Kinetics of Cu²⁺- Catalysed Redox Reaction of n-(2-hydroxylethyl) ethylenediaminetriacetatocobalt(III) with Hydrazine Monohydrate in Aqueous Acid

A. D. Onu, S. O. Idris & B. Y. Abiti

Abstract *The kinetics of the Cu^{2+}-catalysed redox reaction between n-(2-hydroxylethyl) ethylenediaminetriacetatocobalt(III) (hereafter $[Co(HEDTA)OH_2]$) with hydrazine monohydrate (hereafter $N_2H_5^+$) have been successfully investigated in aqueous acidic medium, under the following conditions $T = 298 \pm 1$ K, $I = 0.5$ mol dm^{-3}(NaClO$_4$), $[H^+] = 4.0 \times 10^{-3}$ mol dm^{-3}(HClO$_4$), $[Cu^{2+}] = 5.0 \times 10^{-4}$ mol dm^{-3} and $\lambda_{max} = 550$ nm. Stoichiometric study revealed that two moles of $[Co(HEDTA)OH_2]$ reacted with one mole of $N_2H_5^+$. The rate of the reaction was first order with respect to $[Co(HEDTA)OH_2]$ and $[N_2H_5^+]$, and second order overall, with $k_2 = (9.81 \pm 0.14) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. The rate of the reaction was inversely dependent on $[H^+]$ but directly proportional to $[Cu^{2+}]$ and both plots of k_2 versus $[H^+]^{-1}$ and k_2 versus $[Cu^{2+}]$ were linear from the origin, indicating a one term rate law with respect to both $[H^+]^{-1}$ and $[Cu^{2+}]$. Changes in ionic strength had no effect on the reaction rate and temperature dependent study gave values of activated enthalpy $(\Delta H^{\ddagger})$ and entropy $(\Delta S^{\ddagger})$ as 82.89 KJ mol^{-1} and 17.13 JK^{-1} mol^{-1} respectively. Spectroscopic and kinetic investigations indicated absence of detectable intermediate. Analysis of evidence adduced from the study favour the outer-sphere mechanism and it is proposed for the reaction.*
Key words: *Kinetics, Catalysed Redox Reactions, cobalt(III), Hydrazine Monohydrate.*

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1.0 Introduction

Hydrazine monohydrate has a wide range of applications as a raw material in the synthesis of industrial chemicals (Sanjay and Qiang, 2013; Jiang et al., 2015), agricultural products (Patil and Tanu, 2014) and medical drugs (Muhammad et al., 2013; Anca et al., 2015). The ability of hydrazine monohydrate to form the hydrazinium ion ($N_2H_5^+$) makes it a suitable reductant in many redox reactions (Micheal et al., 1978). To this effect, extensive studies on its catalysed redox property have been carried out as evidence by documented works (Max et al, 1998; 1999; Larsen et al., 2001; Ravi and Brian, 2012; Cantillo et al., 2013; Ghanbari et al., 2013; Shirin et al., 2016). Also, Cu²⁺ has been identified as a potent catalyst for the reduction of hydrazine monohydrate even at small concentration (Carl et al., 1975; Micheal et al., 1978; Mondal and Banerjee, 2009). Studies (Zheng et al., 2005; Ghanbari et al., 2013) on the catalytic redox reactions of hydrazine showed that some of these reactions do not to follow a fixed chemical stoichiometry and also the reactions can follow both the inner – sphere (Patapati et al., 1986; Jhimli et al., 2004; Gain et al., 2011; Streszewski et al., 2014) and the outer – sphere (David, 1984; Rupa et al., 1999; Mshelia et al., 2010) pathways. Although studies on the reactions involving hydrazine and other substrates including binuclear metal complexes of cobalt(III) (Mondal and Banerjee, 2009; Gain et al., 2011) have been reported, there is paucity of kinetic data for the reaction of this reductant with cobalt(III)aminocarboxylato complexes- the oxidant of interest in this study. Due to the bulky nature of the ligands and also, the high charge on the central metal ion (Hamzeh, 2001) reactions of

cobalt(III)aminocarboxylato complexes are slow , thus making it kinetically unfavourable to be monitored. Consequently, to investigate the reduction of n-(2-hydroxylethyl)ethylenediaminetriacetatocobalt(III) by hydrazine via the catalytic action of Cu^{2+} motivated the study with the hope that the kinetic data generated from this reaction will aid in shedding more light on its mechanistic pathway.

2.0 Materials and Methods

All chemical reagents used were of analytical grade, distilled water was used at all times. Stock solution of [CoHEDTAOH$_2$] was prepared using the methods of Dézsi *et al*,. (1976), with some minor modifications, and was characterized using UV/Visible. The UV/Visible spectrum of [CoHEDTAOH$_2$] was scanned between wavelength ranges of 300 - 600 nm and gave λ_{max} of 382 nm and 549 nm respectively, corresponding to values for [CoHEDTAOH$_2$] from previous report (Mansour, 2003). Stock solutions of $N_2H_5^+$ and perchloric acid were made by diluting analar grade 98 % $N_2H_4.H_2O$ (Sigma-Aldrich) of specific gravity 1.032 g cm^{-3} and 70 % perchloric acid (Sigma-Aldrich) of specific gravity 1.66 g cm^{-3}. The prepared acid stock was standardized tritrimetrically using sodium bicarbonate as a primary standard. Stock solutions (0.1 mol dm^{-3}) of copper(II)sulphate, sodium acetate, sodium formate, and potassium perchlorate were prepared in 100 cm^3 volumetric flask by weighing calculated amount of each salt and dissolving with distilled water. The solutions were then made up to mark of the volumetric flask and standardized gravimerically. Analar grade sodium perchlorate was used to maintain constant ionic strength of the reaction medium.

The stoichiometry of the reaction was determined by spectrophotometric titration, using the mole ratio method. The concentrations of [CoHEDTAOH$_2$] and Cu^{2+} were kept constant at 6.0×10^{-3} mol dm^{-3} and 5.0×10^{-4} mol dm^{-3} respectively, while the [$N_2H_5^+$] was varied between $(1.2 –12.0) \times 10^{-3}$ mol dm^{-3} at constant [H^+] $= 2.0 \times 10^{-2}$ mol dm^{-3}, ionic strength, I $= 0.05$ mol dm^{-3} (NaClO$_4$) and a temperature of 298 ± 1 K. The absorbances were obtained $\lambda_{max} = 550$ nm. The reaction was allowed to go to completion indicated by steady value of absorbance. From the graphs of absorbance against

mole ratio ($N_2H_5^+$/[Co(HEDTA)OH$_2$]), the stoichiometry was evaluated.

All kinetic measurements were performed under pseudo - first order conditions with the concentrations of [CoHEDTAOH$_2$] and Cu^{2+} maintained at 6.0×10^{-3} mol dm^{-3} and 5.0×10^{-4} mol dm^{-3} respectively, while the [$N_2H_5^+$] was at least 10 - fold in excess over that of the complex. Reaction rates were monitored by change in absorbance of complex with time at 550 nm on a Corning Colorimeter 252 model. Ionic strength was maintained at 0.5 mol dm^{-3} (NaClO$_4$) and at a constant temperature of 298 ± 1 K. The pseudo – first order rate constants k_1 were obtained from the slopes of the logarithmic plots of log ($A_t - A_\infty$) against time, where A_∞ and A_t are the absorbance at the end of the reaction and at time, t respectively. From these values of k_1, the second order rate constants k_2 were estimated using the relation;

$$k_2 = k_1/[N_2H_5^+] \qquad (6)$$

The effects of [H^+], Cu^{2+} and ionic strength on the rate of the reaction were investigated under the conditions stated in Table 1. The effect of added ions on the reaction rate was studied using CHOO$^-$, CH$_3$CHOO$^-$ and K$^+$ within the concentration range $(0.0 – 2.0) \times 10^{-2}$ mol dm^{-3}, while maintaining a constant concentration for all other reactants as contained in Table2.

Temperature dependent study was carried out between 293 to 313 K using thermostated waterbath to adjust the reaction temperature. After the reagents have attained the temperature of the waterbath they were mixed and quickly transferred into the cuvette of the spectrophotometre and the reaction monitored. At the end of the reaction the temperature of the solution was taken and no variation was observed. From the plot of ln(1/T) against 1/T, the activation enthalpy and entropy were determined.

Spectrophotometric determination of detectable intermediate was carried out by comparing the spectrum of partially oxidized reaction mixtures in the range 400 – 650 nm with the spectrum of [Co(HEDTA)OH$_2$]. The formation of an intermediate complex is often evidenced by an increase in peak height or shift in Λ_{max} of the spectrum of the partially oxidized reaction mixture (Lohdip, 1989).

The Co(II) product of the reaction was determined spectrophotometrically and qualitatively (Hahn and Welcher,1963). N_2, the likely product of $N_2H_5^+$ oxidation was analyzed qualitatively.

3.0   Results and Discussion

The plot of absorbance against mole ratio $[N_2H_5]^+/[Co(HEDTA)OH_2]$ (Fgure 1) gave a mole ratio of 1:2. The stoichiometry of the overall reaction can thus be written as:
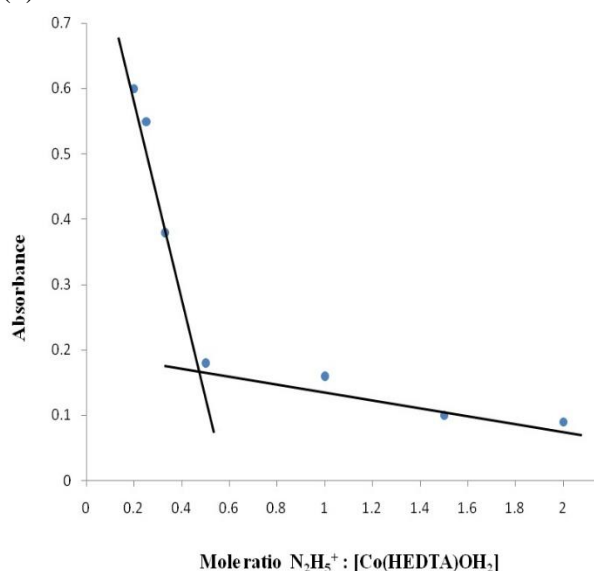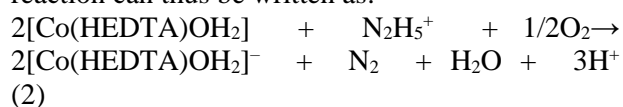
$2[Co(HEDTA)OH_2]$ + $N_2H_5^+$ + $1/2O_2 \rightarrow$ $2[Co(HEDTA)OH_2]^-$ + N_2 + H_2O + $3H^+$ (2)

Fig. 1. Stoichiometric plot for the reduction of $[Co(HEDTA)OH_2]$ by $N_2H_5^+$

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The pseudo – first order plot of log (A_t - A_∞) against time was linear for about 75 % of the reaction time (Figure 2), this shows that the reaction is first order with respect to the [CoHEDTAOH$_2$]. The gradient of the logarithmic plots of log k_1 vs log $[N_2H_5^+]$ (Figure 3) was 1.03, indicating a first order with respect to the $[N_2H_5^+]$. Hence the reaction is second order overall. The second order rate constants determined from $k_1/[oxidant]$ were fairly constant (Table 1). The rate equation can be written thus:

$$-\frac{[CoHEDTAOH]}{dt} = k_2[Co(HEDTA)OH_2][N_2H_5^+]$$

(3)

where $k_2 = (9.81 \pm 0.14) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

The acid dependent study conform to equation (4)

$$k_2 = a\,[H^+]^{-1} \qquad (4)$$

Changing the ionic strength of the reaction medium (0.3 – 0.6 mol dm^{-3}) using NaClO$_4$ showed no effect on the reaction rate (Table 1) evidenced by the fairly constant k_2 values.

Added anions (CHCOO$^-$ and CH$_3$COO$^-$) catalysed the reaction while a marked inhibition was recorded by the cation (K$^+$), Table 2.
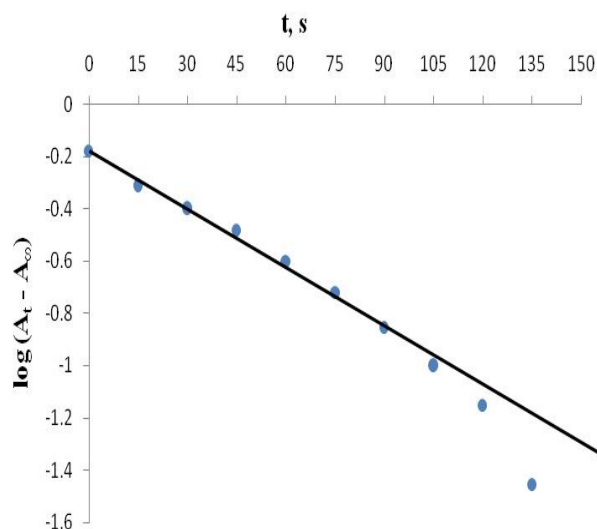

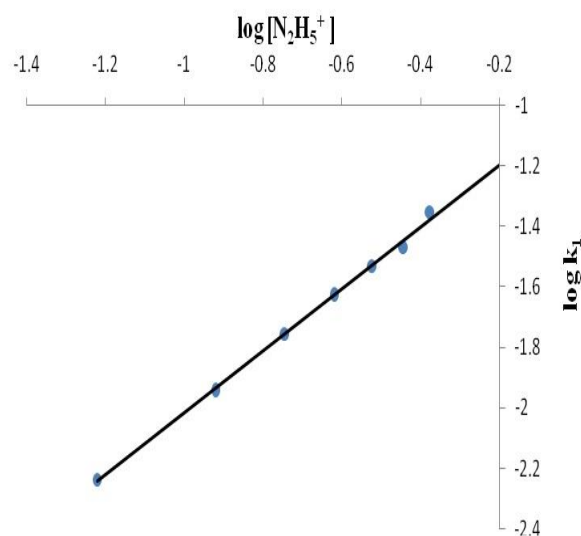**Fig. 2. Pseudo-first order plot for the Cu^{2+}-catalysed $[CoHEDTAOH_2]$ – $N_2H_5^+$ reaction**

Fig. 3. Plot of log k_1 versus log $[N_2H_5^+]$ for the Cu^{2+}-catalysed $[Co(HEDTA)OH_2]$ – $N_2H_5^+$ reaction

Table 1: Pseudo-first order and second order rate constants for the Cu^{2+}catalysed redox reaction of [CoHEDTAOH$_2$] with hydrazine monohydrate in aqueous HClO$_4$ medium at [Co^{3+}] = 6.0 × 10^{-3} mol dm^{-3}, λ$_{max}$ = 550 nm and T = 298 ± 1K.

10[N$_2$H$_5^+$] (M)	10^3[H$^+$] (M)	10^4[Cu^{2+}] (M)	10[I] (M)	10^2 k$_{obs}$s^{-1}	10^{2}k$_2$ M^{-1}s^{-1}
0.6	4.0	5.0	5.0	0.58	9.66
1.2	4.0	5.0	5.0	1.14	9.49
1.8	4.0	5.0	5.0	1.76	9.79
2.4	4.0	5.0	5.0	2.36	9.82
3.0	4.0	5.0	5.0	2.95	9.83
3.6	4.0	5.0	5.0	3.41	9.46
4.2	4.0	5.0	5.0	4.45	10.59
1.2	1.0	5.0	5.0	4.28	35.64
1.2	2.0	5.0	5.0	2.07	17.25
1.2	3.0	5.0	5.0	1.61	13.38
1.2	4.0	5.0	5.0	1.14	9.51
1.2	5.0	5.0	5.0	0.95	7.87
1.2	6.0	5.0	5.0	0.78	6.51
1.2	7.0	5.0	5.0	0.65	5.43
1.2	4.0	2.5	5.0	0.73	5.06
1.2	4.0	5.0	5.0	1.14	9.50
1.2	4.0	7.5	5.0	1.60	13.37
1.2	4.0	10.0	5.0	2.07	17.22
1.2	4.0	12.5	5.0	2.66	22.13
1.2	4.0	15.0	5.0	3.40	28.35
1.2	4.0	5.0	3.0	1.11	9.24
1.2	4.0	5.0	3.5	1.13	9.42
1.2	4.0	5.0	4.0	1.16	9.64
1.2	4.0	5.0	4.5	1.15	9.61
1.2	4.0	5.0	5.0	1.14	9.52
1.2	4.0	5.0	5.5	1.14	9.51
1.2	4.0	5.0	6.0	1.11	9.26

The result for the temperature dependent study (Table 3) and the plot of ln(K/T) against 1/T using Eyring's equation (Atkins and de Paula, 2006) is shown as Figure 4. The spectrum of the reaction product gave a λ$_{max}$ at 509 nm typical of Co(II)aminopolycarboxylacto complexes (Onu, 2015; Arunachalam *et al*., 2015) while addition of KCN to the solution of the product effected a change in colour from pale pink to blue, qualitatively confirming the presence of Co(II).

From the plot, the enthalpy (ΔH*= 82.89 KJ mol^{-1}) and entropy of activation (ΔS* = 17.13 JK^{-1} mol^{-1}) were determined.

Table 2: Effect of added ions on Cu^{2+}- catalysed [Co(HEDTA)OH$_2$] – N$_2$H$_5^+$ reaction at [Co(HEDTA)OH$_2$] = 6.0 × 10^{-3} mol dm^{-3}, [N$_2$H$_5^+$] = 0.12 mol dm^{-3}, [Cu^{2+}] = 5.0 × 10^{-4} mol dm^{-3}, [H$^+$] = 4.0 × 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3} (NaClO$_4$), T = 298 ± 1 K, λ$_{max}$ = 550 nm

10^3 [CHOO$^-$], (M)	10^3 k$_1$, s^{-1}	10^2 k$_2$, dm^3 mol^{-1} s^{-1}
0	11.38	9.48
5.0	15.83	13.19
10.0	24.08	20.07
15.0	35.40	29.50
20.0	41.04	34.20
10^3 [CH$_3$COO$^-$]		
0	11.43	9.52
5.0	17.52	14.60
10.0	19.73	16.44
15.0	22.42	18.68
20.0	27.43	22.86
10^3 [K$^+$]		
0	11.41	9.51
5.0	9.44	7.86
10.0	7.20	6.00
15.0	5.37	4.47
20.0	4.29	3.57

Table 3. Pseudo-first order and second order rate constants for the temperature study on the Cu^{2+} - catalysed redox reaction of [Co(HEDTA)OH$_2$] with hydrazine monohydrate in aqueous HClO$_4$ medium at [Co^{3+}] = 6.0 × 10^{-3} mol dm^{-3}, λ$_{max}$ = 550 nm

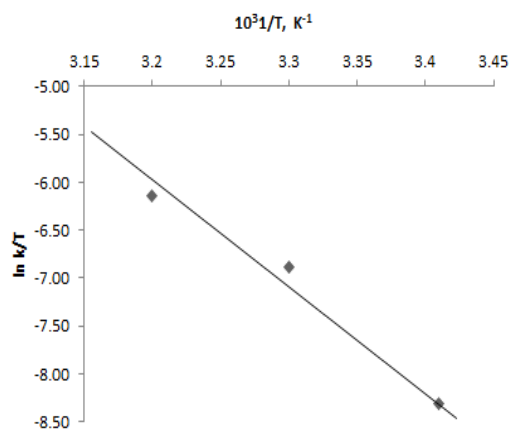| T (K)	10[H$_2$A] (M)	10^3[H$^+$] (M)	10^4[Cu^{2+}] (M)	10[I] (M)	10^2 k$_{obs}$ s^{-1}	10^{2}k$_2$ M^{-1}s^1
293	1.2	4.0	5.0	5.0	0.87	7.27
303	1.2	4.0	5.0	5.0	3.75	31.21
313	1.2	4.0	5.0	5.0	8.12	67.70

Fig. 4: Plot of $\ln\left(\dfrac{k}{T}\right)$ **against** $\dfrac{1}{T}$ **for the Cu^{2+} -**
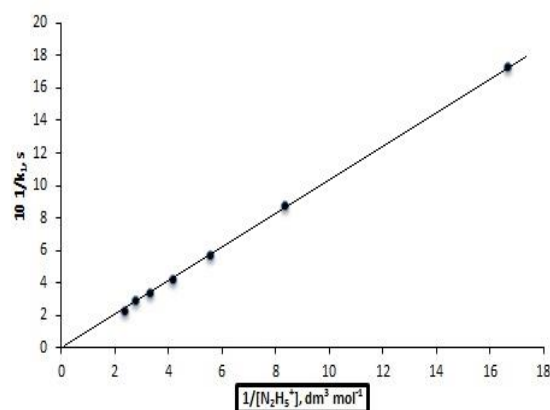
Fig. 5. Plot of k_1^{-1} versus $[N_2H_5^+]^{-1}$ for the Cu^{2+} - catalysed [CoHEDTAOH$_2$] – N$_2$H$_5^+$ reaction

The stoichiometry of 2:1 obtained in this study is similar with the stoichiometry of other $N_2H_5^+$ reactions (Thakuria and Gupta, 1975; Peter et al., 1991; Jhimli et al., 2004; Mshelia et al., 2010; Gain et al., 2011). As a one electron oxidant, two moles of the cobalt(III) complex will be required for oxidation of one mole of hydrazine monohydrate. The stoichiometry obtained is associated with N_2 product of $N_2H_5^+$ oxidation, especially where a two electron transfer process is involved to give diazene (Patapati et al., 1986), followed by oxidation by atmospheric oxygen to give N_2 and H_2O (Wagnerova et al., 1973; Cookson et al., 1977). The linearity of the pseudo – first order plot of log $(A_t - A_\infty)$ against time signifies a first order with respect to [Co(HEDTA)OH$_2$]. The gradient of the

logarithmic plots of log k_1 versus log $[N_2H_5^+]$ was 1.03, indicating a first order with respect to the $[N_2H_5^+]$ and thus a second order overall. Such orders have been known for reactions of $N_2H_5^+$.

The nature of acid dependence obtained which has been reported for the reactions of $N_2H_5^+$ (Thakuria and Gupta, 1975; Al-Subu et al., 1990; Mondal and Banerjee, 2009; Mshelia et al., 2010) implies a deprotonation equilibrium step prior to electron transfer where the deprotonated form is reactive (Onu et al., 2015). Although hydrazinium ion is a weak acid (pK$_a \sim 8$) (Mondal and Banerjee, 2009), in the presence of Cu^{2+} its acidity is enhanced (Carl et al., 1975), with pK$_a$ 4.2 thereby facilitating the deprotonating of H$^+$ to give the inverse acid dependence observed. That Cu^{2+} is a potent catalyst for the reaction is evident from Table 1 showing an increase in the rate of reaction with an increase in [Cu^{2+}]. Of importance in this reaction is the nature and composition of the activated complex. The non-dependence of the reaction on ionic strength is indicative of activated complex, composed of either charged-neutral or neutral –neutral reactant species (Asperger, 2003, Atkins and de Paula, 2006). This result is not unexpected given that the Co(III) complex is neutral. Mondal and Banerjee, (2009) had reported similar result in a related reaction of Co(III) complex.

The catalysis of the reaction by added anions and its inhibition by cation suggest that the activated complex is not composed of bridged species. This observation is further buttressed by the result of the spectroscopic and kinetic tests for the presence of intermediate. The spectroscopic test did not show any shift in the λ_{max} in the spectrum of partially oxidized reaction mixture as well as the kinetic test of plotting $1/k_1$ versus $1/[N_2H_5^+]$ did not give intercept. These observations are common to reactions known to occur via the outer-sphere mechanism (Ali et al., 1990; Onu et al., 2015). Furthermore, the greater disorderliness of the activated complex indicated by the positive activation entropy, $\Delta S^* = 17.13$ JK^{-1} mol^{-1} (James, 2002) lend credence to the lack of bridged species at the activated complex and this is typical of outer-sphere reaction.
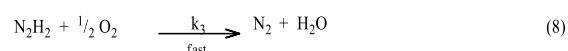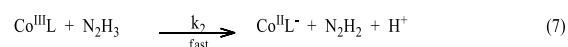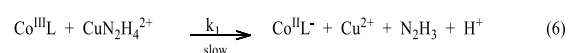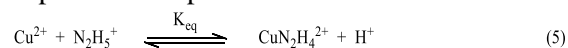
On the basis of the followings:

1. The zero intercept obtained from the plot of k_1^{-1} versus $[N_2H_5^+]^{-1}$

2. The positive value of the change in entropy of activation.

3. The catalysis and inhibition by anions and cation respectively.

4. The lack of spectroscopically determinable intermediate,

The reaction is proposed to occur via the outer-sphere mechanism. The mechanistic scheme below explains the experimental data.

$$Cu^{2+} + N_2H_5^+ \overset{K_{eq}}{\rightleftharpoons} CuN_2H_4^{2+} + H^+ \qquad (5)$$

$$Co^{III}L + CuN_2H_4^{2+} \overset{k_1}{\underset{slow}{\longrightarrow}} Co^{II}L^- + Cu^{2+} + N_2H_3 + H^+ \qquad (6)$$

$$Co^{III}L + N_2H_3 \overset{k_2}{\underset{fast}{\longrightarrow}} Co^{II}L^- + N_2H_2 + H^+ \qquad (7)$$

$$N_2H_2 + \tfrac{1}{2}O_2 \overset{k_3}{\underset{fast}{\longrightarrow}} N_2 + H_2O \qquad (8)$$

Given that $Co^{III}L$ and $Co^{II}L^-$ are $[Co(HEDTA)OH_2]$ and $[CoHEDTAOH_2]^-$ respectively, from equation 6:

Rate $= k_1[CuN_2H_4^{2+}][Co(HEDTA)OH_2]$ (9)

From equation (5),

$$K_{eq} = \frac{[CuN_2H_4^{2+}][H^+]}{[Cu^{2+}][N_2H_5^+]} \qquad (10)$$

$[CuN_2H_4^{2+}] = K_{eq}[H^+]^{-1}[Cu^{2+}][N_2H_5^+]$
(11)

Thus, Rate $= k_1 K_{eq} [H^+]^{-1}[Cu^{2+}][CoHEDTAOH_2][N_2H_5^+]$
(12)

At constant $[H^+]$ and $[Cu^{2+}]$,

Rate $= k[CoHEDTAOH_2][N_2H_5^+]$
(13)

Where $k = k_1 K_{eq} [H^+]^{-1} [Cu^{2+}]$, this conforms to the experimental rate law.

4.0   Conclusion

5.0   References

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