relationship at low persulfate concentrations. A least-squares quadratic fit to these data gave an R^2 value of 0.91, only a small improvement in reproducibility over the results in Figure 9 and Figure 10.

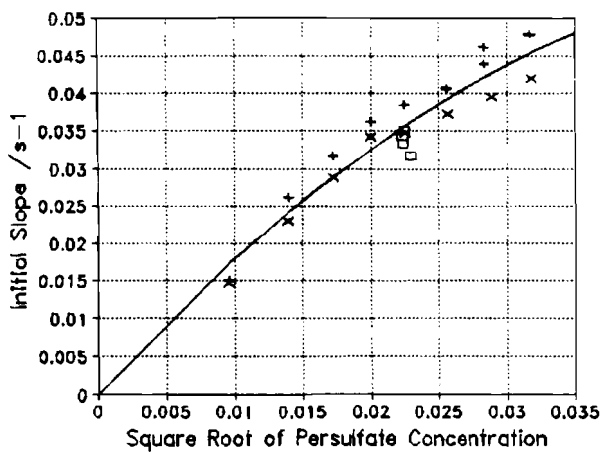


Figure 11: Variation of Initial Slope with Square Root of Persulfate Concentration (Double Injection Technique)

4.3 Dependence on pH Value

The dependence of the rate of this reaction on pH was investigated by adding different volumes of NaOH solution when preparing the reaction mixture. This scheme was adopted in order to avoid using buffer mixtures. As a consequence, all solutions investigated had a pH in excess of 10.3.

Five sets of runs were performed. In all runs the initial concentration of CuSO_4 was set at 5.0×10^{-5} mol/L and that of Na_2dmg and $\text{K}_2\text{S}_2\text{O}_8$ were both set at 5.0×10^{-4} mol/L. In each set the same volume of 2×10^{-3} mol/L NaOH was added. In the first set, for example, no extra NaOH was added, in the second set 10 mL, in the third set 25 mL and so on. Again the total volume of the solution was always 200 ± 0.1 mL. The double-injection technique was used to add first the CuSO_4 solution and then the $\text{K}_2\text{S}_2\text{O}_8$ solution.

Table V. Effect of Added NaOH on Initial Rates

Set Label	Vol /mL	Initial Slopes/ s^{-1}					Mean	Std. Devn.
BD500H0	0	0.0353	0.0364	0.0369	0.0373	0.0399	0.037	0.0015
ED50010	10	0.0385	0.0405	0.039	0.0347	0.0397	0.038	0.0020
GD50025	25	0.025	0.0286	0.0281	0.0266	0.0275	0.027	0.0013
DD50050	50	0.0434	0.046	0.0472	0.044	0.0521	0.046	0.0031
ID50075	75	0.0275	0.0266	0.0264	0.028	0.0252	0.026	0.00097
FD50010	100		0.037	0.0342	0.0383		0.036	0.0014

The results obtained for the initial rate in all 5 sets, along with the volume of NaOH used in each set, are given in Table V. The results are also plotted in Figure 12. Each run shows a relative standard deviation between 3.6 and 6.7 percent, a fairly satisfactory result.

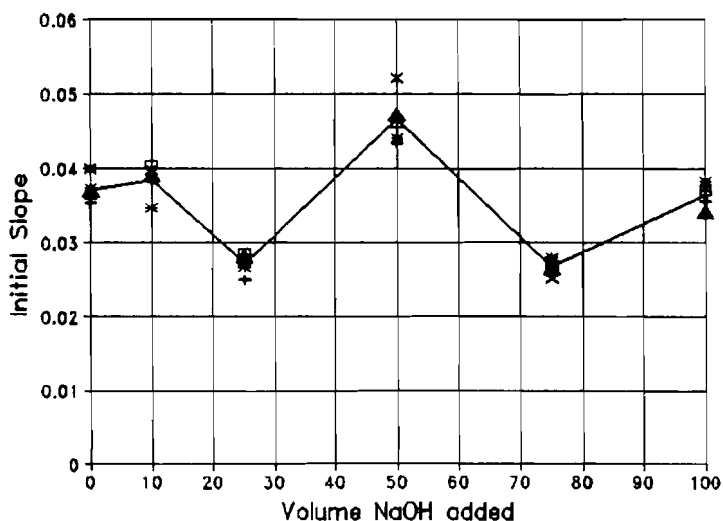


Figure 12: Variation of Initial Slope with Added NaOH

The overall variation with hydroxide ion, however, is more puzzling. In Figure 12, all 30 points are plotted. The line in this figure connects the mean values for each set. The W-shaped form of this plot suggests that the reaction must be quite complex at high pH values. There is some visual indication that this is so. When no hydroxide is added, the reaction produces a pink color which then slowly fades. As higher volumes of hydroxide are used, the color produced in the reaction changes from pink to an orange-brown color.

4.4 Dependence on Copper(II) Concentration

In this series of experiments, the concentrations of both sodium dimethylglyoximate and potassium persulfate were held constant and only the concentration of copper sulfate was varied. The initial concentration of Na_2dmg used in the reaction flask was 5×10^{-4} mol/L and that of $\text{K}_2\text{S}_2\text{O}_8$ was 2.5×10^{-5} mol/L throughout this section of the work.

As in previous experiments, Na_2dmg solution was first added to the reaction vessel and diluted to about 200 mL. An appropriate volume of CuSO_4 solution was then injected. The concentration of this solution was either 1, 2, or 4×10^{-2} mol/L. Following this, the $\text{K}_2\text{S}_2\text{O}_8$ solution was injected. The total volume of the solution in the reaction vessel was always 200 ± 0.1 mL.

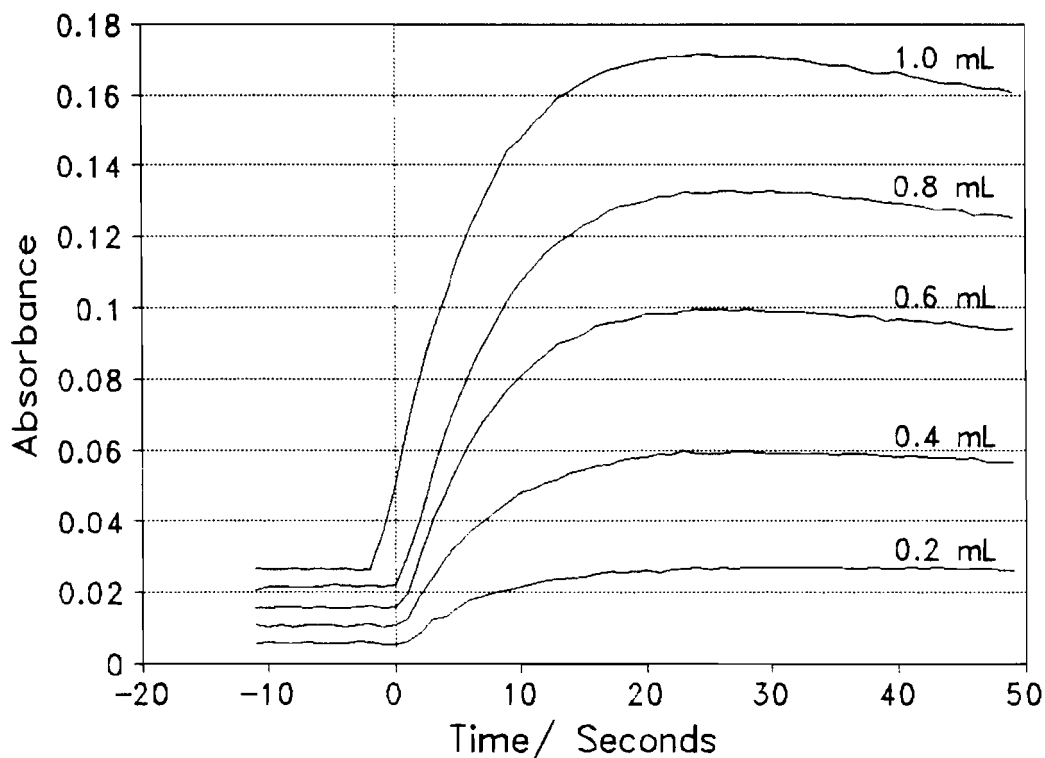


Figure 13: Variation of Absorbance with Time for Cu(II) Concentrations below 5×10^{-5} mol / L

Figure 13 illustrates the variation of absorbance with time obtained for a set of five runs, each with a different injected volume of 0.01M CuSO_4 . As the Cu(II) concentration increases, so does the initial slope of the reaction and also the maximum absorbance achieved.

All these runs were performed using the double-injection technique, but

the variation of absorbance with time is only drawn after the first injection. In all cases, the initial absorbance, before the injection of CuSO_4 , was zero. In other words, each run showed a behavior similar to that shown in Figure 8. For reasons of space, however, the initial zero portion of these curves has been omitted.

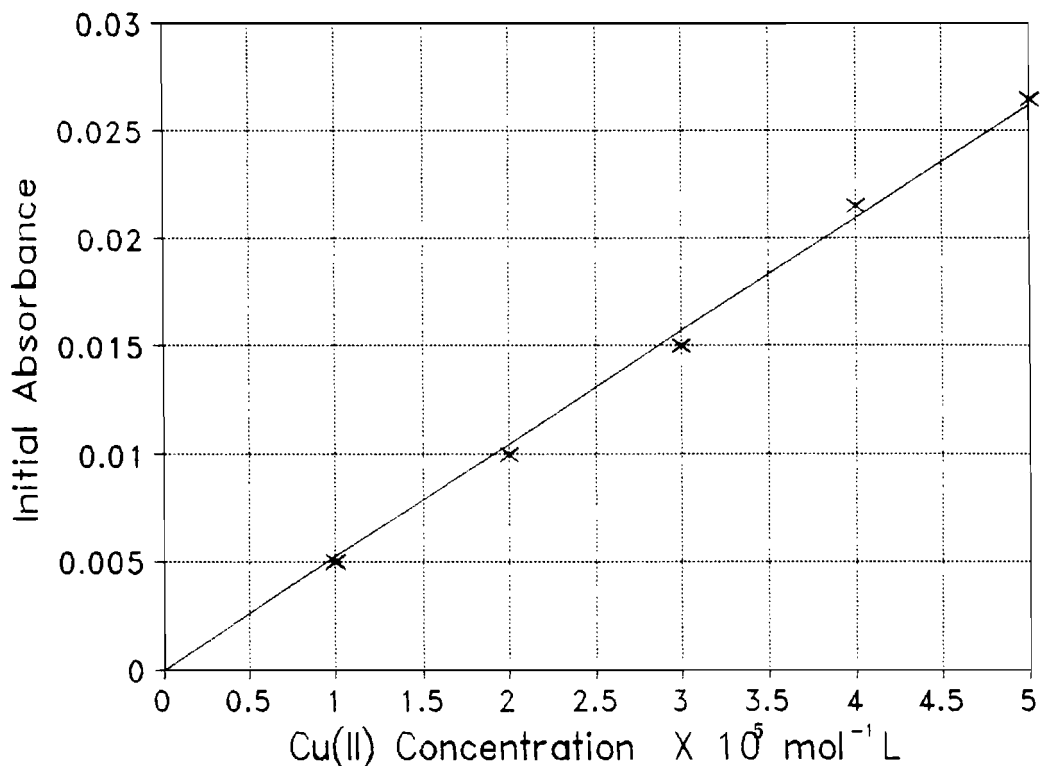


Figure 14: Variation of Initial Absorbance with Cu(II) Concentration

Note in Figure 13 how the initial constant absorbance value before the injection of persulfate varies from run to run and increases with Cu(II) concentration. This initial absorbance corresponds to the absorbance of the complex (or complexes) formed when the Cu(II) solution is added to the Na_2dmg solution. As shown in Figure 14 the value of this initial absorbance is

proportional to the Cu(II) concentration. In other words Beer's Law is obeyed by the solutions existing before the addition of persulfate. The data plotted are for the same five runs shown in Figure 13. An excellent straight line through the origin with an R^2 value of 0.996 is obtained.

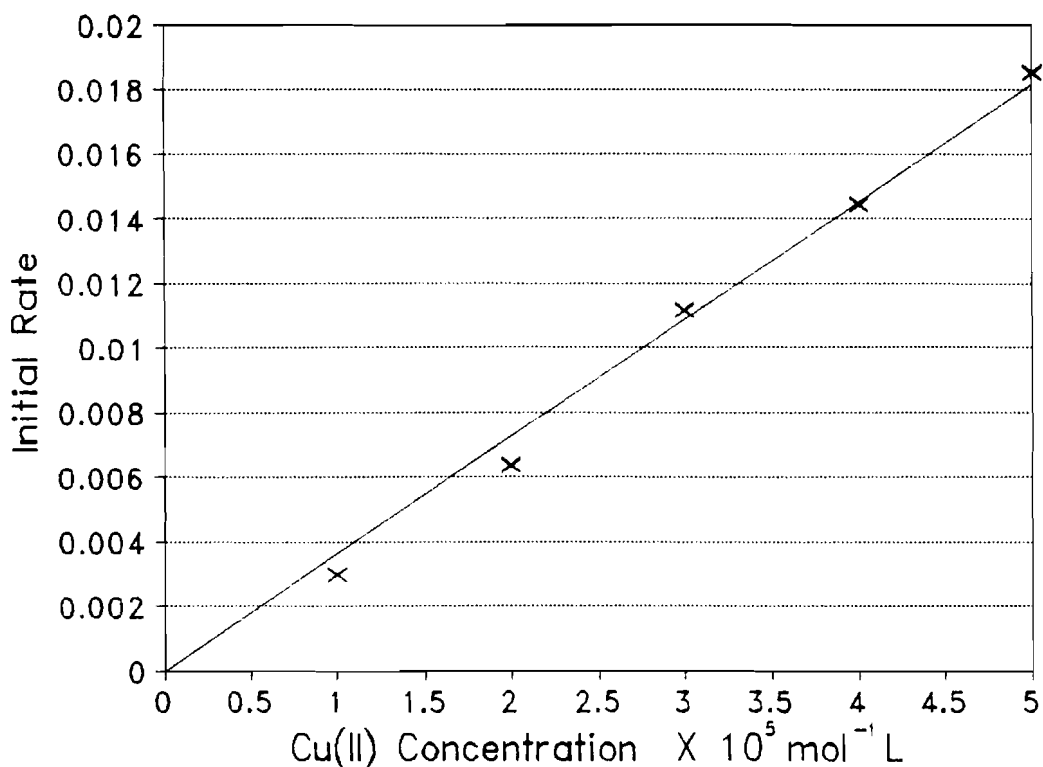


Figure 15: Variation of Initial Slope with Cu(II) Concentration

In Figure 15 the value of the initial slope of each of the runs shown in Figure 13 is plotted against the Cu(II) concentration. Regression analysis gives a good straight line going through the origin with an R^2 value of 0.990. At these concentrations, therefore, the initial rate of increase of absorbance with time is first order with respect to the concentration of copper(II).

At higher concentrations of copper(II), this simple relationship between initial slope and Cu(II) concentration is no longer maintained. In Figure 16

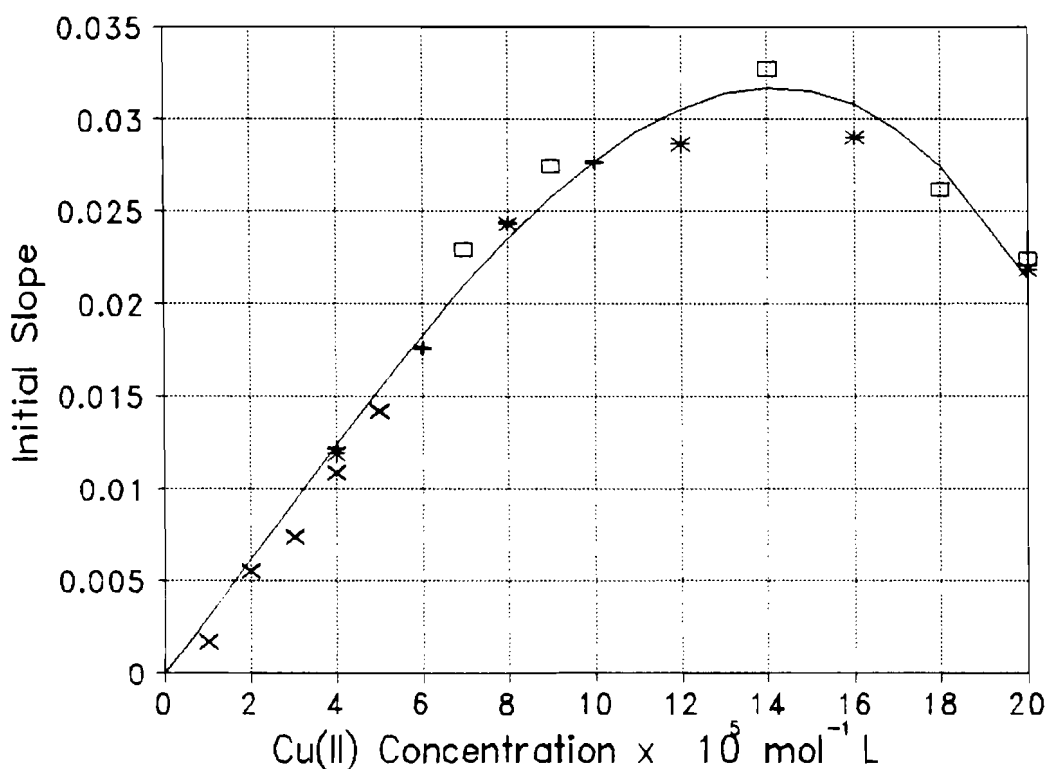


Figure 16: Variation of Initial Slope with Cu(II) Concentration up to $2 \times 10^{-4} \text{ mol/L}$

values for the initial slope of the reaction are plotted against the initial concentration of Cu(II), but this time the maximum Cu(II) concentration is four times that of Figure 15. At low concentrations (up to about $8 \times 10^{-5} \text{ mol/L}$), the slope is indeed proportional to the Cu(II) concentration. At higher concentrations, though, there is a pronounced curvature. Eventually the value of the slope begins to decrease with increasing Cu(II) concentration. The curve through the points given in Figure 16 is the best cubic fit.

Although the variation of the initial slope of the absorbance with Cu(II) concentration shown in Figure 16 is quite complex, the behavior of the initial absorbance value before the addition of oxidant is fairly simple. In Figure 17 the initial absorbances for all the 19 runs plotted in Figure 16 are plotted

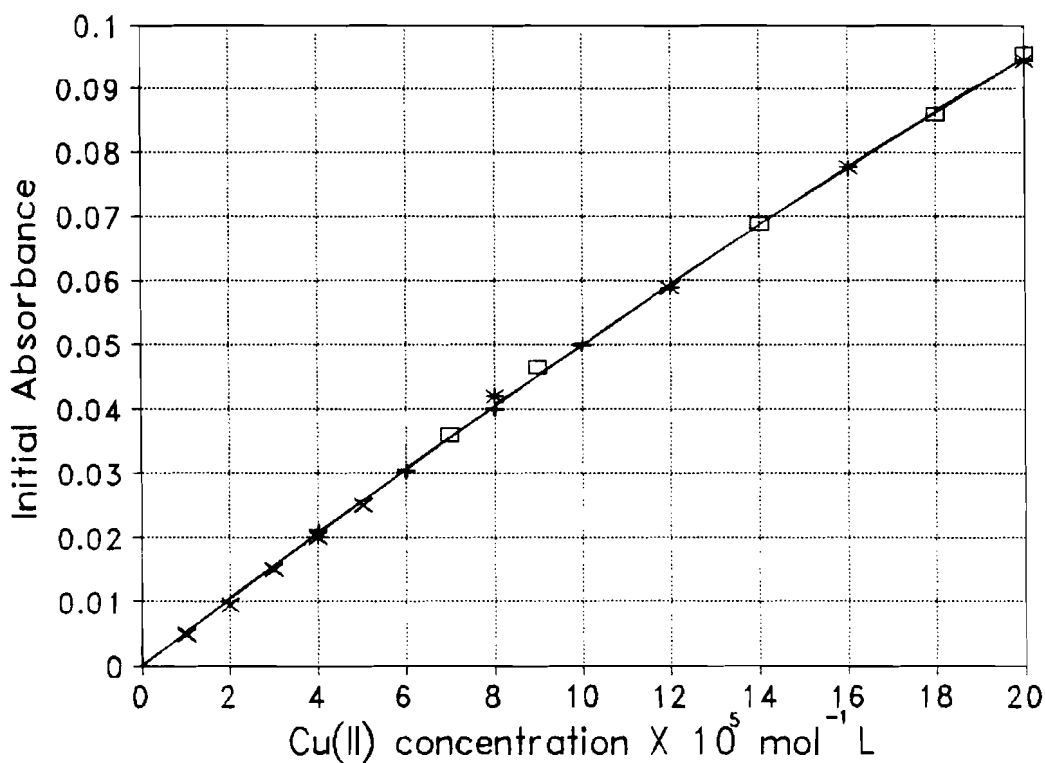


Figure 17: Variation of Initial Absorbance with Cu(II) Concentrations up to $2 \times 10^{-4} \text{ mol/L}$

against the initial Cu(II) concentration. As can be seen from this figure, deviations from Beer's Law, though present, are quite small. The best quadratic fit of these points gives an excellent R^2 value of 0.999. However, the R^2 value of the best straight line fit is almost as good, namely 0.997. This closeness to linearity suggests that these solutions contain essentially only one Cu(II) complex before the addition of oxidant.

Figure 18 shows how the absorbance changes with time at higher Cu(II) concentrations. The five runs shown here are from the run QUATB. These are the points indicated by asterisk in Figure 16. The labels on each curve refer to the volume of 0.04M CuSO_4 injected into the reaction vessel. The general appearance of the four most dilute solutions is fairly similar to that shown

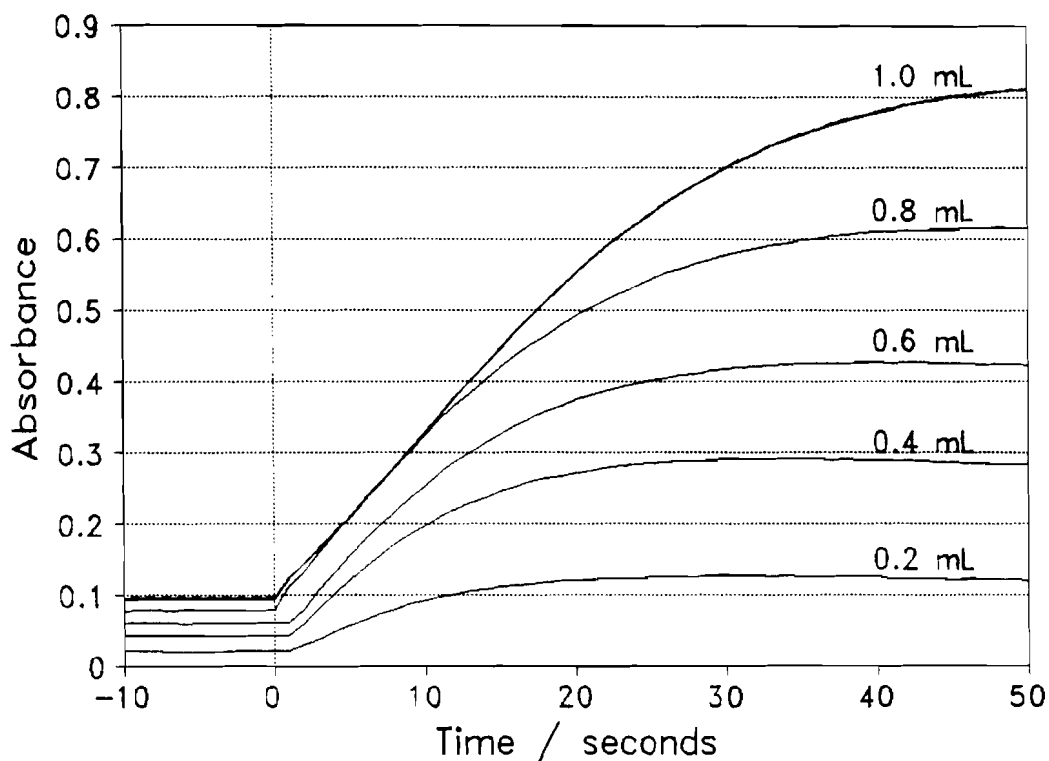


Figure 18: Variation of Absorbance with Time at Cu(II) Concentrations above 4×10^{-5} mol/L

earlier in Figure 13. The behavior of the run of highest Cu(II) concentration (run 1.0 mL) is anomalous. The color of this solution was also observed to be different. Instead of the regular pink, an orange-brown color was produced.

Discussion

5.1 Conclusions

The investigations described in this thesis have had two positive results. In the first place, a novel, inexpensive, and simple method has been developed for investigating the kinetics of a reaction accompanied by a color change. In the second place, real progress has been made in unravelling the nature of the color reaction which occurs when basic solutions containing Cu(II) and dimethylglyoxime are oxidized by persulfate ions. The order of this reaction with respect to several components has been established.

As the above work has shown, the combination of a dipping-probe colorimeter and a jacketed beaker like that shown in Figure 4 provides a very convenient method for investigating the kinetics of a reaction in which a color change occurs. By putting the colorimeter in the solution instead of the more traditional method of putting the solution in the colorimeter, a much greater flexibility is achieved. An instance of this flexibility occurred in the investigation just described. The technique being developed required an initial addition of CuSO_4 solution followed almost immediately by the addition of $\text{K}_2\text{S}_2\text{O}_8$ solution to the reaction vessel. This was easy to do in an open vessel, but would have been much more difficult to implement in a stopped flow apparatus or with any other technique involving a closed container.

The dipping-probe method developed here has, of course, its limitations. With the simple techniques used here, mixing would only be achieved in about a second. This would restrict investigation to reactions with a half-life

greater than about ten seconds. A second draw back is the necessity for using an interference filter. This restricts investigation to only a few wavelengths.

A further possible difficulty is the reproducibility of successive runs. In the work described above excellent reproducibility (R^2 greater than 0.995) was obtained for measurements of steady absorbances. A similar internal agreement was found for absorbance measurements in any given run. When repetitions of the same run were compared, though, a much inferior reproducibility was observed. A major reason for this lack of reproducibility proved to be differences in the way that reactants had been prepared and mixed. Use of the double-injection technique standardized the mixing history of the solutions and resulted in a distinct improvement in reproducibility ($R^2 \approx 0.95$).

Part of the difficulty experienced in obtaining reproducibility in this work may have been the result of using fairly basic solutions. Mopurgo and Tomlinson² noticed a tendency for a precipitate with the approximate formula $\text{Cu}(\text{Hdmg})(\text{OH})$ to be formed in basic solutions. The effect of using less basic solutions on the reproducibility of the initial rate of this reaction deserves investigation.

The work just described also made progress toward elucidating the kinetics of this color reaction. These investigations were restricted to basic unbuffered solutions obtained by mixing CuSO_4 solutions with Na_2dmg solutions and then adding $\text{K}_2\text{S}_2\text{O}_8$. In a typical run the $\text{Cu}(\text{II})$ solution was in the neighborhood of 5×10^{-5} mol/L while both Na_2dmg and $\text{K}_2\text{S}_2\text{O}_8$ were both in the neighborhood of 5×10^{-4} mol/L (i.e. about ten times the $\text{Cu}(\text{II})$ concentration). The pH of these solutions was always between 10.2 and 10.5 except for those

runs in which excess NaOH was added in investigating the effect of pH on the rate of the reaction.

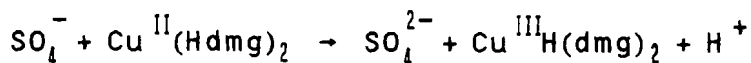
In solutions of this type it was established that the production of the pink color is half order with respect to $K_2S_2O_8$ for concentrations below about 5×10^{-4} mol/L. The reaction was also found to be first order with respect to Cu(II) for a concentration up to about 8×10^{-4} mol/L and a Na₂dmg/Cu(II) ratio in excess of 5:1. However, the dependence of this reaction on the hydrogen ion concentration was not clearly established. The results displayed in Figure 12 are open to two interpretations. If the best line is drawn through all 30 points, then the reaction rate changes very little with pH. On the other hand, if the mean values for each volume are to be regarded as more reliable, then the dependence of rate on pH is the complex W-shaped line shown in Figure 12.

Apart from the pH-dependence, these results are in conformity with what other workers have found. Many reactions involving persulfate ion are known in which $SO_4^{\cdot -}$ radicals are involved and the reaction is half order with respect to the persulfate ion concentration (e.g. Pennington¹¹). Invariably these reactions are one-electron oxidations in which the $SO_4^{\cdot -}$ radical accepts an electron and is converted into a sulfate ion SO_4^{2-} .

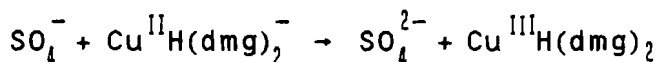
Only one kinetic study on the oxidation of copper-dimethylglyoxime complexes to form the pink compound can be found in the literature. This is the work done by Sulfab⁹ described in the introduction on page 5. Again this is a one electron transfer reaction.

If the reaction is half order with respect to persulfate and first order with respect to copper, this means that half a persulfate ion (i.e. an $SO_4^{\cdot -}$ radical) and a copper(II) species are involved in the rate-determining step.

Presumably the pink color produced is the same Cu(III) complex inferred by Sulfab. A reasonable formulation for the rate determining step is therefore:



However, since the order of the reaction with respect to H^+ has not been satisfactorily established, one should realize that alternative formulations of the rate determining step are also possible differing from it by the presence or absence of a proton, for example:



5.2 Suggestions for Further Work

Although much progress has been made in the work described above, more remains to be done before the oxidation of Cu(II)-dimethylglyoxime complexes with persulfate can be said to be well-understood.

In the work just described, attention was confined to rather basic solutions ($\text{pH} \approx 10.5$), partly to avoid the use of buffers, and partly because the reaction seemed to be simpler in basic solutions. A much better understanding of the reaction would be obtained if it were extended to lower pH values. In previous work (Welsh⁶) it was found that the results obtained seemed to depend on the nature of the buffer. However, Sulfab's work⁹ on the electrolytic oxidation of $\text{Cu}^{\text{II}}(\text{Hdmg})_2$ used three different buffers and the results obtained were buffer-independent in the range pH 5 to pH 8.5. Sulfab's results indicate that it would be worthwhile to make another attempt to obtain buffer-independent results at lower pH values for the persulfate oxidation.

In extending this work to lower pH values, another factor needs to be

considered, namely the rate of the reaction. In the work described above, the investigations into pH dependence gave an ambiguous result. If anything they indicated that the rate of the reaction will be slower in more acidic solutions. If this is actually the case, it will be easy to following the reaction with our present apparatus. However, the oxidation of $\text{Cu}^{\text{II}}(\text{Hdmg})_2$ by $[\text{Cu}^{\text{III}}(\text{dgen})]^+$ studied by Sulfab often involved a half-life of a few centiseconds. This is much too fast to study with our apparatus. Although the reaction studied by Sulfab is similar to the one studied here, it does not follow that its rate will be similar. If the persulfate oxidation reaction proceeds through the production of SO_4^- radicals, then an O-O bond must first be broken when the $\text{S}_2\text{O}_8^{2-}$ is dissociated. This would require a higher activation energy than for Sulfab's reaction and hence result in a much slower rate.

It is now clear that much smaller persulfate concentrations should be use in further work. Up to this point, investigations at E.S.U. have tended to use solutions in which the persulfate ion concentration was in considerable excess: as high as 10 persulfate ions to one copper ion. Every effort should be made to reduce the persulfate ion to a much lower ratio. The persulfate ion is a powerful oxidizing agent and our results indicate that an excess results in further oxidation reactions after the initial production of the pink color. In his studies on the oxidation of $\text{Cu}^{\text{II}}(\text{Hdmg})_2$ by $[\text{Cu}^{\text{III}}(\text{dgen})]^+$, Sulfab was able to use a ratio of oxidizing to reducing agent of about 1 to 10. As a result, he was able to achieve a situation in which essentially only one reaction was occurring. The production of the pink color, in other words, went essentially to completion while following a simple first-order rate law. This is in contrast to the very complex behavior shown, for instance, by the reaction in Figure 3,

where the absorbance, instead of increasing in a regular manner, actually alternates between increasing and decreasing several times as a succession of reactions occurs.

Another obvious direction for further investigation is to determine the nature of the Cu(II) complexes present in dimethylglyoxime solutions before the addition of oxidant. Though Mopurgo and Tomlinson's work² in this connection has value, it is far from being definitive. In particular, though they measured many spectra, they did not make any quantitative deductions from their spectrophotometric measurements. A useful constant to know accurately would be the pK_a for $Cu^{II}(Hdmg)_2$. The best literature value for this constant is 10.6 obtained by Dyrrsen and Hennichs¹² in 1961 using a solvent extraction method. The loss of a proton by this complex is almost certain to produce a spectral change which can be followed photometrically. This would make it possible to measure this pK_a very accurately with our apparatus. Another related investigation which would be worthwhile would be a series of experiments to determine under what circumstances solutions of Copper (II) and dimethylglyoxime actually obey Beer's Law. As shown in Figure 14 and Figure 17, the dipping-probe colorimeter lends itself particularly well to this kind of work.

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Yang Cao

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July 31, 91

Date

Kinetics of Oxidation of Cu(II) in Basic

Solutions of Dimethylamine by Persulfate Ion

Title of Thesis

Jackie Sollert

Signature of Graduate Office Staff Member

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