Determination of dielectric constant, the activation parameters, and the Arrhenius parameters on the electron-transfer reaction of [N-(2-hydroxyl-ethyl) ethylenediamine-N, N', N', - triacetate cobalt (II) by copper (II) cation.

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ABSTRACT

The effects of dieletric constant and temperature in the Kinetics of the oxidation- reduction reactions (involing electron transfer) of N-(2- hydroxyl-ethyl) ethylenediamine- N,N', N' -triacetatocobalt (II) by Cu^{2+} cation were determined. The effect of diaelectric constant (D) on the rate of reactions between the ($CoHEDTAH_2O$) and Cu^{2+} ions was investigated at constant concentration of oxidant and reductant. While the temperature, acidity and ionic strength of the medium were kept constant, the dielectric constant of the medium was varied from 63.25 to 43.78, using acetone and water mixture. It was found that the rates of reaction did not show any appreciable change. The temprature dependence of rates on this reaction was investigated at 35°C, 40°C, 50°C, 55°C, and 60°C respectively. Hence, the activation parameters and the Arrhenius parameters were calculated.

INTRODUCTION

A vitamin known as coenzymes B_{12} is the only organometallic compound in nature containing metal-carbon $_{\delta}$-bond (Crosanoe et al, 2002)[1,2]. It incorporates cobalt into a corrin ring- structure.

Vitamin B_{12} is an important Co complex. The vitamin was isolated from liver after it was found that eating large quantities of raw liver was an effective treatment for pernicious anemia. Injection of vitamin B_{12} are now used for treatment (more pleasant than eating raw liver).

Vitamin B_{12} is a coenzyme, and serves as a prosthetic group which is tightly bound to several enzymes in the body. The precise role of vitamin B_{12} is not fully understood (Lee, 1996)[3] hence this study.

Dorothy Crowfoot Hodgkin was awarded the Nobel Prize for Chemistry in 1964 for X-ray crystallographic work including solving the structure of this enzymes[3].

Vitamin B_{12} is required in humans for several transformations, such as the AdoCbl- dependent conversion of (R) – methylmalonyl co- enzyme A(CoA) into succinyl CoA[4].

And the MeCbl –dependent conversion of (S) homocysteine into methionine[4]:

$$HSCH_2CH_2CH(NH_3^+)COO^- \quad \text{--->} \quad MeSCH_2CH_2CH(NH_3^+)COO^-$$

There are a number of related reactions in which a substrate >CH-CX < is rearranged to >CX – CH<. The mechanistic details are obscured (Golding, 1990)[4].

Cobalt is biologically important in some enzymes, glutamic mutase is involved in the metabolism of amino acids and ribonucleotide reductase in the biosynthesis of DNA[3].

Traces of cobalt (1 – 1.5ppm) are added to beer to make it froth better. This has been linked with an increased rate of heart failure among heavy beer drinkers who have a dietary deficiency of protein or thiamine (Nicholls, 1973; Phipps, 1976)[5,6].

EXPERIMENT

All reagents used were of analar grade. The stock solutions of [$CoHEDTAOH_2$] were prepared according to the method of Mansour (2003)[7-9], 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 $0.05 moldm^{-3}$ ($NaClO_4$) 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.

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

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 $k_1/[Cu^{2+}]$.

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= $0.05 moldm^{-3}$ ($NaClO_4$) 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+}] / [$CoHEDTAOH_2$][10-13].

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 the reaction is presented as equation 2.

$$[CoHEDTAOH_2] + Cu^{II} \;\text{---->}\; [CoHEDTAOH_2]^- + Cu^{I} \qquad (2)$$

THE EFFECT OF DIELECTRIC CONSTANT[14-17]

The effect of dielectric constant (D) on rate of reactions between the ($Co^{11}HEDTAH_2O$) and Cu^{11} ions was investigated at constant concentration of oxidant and reductant.

While the temperature, acidity and ionic strength of the medium was kept constant, the dielectric constant of the medium was varied using acetone and water mixture.

The oxidation of $(Co^{11}HEDTAH_2O)^-$ by Cu^{11} at $[H^+] = 5.0 \times 10^{-3}$ moldm^{-3}, I = 0.05 moldm^{-3}, ($NaClO_4$) and T = 29.0 ± 1 °C showed independence of rates on the dielectric constant D[13].

Decreasing the dielectric constant from 63.25, 61.09, 58.93, 56.76, 54.60, 52.44, and 43.78 (CH_3COCH_3/H_2O) as shown in Table 1 below, did not change k_{obs}.

TABLE 1: Dependence of rate on dielectric constant (D) for oxidation of $[Co^{11}HEDTAH_2O]$ by Cu^{2+} at $[Cu^{2+}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[Co^{11}HEDTAH_2O] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, I = 0.05 mol dm^{-3} ($NaClO_4$), λ = 510nm, T= 29 ± 1^0C

D	63.25	61.09	58.93	56.76	54.60	52.44	43.78
$10^3 k_{obs}$ (S^{-1})	2.44	2.63	2.63	2.07	1.92	1.91	2.99

From the table above, it is noticed that the rate of reaction is fluctuating as the dielectric constant is decreased from 63.25-43.78.

TEMPERATURE DEPENDENCE OF RATES OF REACTIONS

The dependence of temperature on the rates of the reactions for the oxidation of $[Co^{II}HEDTAH_2O]^-$ by Cu^{2+} was investigated at 35 ^{0}C, 40 ^{0}C, 50 ^{0}C, 55 ^{0}C and 60 ^{0}C respectively. The rate constants determined are reported in Table 2.

From Eyring equation and thermodynamics[18],

$$\text{Log } k_{obs}/T = \log k/h + \Delta S^{\#}/2.303R - \Delta H^{\#}/2.303RT^2 \qquad (3)$$

Where k_{obs} = Temperature dependent rate constant.

k= Boltzmann's constant

h= Planks constant

$\Delta S^{\#}$ = Entropy of activation

$\Delta H^{\#}$ = Enthalpy of activation

R = universal gas constant

T = Temperature

From the plots of log k_{obs}/T versus $1/T^2$, the activation parameters were determined from the slopes and intercepts as in figure 1.

Table 2: Temperature dependence of rate constants for the oxidation - reduction reaction of [Co ^{II}HEDTAH$_2$O] and Cu^{2+}, at [Co ^{II}HEDTAH$_2$O] = 1.0 x 10^{-4} mol dm^{-3}, [Cu^{2+}] = 2.0 x 10^{-3} mol dm^{-3}, [H$^+$] = 5.0 x 10^{-3} mol dm^{-3}, I= 0.05 mol dm^{-3}, (NaClO$_4$), λ_{max} = 510nm.

Temp. (K)	**10^2 k_{obs}(S^{-1})**	**Logk_{obs}/T**	**10^5 $1/T^2$**
308	1.7	- 4.26	1.05
313	1.9	-4.22	1.02
323	2.1	-4.19	0.96
328	3.2	-4.01	0.93
333	3.5	-3.98	0.90

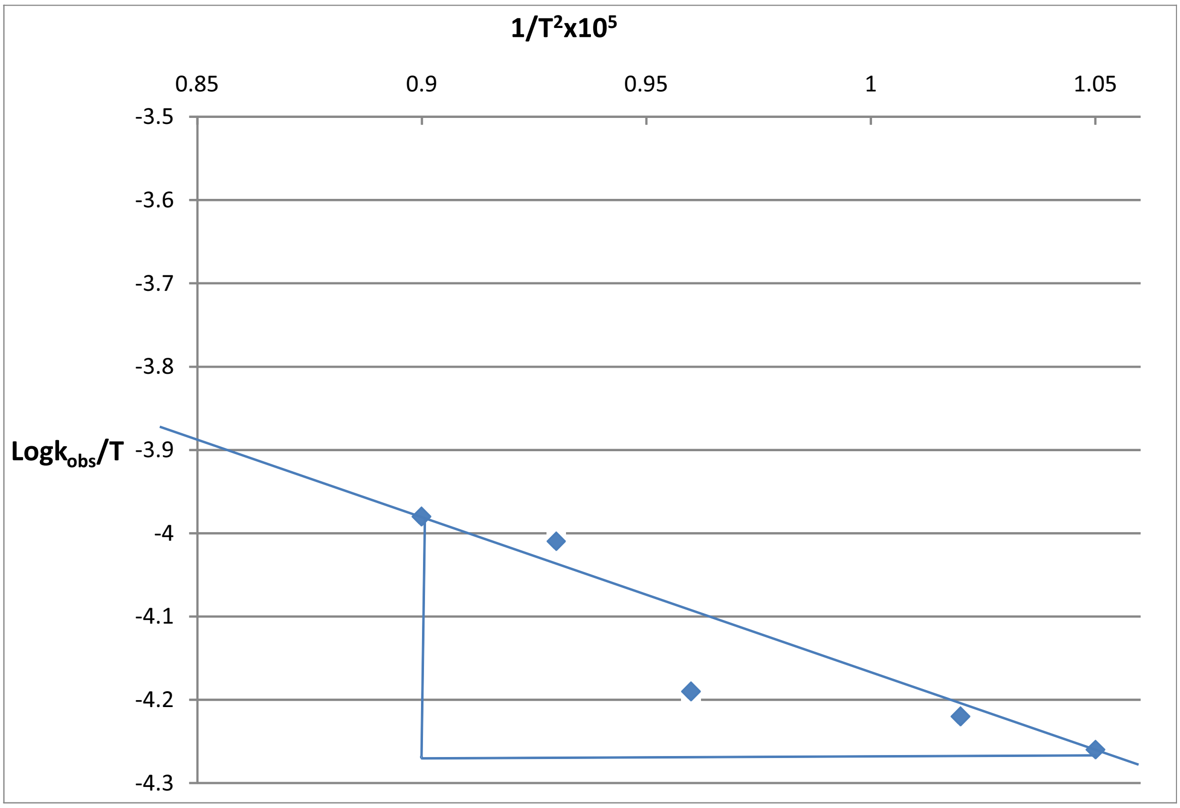

Fig 1. A graph of logk_{obs} / T versus $10^5 1/T^2$

Table 3: Activation parameter for the oxidation - reduction reaction of [Co^{II}HEDTAH$_2$O] and Cu^{2+}, at [Co ^{II}HEDTAH$_2$O] = 1.0 x 10^{-4} mol dm^{-3}, [Cu^{2+}] = 2.0 x 10^{-3} mol dm^{-3}, [H$^+$] = 5.0 x 10^{-3} mol dm^{-3}, I= 0.05 mol dm^{-3}, (NaClO$_4$), λ_{max} = 510nm.

Oxidant	**$\triangle H^\#$ (kJmol^{-1})**	**$\triangle S^\#$ (JK^{-1}mol^{-1})**	**$\triangle G^\#$(kJmol^{-1})**
Cu^{2+}	**-3622.52**	**-272.63**	**-3713.31**

For the determination of Ea (activation energy and the frequency factor A) Arrhenius equation $K = Ae^{-Ea/RT}$ is used. The constant A is called the frequency factor or pre-exponential factor; Ea is the activation energy. Collectively, the two quantities are called Arrhenius parameters[18,19]. Converting the above equation to logarithmic form, gives

$$\text{Log}_{10}K = \text{Log}_{10}A - Ea^{\#}/2.303RT \qquad (4)$$

It is apparent that by determining the values of K at several temperatures, the plot of $\log_{10}k$ versus 1/T will yield the activation energy from the slope of the curve and the frequency factor from the intercept. Although the frequency factor may depend slightly on temperature, unless the temperature range is very great. The determination of the activation energy is an important objective of any kinetic investigation.

Table 4: Table for graph of Logk $_{obs}$ versus 1/T(k^{-1}).

Temp.	**k_{obs}**	**Log k_{obs}**	**10^3 1/T$^{(k-1)}$**
308	0.017	-1.77	3.25
313	0.019	-1.72	3.19
323	0.021	-1.68	3.10
328	0.032	-1.49	3.04
333	0.035	-1.46	3.00

From the Table 4, it is seen that the rate of reaction increases as the temperature of the reaction increases.

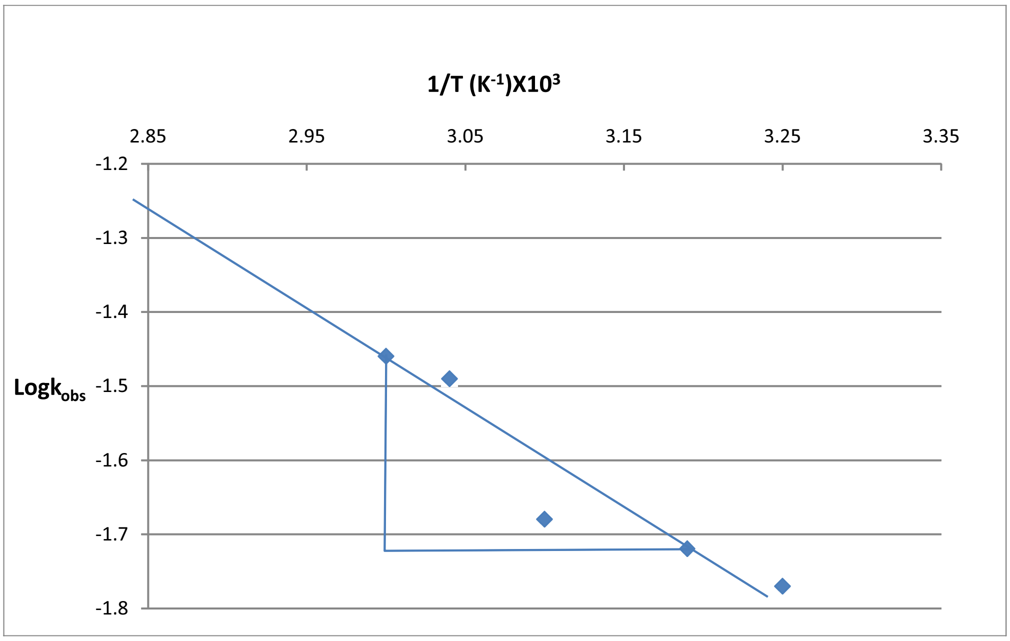

Fig 2. A graph of k_{obs} versus 1/T

From the graph, the intercept is -1.26 = 0.055 = A.

Hence, the Arrhenius parameters are as shown in table 5.

Table 5: The Arrhenius parameters for the reactions of [Co ^{II}HEDTAH$_2$O] and Cu^{2+}.

Oxidant	**Ea$^{\#}$**(kJ mol^{-1})	**A**
Cu^{2+}	-23.188	0.055

CONCLUSION

We have been able to establish the effects of dielectric constant and have calculated both the activation parameters and Arrhenius parameters in the reaction in question. Our next step is to establish mechanism of this reaction and hence compare it with some of the already known mechanisms of enzymatic reactions that are going on in some biological processes.

Acknowledgement: The authors thank very sincerely the Faculty of Natural and Applied Sciences, Godfrey Okoye University Enugu for all the encouragements and supports of this work.

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