**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 =280C, 1=0.05moldm-3 (NaCIO4), [H+]= 5x10-3 moldm-3. The stoichiometric studies showed that for every mole of [CoHEDTA(H2O)], one mole of Cu(II) was consumed. The rate data for the oxidation of [CoHEDTA(H2O)] 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(At -A∞) against time (t). pseudo- first order rate constants were determined from the slope of the plot, based on the following equation:

(A∞-At) – (A∞-A0)e-kobs.t

The logarithmic plot of the difference in absorbance of the reacting solution at 510nm against time was linear and the kobs increased with [Cu(II)]. The plot of logkobs versus log[CU2+] 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:

*-d[Cu2+] = {c + d[H+]}[CoIIHEDTA(H2O)][Cu2+]*

 *dt*

**INTRODUCTION**

Copper is one ofthe transition elements frequently found at the active site of proteins1-3. 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 transfer5, dioxygen transport6, oxygenation, oxidation, reduction and disproportionation7-9

In nature, a variety of copper proteins are essential constituents of aerobic organisms10, including hemocyanins (arthropodal and molluskan O2 carriers) and enzymes that "activate" O2, promoting oxygen atom incorporation into biological substrates (Holm etal, 1996)11.

The latter include tyrosinase (a monooxygenase, incorporating oneoxygen 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 O2 to water14.

**EXPERIMENTAL**

All reagents used were of analar grade. The stock solutions of [CoHEDTAOH2] 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 𝝀max (510nm) was determined by running the electronic spectrum of the solution of [CoHEDTAOH2] 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 (NaClO4) was used to maintain the ionic strength.

**KINETICS**

The wavelength of maximum absorption, 𝝀max of [CoHEDTAOH2] – was 510nm using spectrum lab 330 – 1000 spectronic 23A spectrophotometer. The rate of the reaction of [CoHEDTAOH2] – with Cu2+ ion was studied at this 𝝀max by observing the change in absorbance of [CoHEDTAOH2] – at 28oC and 0.05moldm-3 (NaClO4) ionic strength.

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

Log (At - A∞) = K1t + log ( AO –A∞)………………………………… (I).

 2.303

Where A∞, At are the absorbances of the reaction mixture at time infinity, and t, respectively. The second order rate constants (k2) were obtained from k, as k1 /[Cu2+]. The results are presented in table 1.

**RESULTS/ DISCUSSION**

**STOICHIOMETRY**

The stoichiometry of the [CoHEDTAOH2] - with Cu2+ reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of the [CoHEDTAOH2] - was kept constant at 1x 10-4moldm-3, while that of Cu2+ was varied from 1.5 x 10-5 - 1x10-4moldm-3 at ionic strength, 1= 0.05moldm-3 (NaClO4) and [H+] = 5x 10-3moldm-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 [Cu2+]/ [CoHEDTAOH2]-. 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 [CoHEDTAOH2]reacted with one mole of [Cu2+]. The stoichiometric equation for reaction is presented as equation 2.

/[CoHEDTAOH2] – + Cu II  [CoHEDTAOH2]+ Cu I …………………….(2).

**ORDER OF REACTION**

The pseudo – first order plots of log (At - 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 [CoHEDTAOH2]19-20.

From the slopes of the plots, the pseudo – first order rate constants (kobs) were obtained. Analysis of the plot of log kobs versus log [Cu2+](fig 2), gave a slope of 0.46, indicating half – order dependence of rate on [Cu2+].

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

d[CoHEDTAOH2] = kobs [CoHEDTAOH2] [Cu2+]………… (3).

 at

The effect of [H+] on the rate of the reaction was investigated using perchloric acid in the range 3.0 < H+ < 11.0 x 10-3 moldm-3, while the [CoHEDTAOH2]- and [CU2+] were kept constant. The reaction was carried out at 280C and 1 = 0.05moldm-3 (NaCIO4).

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 k2 versus [H+] was linear with intercept on the k2 axis as shown in figure 3.

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

k2 = c + d [H+]. (4).

The overall rate equation in the acid range investigated is

–d[Cu2+] = (c+d[H+])[CoHEDTAOH2][Cu2+] (5).

 dt

Acid dependence of this type shows that there are two parallel reaction pathways; one which is acid dependent and the other that is acid – independent16, 17, 21.

The effect of ionic strength on the rate of the reaction was investigated in the range 1 = 0.02 – 0.06moldm-3 (NaCIO4), 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 logk2 versus √1 was linear.

**Table 1:** Pseudo-first order rate constant for the reaction of [CoIIHEDTA(H2O)] and [CuII] at [CoIIHEDTA(H2O)]=1×10-4 (moldm-3), T=29±1oC and ٨max =510nm.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **103 [Cu2+] (moldm-3)**  | 103 [H+] (moldm-3)  | I, NaClO4(moldm-3)  | 103 kobs (S-1)  | K2 dm3mol-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 (At-A∞) versus time**

**Fig. 2:** Plot of log kobs versus log [Cu2+] at constant [H+] and constant ionic strength.

**Fig. 3:** Plot of k2 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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