The Kinetics of The Oxidation of [N-(2-hydroxy-ethyl)ethlyenediamine- N, N', N'-triacetatocobalt (II)] by Copper (II) Ion.

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ABSTRACT

The kinetics of the oxidation of N-(2-hydroxy-ethyl) ethylenediaminetriacetatocobaltate (II) ions by Cu(II) in aqueous perchloric acid medium was studied under pseudo- first order conditions of large excess of Cu(II) at T $=28^0$C, $1=0.05$moldm^{-3} ($NaClO_4$), $[H^+]= 5x10^{-3}$ moldm^{-3}. The stoichiometric studies showed that for every mole of [CoHEDTA(H_2O)], one mole of Cu(II) was consumed. The rate data for the oxidation of [CoHEDTA(H_2O)] by Cu(II) were obtained as a decrease in absorbance of the resulting mixture at 510nm.

The kinetic curves obtained under this conditions were exponential and the rate constant were obtained from the logarithmic plot of absorbance difference log(A_t -A∞) against time (t). pseudo- first order rate constants were determined from the slope of the plot, based on the following equation:

$$(A\infty-A_t) – (A\infty-A_0)e^{-kobs.t}$$

The logarithmic plot of the difference in absorbance of the reacting solution at 510nm against time was linear and the k_{obs} increased with [Cu(II)]. The plot of logk_{obs} versus log[CU^{2+}] at constant [H^+] and constant ionic strength was linear with negligible intercept and a slope of 0.5 indicating half-order dependence of rate with respect to [Cu(II)]. The reaction showed positive acid dependence, negative Bronsted-Dye primary salt effect. The plausible rate of constant acid concentration is given as:

$$\frac{-d[Cu^{2+}]}{dt} = \{c + d[H^+]\}[Co^{II}HEDTA(H_2O)][Cu^{2+}]$$

INTRODUCTION

Copper is one of the transition elements frequently found at the active site of proteins[1-3]. The copper-containing enzymes and proteins constitute an important class of biologically active compounds (Mukherjee, 2003).[4] The biological functions of copper proteins/enzymes include electron transfer[5], dioxygen transport[6], oxygenation, oxidation, reduction and disproportionation[7-9]

In nature, a variety of copper proteins are essential constituents of aerobic organisms[10], including hemocyanins (arthropodal and molluskan O_2 carriers) and enzymes that "activate" O_2, promoting oxygen atom incorporation into biological substrates (Holm etal, 1996)[11].

The latter include tyrosinase (a monooxygenase, incorporating one oxygen atom to the substrate and reducing the other to water)[12] and dopamine β -hydroxylase (a monooxygenase). "Blue" multicopper oxidases [e.g.. laccase (phenol and diamine oxidation)[13], ascorbate oxidase (oxidation of l- ascorbate) and ceruloplasmin] promote substrate one- electron oxidation while reducing O_2 to water[14].

EXPERIMENTAL

All reagents used were of analar grade. The stock solutions of [$CoHEDTAOH_2$] were prepared according to the method of Mansour (2003)[15-17], Copper (II) tetraoxosulphate (VI) was prepared by dissolving accurate weighed amount of the salt in a known volume of distilled water. The $_{max}$(510nm)

was determined by running the electronic spectrum of the solution of [CoHEDTAOH$_2$] in the wavelength range of 340 -700nm, and plotting a graph of the absorbance against wavelength.

A stock solution of perchloric acid was made by diluting analar grade acid (70%, specific gravity 1.67) and standardizing titrimetrically. Analar grade sodium perchlorate ($NaClO_4$) was used to maintain the ionic strength.

KINETICS

The wavelength of maximum absorption, $_{max}$ of [CoHEDTAOH$_2$]$^-$ was 510nm using spectrum lab 330

– 1000 spectronic 23$_A$ spectrophotometer. The rate of the reaction of [CoHEDTAOH$_2$]$^-$ with Cu^{2+} ion

was studied at this $_{max}$ by observing the change in absorbance of [CoHEDTAOH$_2$]$^-$ at 28°C and

0.05moldm^{-3} ($NaClO_4$) ionic strength.

The plots of log (A_t - A∞) versus time were made. From the gradient, the pseudo – first order rate constants k, were determined as given by the equation.

$$\text{Log}\,(A_t - A_\infty) = \frac{K_1 t}{2.303} + \log\,(A_O - A_\infty) \ldots\ldots\ldots\ldots \quad \text{(I).}$$

Where A∞, A_t are the absorbances of the reaction mixture at time infinity, and t, respectively. The second order rate constants (k_2) were obtained from k, as $k_1/[Cu^{2+}]$. The results are presented in table 1.

RESULTS/ DISCUSSION

STOICHIOMETRY

The stoichiometry of the [CoHEDTAOH$_2$]$^-$ with Cu^{2+} reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of the [CoHEDTAOH$_2$]$^-$ was kept constant at 1x 10^{-4}moldm^{-3}, while that of Cu^{2+} was varied from 1.5 x 10^{-5} - 1x10^{-4}moldm^{-3} at ionic strength, 1= 0.05moldm^{-3} ($NaClO_4$) and $[H^+]$ = 5x 10^{-3}moldm^{-3}.

The reactions were allowed to go to completion and the absorbances of the solutions were taken at 510nm. The stoichiometry was determined from the plot of absorbance versus mole ratio $[Cu^{2+}]$ / [CoHEDTAOH$_2$]$^-$.[18]

On the basis of the stoichiometry, final absorbances at completion of reaction were plotted against mole ratio. The result indicated that one mole of [CoHEDTAOH$_2$] reacted with one mole of $[Cu^{2+}]$. The stoichiometric equation for reaction is presented as equation 2.

$$/[\text{CoHEDTAOH}_2]^{-+}\,\text{Cu}^{II} \qquad [\text{CoHEDTAOH}_2] + \text{Cu}^{I} \ldots\ldots\ldots\ldots(2).$$

ORDER OF REACTION

The pseudo – first order plots of log (A_t - A∞) versus time were linear to greater than 75% extent of the reaction respectively.

The linearity of the plot indicates that the reaction is first order with respect to $[CoHEDTAOH_2]$[19-20].

From the slopes of the plots, the pseudo – first order rate constants (k_{obs}) were obtained. Analysis of the plot of log kobs versus log $[Cu^{2+}]$(fig 2), gave a slope of 0.46, indicating half – order dependence of rate on $[Cu^{2+}]$.

The reaction is (1½) order overall. The rate law at constant $[H^+]$ is represented as in equation 3.

$$\frac{d[CoHEDTAOH_2]}{at} = k_{obs} [CoHEDTAOH_2] [Cu^{2+}] \ldots\ldots\ldots\ldots (3).$$

The effect of $[H^+]$ on the rate of the reaction was investigated using perchloric acid in the range $3.0 \leq H^+ \leq 11.0 \times 10^{-3}$ moldm^{-3}, while the $[CoHEDTAOH_2]^-$ and $[CU^{2+}]$ were kept constant. The reaction was carried out at 28^0C and 1 = 0.05moldm^{-3} ($NaClO_4$).

The results are presented in table 1. The results shows that the rate of reaction increased with increase in $[H^+]$ in the range investigated. The plot of k_2 versus $[H^+]$ was linear with intercept on the k_2 axis as shown in figure 3.

The acid dependent rate constant is represented as in equation 4.

$$k_2 = c + d [H^+]. \qquad (4).$$

The overall rate equation in the acid range investigated is

$$\frac{-d[Cu^{2+}]}{dt} = (c+d[H^+])[CoHEDTAOH_2][Cu^{2+}] \qquad (5).$$

Acid dependence of this type shows that there are two parallel reaction pathways; one which is acid dependent and the other that is acid – independent[16,17,21.]

The effect of ionic strength on the rate of the reaction was investigated in the range 1 = 0.02 – 0.06moldm^{-3} ($NaClO_4$), while the concentration of other reagents was kept constant. The results are presented in table 1. Ionic strength dependence studies show a general trend of decrease in reaction rate with increase in ionic strength of the reaction medium, as shown in table 1. Decrease in reaction rate with increase in ionic strength of the medium is noted to occur in reaction that involves oppositely charged ions[17,22–24]. The plot of logk_2 versus √1 was linear.

Table 1: Pseudo-first order rate constant for the reaction of [$Co^{II}HEDTA(H_2O)$] and [Cu^{II}] at [$Co^{II}HEDTA(H_2O)$]=1×10^{-4} ($moldm^{-3}$), T=29±1°C and ʎmax =510nm.

10^3 [Cu^{2+}] ($moldm^{-3}$)	10^3 [H^+] ($moldm^{-3}$)	I, $NaClO_4$($moldm^{-3}$)	10^3 k_{obs} (S^{-1})	K_2 dm^3mol^{-1}(S^{-1})
2.0	5.0	0.05	4.2989	21.4945
5.0	5.0	0.05	4.606	9.212
7.0	5.0	0.05	5.066	7.237
10.0	5.0	0.05	6.333	63.33
12.0	5.0	0.05	8.0605	67.171
7.0	3.0	0.05	5.389	7.699
7.0	5.0	0.05	6.275	8.964
7.0	7.0	0.05	6.37	9.1
7.0	9.0	0.05	7.860	11.229
7.0	11.0	0.05	9.81	14.014
6.0	5.0	0.02	10.608	17.68
6.0	5.0	0.03	7.64696	12.743
6.0	5.0	0.04	5.47485	9.125
6.0	5.0	0.05	3.915	6.525
6.0	5.0	0.06	3.247	5.412

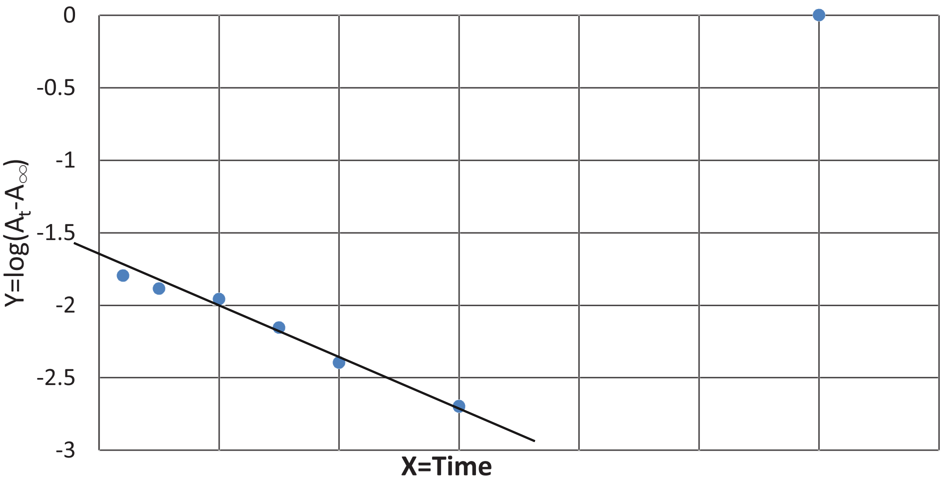

Fig. 1: Graph of log (A_t-A_∞) versus time

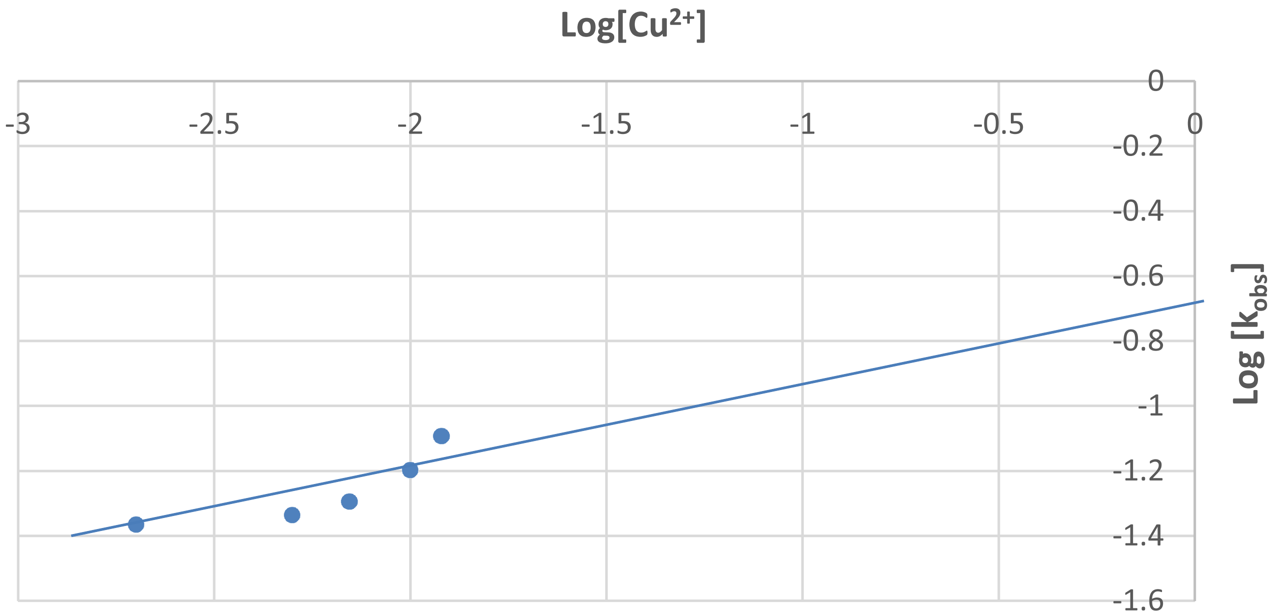

Fig. 2: Plot of log k_{obs} versus log $[Cu^{2+}]$ at constant $[H^+]$ and constant ionic strength.

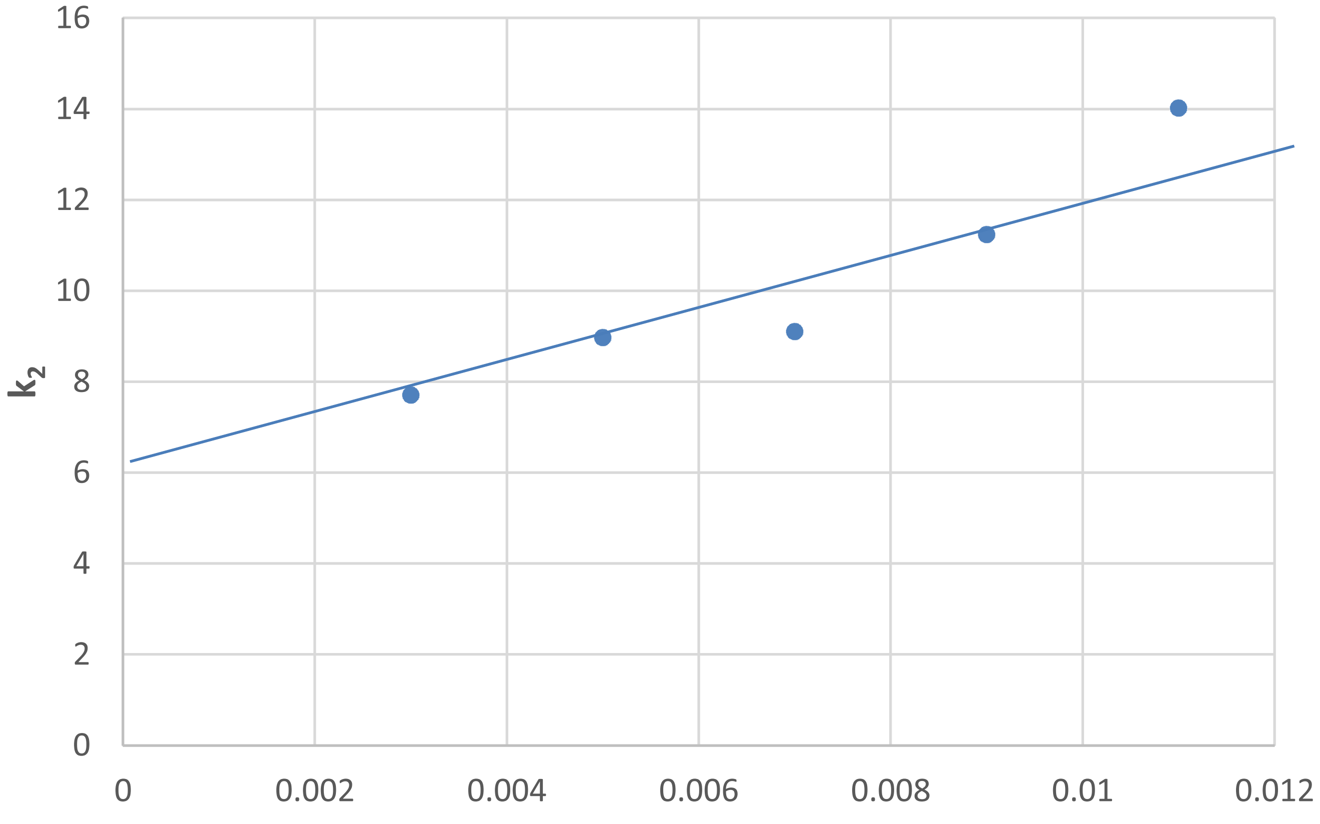

Fig. 3: Plot of k_2 versus $[H^+]$

CONCLUSION

We are preparing to investigate the effect of other interesting parameters like dielectric constant (D), activation parameters and some other things such as catalysis and the presence of free radicals in this reacting system. This will enable us to formulate plausible mechanism for this reaction. If we are able to do this, then we are fulfilling our ultimate aim which is to avail more understanding in the numerous important reactions that are going on in biomolecules (copper protein/enzymes).

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