



# KINETICS AND MECHANISM OF THE CATALYSED REDUCTION OF ETHYLENEDIAMINETETRAACETATOCOBALTATE(III) ION BY L-ASCORBIC ACID IN AQUEOUS ACIDIC MEDIUM



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**Abstract:** The kinetics of the copper(II) catalysed reduction of ethylenediaminetetraacetatocobaltate(III) ion (hereafter [Co(III)EDTA]<sup>-</sup>) by L-ascorbic acid (hereafter H<sub>2</sub>A) has been investigated spectrophotometrically in aqueous acidic medium at  $\lambda_{\max} = 535$  nm. The reaction follows a stoichiometry of 1:2 for H<sub>2</sub>A to [Co(III)EDTA]<sup>-</sup>. The order of reaction was first order with respect to both H<sub>2</sub>A and [Co(III)EDTA]<sup>-</sup> with a second order rate constant,  $k_2$ , value of  $(9.88 \pm 0.065) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Pseudo – first order rate constant,  $k_{\text{obs}}$ , values were stable with changes in [H<sup>+</sup>]  $\{(0.5 - 8.0) \times 10^{-3} \text{ mol dm}^{-3}\}$ , while a negative kinetic salt effect was noticed with changes in ionic strength (Na<sub>2</sub>SO<sub>4</sub>). The experimental data fits the rate law  $\text{Rate} = K_{\text{eq}} k_1 [\text{Cu}^{2+}] [\text{H}_2\text{A}] [\text{Co}(\text{EDTA})^-]$ . Activated parameters were obtained as  $\Delta H^\ddagger = 61.85 \text{ KJ mol}^{-1}$  and  $\Delta S^\ddagger = -77.09 \text{ JK}^{-1} \text{ mol}$ . The effect of added anions inhibition and absence of intermediate as seen from the Michaelis-Menten plot led to the conclusion that the reaction follows an outer – sphere mechanistic path.

**Keywords:** Catalyst, ethylenediaminetetraacetatocobaltate(III), kinetics, L-ascorbic acid, outer-sphere, reduction

## Introduction

The activity of ascorbic acid in many natural and industrial processes is due to its availability and natural existence, as it is a biosynthetic product of many plant (Isherwood *et al.*, 1954; Carlos *et al.*, 2000) and animals (Chatterjee *et al.*, 1961). Thus, being readily available, its chemical interaction with both biological and non biological substrates as a reducing agent is well pronounced (Hacisevki, 2009). The ability of ascorbic acid to serve as a good reductant is due to the presence of grouping C(OH)=C(OH)-C=O containing conjugated double bonds (Sadhana *et al.*, 2014). These has led to studies in many reduction reactions involving ascorbic acid with various oxidizing metal complexes (Lappin *et al.*, 1981; Davis, 1992; Leal *et al.*, 1993; Saha *et al.*, 1995), and have been documented to follow both the inner – sphere (Maity *et al.*, 2007; Mondal *et al.*, 2009; Lawrence *et al.*, 2012) and the outer – sphere (Lemma *et al.*, 2002; Khan *et al.*, 2005; 2013) mechanistic pathways. Of particular interest are the reductions of Cobalt(III) metal complexes by L-ascorbic acid (Abdur-Rashid *et al.*, 1996; Majumdar *et al.*, 2010; Sadhana *et al.*, 2014; 2015).

Although, many cobalt(III) complexes are kinetically inert, introducing a catalyst to fasten the reaction rate has thus presented important opportunities in the study of their kinetics. In fact Cu(II) ion has been used to catalyse the reduction of other forms of Co(III) complexes (Singh *et al.*, 2014) and in the oxidation of ascorbic acid (Luty-Blocho *et al.*, 2013). In a study on the reduction of various cobalt(III) complexes by L-ascorbic acid (Hamzeh, 2001; Sadhana *et al.*, 2015), it was observed that although L-ascorbic acid reacts with ethylenediaminetetraacetatocobaltate(III) ion in aqueous medium, the reaction was however very slow and could not be kinetically monitored, hence kinetic data were not generated. The reason given for this observation was the bulky nature of the ligand (EDTA) which leads to the slow rate of the reaction, due to the low rate at which electrons tunnel through the ligand.

This study therefore seeks to explore the use of Cu(II) ions as a potential catalyst in the reduction of aminocarboxylatocobaltate(III) ions by L-ascorbic acid, in order to gain knowledge on the kinetics of the redox process.

## Materials and Methods

### Experimental

#### Materials

All materials and reagents used were of standard analytical grade, preparation of reagents were done using distilled water at all times. The complex was prepared from cobaltous nitrate (BDH) and ethylenediaminetetraacetic acid disodium salt (Sigma Aldrich), according to the method of Szabolcs *et al.* (2005). The complex was characterized using UV/Visible between wavelength ranges of 300 - 600 nm and gave  $\lambda_{\max}$  of 382 and 536 nm. This corresponds to values from previous literature (Bengt, 1970; Perveen *et al.*, 2013). Analar grade L-ascorbic acid (BDH) with a molar mass of 176.12 g mol<sup>-1</sup> was used to prepare the solution of ascorbic acid by dissolving 8.8 g of the solid ascorbic acid in 20 cm<sup>3</sup> of distilled water; this was then carefully transferred into a 50 cm<sup>3</sup> volumetric flask and topped to the mark with freshly prepared distilled water to get a 1M ascorbic acid solution. A 0.05M stock solution of sulphuric acid (analar grade) was made by diluting 98% sulphuric acid of specific gravity 1.84 g cm<sup>-3</sup>. The sulphuric acid was then standardized volumetrically. Solutions of CuSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>SO<sub>4</sub>, ZnSO<sub>4</sub>, CH<sub>3</sub>COONa, and CHONa were all prepared by dissolving known weight of the respective salts in known volume of distilled water. All salts were of analytical grade.

#### Stoichiometric study

The stoichiometry of the reaction was carried out by spectrophotometric titration using the mole ratio method (Mamman and Iyun, 2007; Onu *et al.*, 2009). The concentration of [Co(III)EDTA]<sup>-</sup> was kept constant at  $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ , catalyst (CuSO<sub>4</sub>) and acid concentration were also kept constant at  $2.0 \times 10^{-3}$  and  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  respectively, while that of [H<sub>2</sub>A] was varied from (0.6 - 6.6)  $\times 10^{-3} \text{ mol dm}^{-3}$ . The reactions were allowed to go to completion with a constant ionic strength maintained at 0.05 mol dm<sup>-3</sup> (Na<sub>2</sub>SO<sub>4</sub>). The absorbance of the solutions was taken at 535 nm during the course of the reaction and a stable absorbance marks an end to the reaction. The stoichiometry was determined from the plot of absorbance versus mole ratio [H<sub>2</sub>A]:[Co(III)EDTA]<sup>-</sup> (Fig. 1).

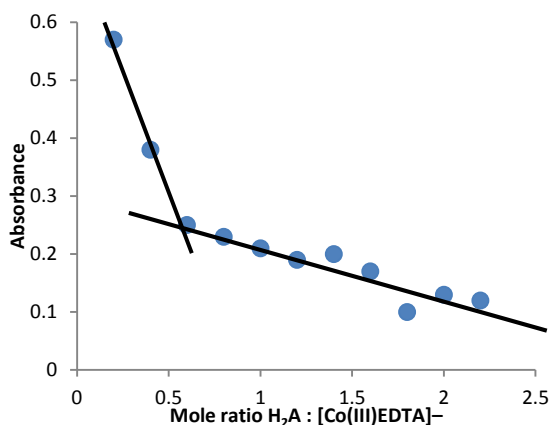


Fig 1: Stoichiometric plot for the catalysed reduction of [Co(III)EDTA]<sup>-</sup> by H<sub>2</sub>A

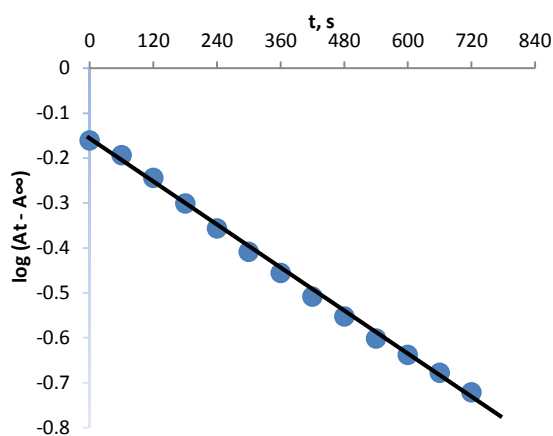


Fig 2: Typical pseudo - first order plot for reduction of [Co(III)EDTA]<sup>-</sup> by H<sub>2</sub>A

### Kinetic study

The rates of the reactions were monitored on an Agilent 8453 spectrophotometer. The rate was studied by monitoring decrease in absorbance of the cobalt complex at 535 nm. The kinetic measurements were carried out under pseudo-first order conditions with [H<sub>2</sub>A] at least a 20 fold excess to that of [Co(III)EDTA]<sup>-</sup> (3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>) at constant [H<sup>+</sup>], [catalyst], temperature and ionic strength. The plots of log (A<sub>t</sub> - A<sub>∞</sub>) versus time (Fig. 2) were made and the pseudo-first order rate constants, k<sub>obs</sub> were determined. The second order rate constant (k<sub>2</sub>) was gotten as k<sub>obs</sub>/[Oxidant]. The influence of H<sup>+</sup>, catalyst (CuSO<sub>4</sub>) and ionic strength (Na<sub>2</sub>SO<sub>4</sub>) on the rate of the reaction were investigated within the ranges of [H<sup>+</sup>] = (0.5 - 8.0) × 10<sup>-3</sup> mol dm<sup>-3</sup>, [CuSO<sub>4</sub>] = (0.3 - 1.3) × 10<sup>-2</sup> mol dm<sup>-3</sup> and I = (3.0 - 5.5) × 10<sup>-1</sup> mol dm<sup>-3</sup> respectively while keeping all other parameters constant.

### The effect of added anions and cations on the reaction rate

Effect of added anions CH<sub>3</sub>COO<sup>-</sup> (0.5 - 10.0) × 10<sup>-2</sup> mol dm<sup>-3</sup> and CHOO<sup>-</sup> (0.5 - 7.5) × 10<sup>-2</sup> mol dm<sup>-3</sup>, and cations Zn<sup>2+</sup> and Li<sup>+</sup> (0.5 - 8.5) × 10<sup>-2</sup> mol dm<sup>-3</sup> were investigated while all other parameters were kept constant. Ionic strength was maintained at 0.4 mol dm<sup>-3</sup> for anions and 0.5 mol dm<sup>-3</sup> for cations, respectively.

### Tests for free radical

About 5 cm<sup>3</sup> of acrylamide was added to partially oxidized reaction mixture of ascorbic acid and [Co(III)EDTA]<sup>-</sup> and allowed to stand for a few minutes, this was followed by a large excess of methanol. The acrylamide was also added to a solution each of ascorbic acid and [Co(III)EDTA]<sup>-</sup> separately, this served as control.

### Temperature dependent study

The temperature dependent study was carried out to show the effect of change in temperature on the reaction rate. The reactions were investigated at temperatures of 299, 313, 323 and 333 K, while all other reaction parameters were kept constant. A Grant JB Nova water bath was used to heat up and maintains the reactants at desired temperatures; the reactants were carefully mixed and quickly transferred to the spectrophotometer where the decrease in absorbance was taken with respect to time. Care was taken to prevent any significant loss in temperature, the temperatures of the reactants before the reaction and the products after the reaction were checked for any significant loss in temperature during the course of the reaction.

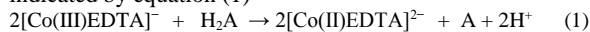
### Product analysis

Qualitative test was carried out to determine if Co<sup>2+</sup> ions were present in the product mixture using potassium thiocyanate according to the method developed by Hahn and Welcher (1963). Small sample of the reaction product was mixed with potassium thiocyanate, a colour change to faint blue would suggest the formation of [Co(SCN)<sub>4</sub>]<sup>2-</sup>, indicating the presence of Co(II) ions. In addition, the method of Tipson (1945) was used to check for the presence of dehydroascorbic acid as a possible product. A further spectrophotometric test was carried out for possible Co(II) complex products, by determining the λ<sub>max</sub> of the products to see if it matches with the range of 490 - 510 nm for Cobalt(II)aminocarboxylato complexes (Onu *et al.*, 2009; Arunachalam *et al.*, 2015).

## Results and Discussion

### Stoichiometry

The stoichiometry of the reaction showed a ratio of 2:1 as indicated by equation (1)



Where: A is dehydroascorbic acid

The observed stoichiometry obtained shows that H<sub>2</sub>A is undergoing a two electron transfer oxidation. This stoichiometry was supported by the UV/Visible spectrum of the reaction product which was scanned between wavelength ranges of 300 - 600 nm and a λ<sub>max</sub> of 507 nm was obtained, which agrees with literature value of the range 490 - 510 for Co(II) product (Onu *et al.*, 2009; Arunachalam *et al.*, 2015). The change in colour observed from faint pink to blue upon the qualitative test for Co(II) indicates the formation of [Co(SCN)<sub>4</sub>]<sup>2-</sup> signifying the presence of Co(II) (Hahn and Welcher, 1963), whose presence is as a result of the reduction of Co(III) by H<sub>2</sub>A. Also, the blue - green colour observed upon treating the reaction mixture with pyrrole in excess trichloroacetic acid confirms the presence of dehydroascorbic acid in the reaction product (Tipson, 1945). All these justify the stoichiometry obtained. A similar stoichiometry has been recorded in the reduction of some metal complexes by ascorbic acid (Abdur-Rashid *et al.*, 1996; Maity *et al.*, 2007; Mondal *et al.*, 2009; Lawrence *et al.*, 2012; Bitziou *et al.*, 2013).

### Kinetic study

The pseudo-first order plot for the reaction was linear (Fig. 2), confirming a first order dependence on [Co(III)EDTA]<sup>-</sup>. The logarithmic plot of k<sub>obs</sub> versus [H<sub>2</sub>A] was also linear (Fig. 3), with a gradient of 1.02. This shows that the reaction is first-order with respect to both [Co(III)EDTA<sup>-</sup>] and [H<sub>2</sub>A] respectively and a second order overall, with a second order rate constant (k<sub>2</sub>) of (9.88 ± 0.065) × 10<sup>-3</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Similar orders have been documented for H<sub>2</sub>A and other forms of Co(III) complexes in earlier works (Hamzeh, 2001; Lemma *et al.*, 2002; Khan *et al.*, 2005; Sailani *et al.*, 2011; Luty-Blocho *et al.*, 2013).

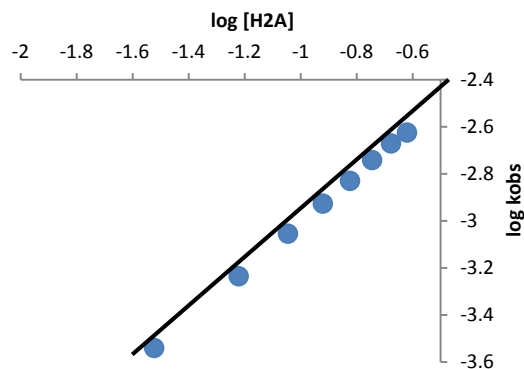


Fig 3: Plot of log k<sub>obs</sub> versus log [H<sub>2</sub>A] for the catalysed reduction of [Co(EDTA)]<sup>-</sup> by H<sub>2</sub>A at [Co(III)EDTA]<sup>-</sup> = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>A] = (3.0 – 21.0) × 10<sup>-2</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [Cu<sup>2+</sup>] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.4 mol dm<sup>-3</sup>, T = 299 ± 1 K, λ<sub>max</sub> = 535 nm

From the study of the effect of acid on the reaction, it was found that the reaction was independent of [H<sup>+</sup>] (Table 1) which suggests that the protonation or otherwise of H<sub>2</sub>A was not important in initiating this reaction (Davis, 1992). The rate of reaction was also first order with respect to [catalyst], which conforms to results obtained by earlier workers (Taqi and Ram, 1988; Sadhana *et al.*, 2014). The plot of k<sub>2</sub> versus [Cu<sup>2+</sup>] was linear with near zero intercept with a slope of 3.9. Investigation on the effect of ionic strength on the reaction species showed a decrease in the rate of the reaction with increase in concentration of inert salt (Table 1), indicating a negative kinetic salt. This result suggests the presence of oppositely charged species at the rate determining step (Singh *et al.*, 2014; Idris *et al.*, 2015).

Table 1: Pseudo – first order and second order rate constants for the catalysed reduction of [Co(EDTA)]<sup>-</sup> by H<sub>2</sub>A at [Co(III)EDTA]<sup>-</sup> = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, T = 299 ± 1 K, λ<sub>max</sub> = 535 nm

10[H <sub>2</sub> A], mol dm <sup>-3</sup>	10 <sup>3</sup> [H <sup>+</sup> ], mol dm <sup>-3</sup>	10 <sup>3</sup> [Cu <sup>2+</sup> ], mol dm <sup>-3</sup>	10[I], mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>obs</sub> , s <sup>-1</sup>	10 <sup>2</sup> k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
0.30	1.00	5.00	4.00	0.29	0.97
0.60	1.00	5.00	4.00	0.58	0.97
0.90	1.00	5.00	4.00	0.88	0.98
1.20	1.00	5.00	4.00	1.18	0.98
1.50	1.00	5.00	4.00	1.48	0.99
1.80	1.00	5.00	4.00	1.82	1.00
2.10	1.00	5.00	4.00	2.14	1.02
2.40	1.00	5.00	4.00	2.38	0.99
2.10	0.50	5.00	4.00	1.98	0.94
2.10	1.00	5.00	4.00	2.14	1.02
2.10	2.00	5.00	4.00	1.94	0.92
2.10	4.00	5.00	4.00	2.23	1.06
2.10	6.00	5.00	4.00	2.12	1.00
2.10	8.00	5.00	4.00	2.17	1.03
2.10	10.00	5.00	4.00	2.26	1.07
2.10	1.00	3.00	4.00	1.33	0.63
2.10	1.00	5.00	4.00	2.14	1.02
2.10	1.00	7.00	4.00	3.25	1.55
2.10	1.00	9.00	4.00	4.56	2.17
2.10	1.00	11.00	4.00	5.74	2.73
2.10	1.00	13.00	4.00	6.93	3.30
2.10	1.00	5.00	3.00	5.36	2.55
2.10	1.00	5.00	3.50	2.99	1.42
2.10	1.00	5.00	4.00	2.14	1.02
2.10	1.00	5.00	4.50	1.43	0.68
2.10	1.00	5.00	5.00	1.18	0.56
2.10	1.00	5.00	5.50	1.06	0.51

Table 2: Effect of added ions on the catalysed reaction of L- ascorbic acid and [Co(III)EDTA]<sup>-</sup> at [Co(III)EDTA]<sup>-</sup> = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>A] = 0.21 mol dm<sup>-3</sup>, [H] = 1.0 × 10<sup>-3</sup>, I = 0.4 mol dm<sup>-3</sup>, [Cu<sup>2+</sup>] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, T = 299 ± 1 K, λ<sub>max</sub> = 535 nm

X, mol dm <sup>-3</sup>	10 <sup>4</sup> k <sub>obs</sub> , s <sup>-1</sup>	10 <sup>3</sup> k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
10 <sup>3</sup> [HCOO <sup>-</sup> ]		
5	7.9	5.4
25	5.1	3.5
35	3.9	2.7
50	2.2	1.5
60	1.3	0.9
75	0.7	0.5
10 <sup>3</sup> [CH <sub>3</sub> COO <sup>-</sup> ]		
5	31.8	21.7
25	23.0	15.7
50	21.7	14.8
75	16.6	11.3
85	12.6	8.6
100	8.5	5.8
10 <sup>3</sup> [Li <sup>+</sup> ]		
5	7.6	5.2
15	8.8	6.0
25	9.9	6.8
35	18.0	12.3
50	22.3	15.2
75	31.3	21.3
85	35.3	24.1
10 <sup>3</sup> [Zn <sup>2+</sup> ]		
5	8.8	6.0
15	19.5	13.3
25	28.3	19.3
35	33.9	23.1
50	40.3	27.5
75	53.1	36.2
85	58.0	39.5

Effect of added anions and cations

The reaction was catalyzed upon the addition of cations as evidenced by an increase in rate that accompanied increasing cation concentration for Li<sup>+</sup> and Zn<sup>2+</sup> (Table 2). The reverse was observed in the cases of formate and acetate ions, in which increase in anionic concentration led to a marked drop in rate (Table 2). The inhibition by added anions is in order, as the added anions would further increase the distance between the reactants species at the activated complex by repelling the [Co(EDTA)]<sup>-</sup> specie and hence, reduce the rate of electron transfer. The observed effect of added ions shows that the reactant ions maintain their coordination integrity in the activated complex prior to and during electron transfer (Sharpe, 1981).

Free radicals

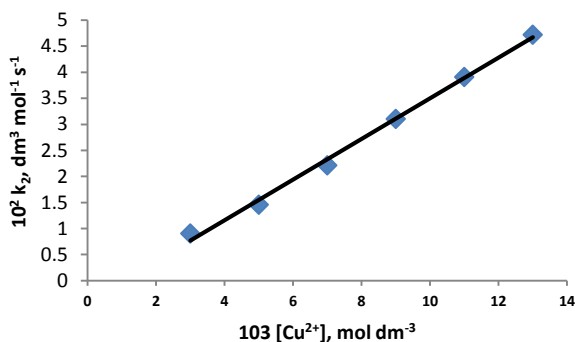
A gelatinous precipitate was detected when acrylamide was added to the reaction mixture followed by an excess of methanol. This is an indication that a free radical was present in the reaction mixture to have initiated polymerisation of the acrylamide, while the methanol was responsible in trapping this polymer as an insoluble precipitate (Gromov *et al.*, 1966). The majority of studies of oxidation of ascorbic acid by metal ions have proposed the formation of ascorbate free radical (Sailani *et al.*, 2011; Khan *et al.*, 2013), with dehydroascorbic acid as product (Davis, 1992).

Temperature study

As stated, the reaction was varied across temperatures ranging from 313 – 333 K (Table 3). An increase in temperature led to an increase in rate. From the Eyring Plot of  $\ln\left(\frac{k}{T}\right)$  versus  $\frac{1}{T}$ , the activated parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) were gotten from the slope ( $-7439.31$ ) and intercept ( $14.4876$ ) respectively. For  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $k_b = 1.381 \times 10^{-23} \text{ J/K}$ ,  $h = 6.626 \times 10^{-34} \text{ Js}$ , we can estimate  $\Delta H^\ddagger$  ( $61.85 \text{ KJ mol}^{-1}$ ) and  $\Delta S^\ddagger$  ( $-77.09 \text{ JK}^{-1} \text{ mol}$ ).

**Table 3: Temperature dependence on the rate of the reaction for  $[\text{Co(III)EDTA}]^-$  and  $\text{H}_2\text{A}$  at  $[\text{Co(III)EDTA}]^- = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{A}] = 0.21 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-3}$ ,  $\text{I} = 0.4 \text{ mol dm}^{-3}$ ,  $[\text{Cu}^{2+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 535 \text{ nm}$**

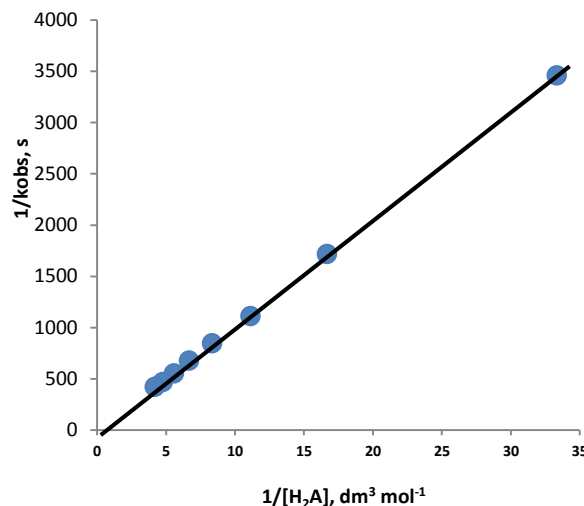
Temperature K	$10^3 k_{\text{obs}} \text{ s}^{-1}$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Activated Parameters
299	2.14	1.02	$\Delta S^\ddagger = -77.09 \text{ JK}^{-1} \text{ mol}$
313	3.69	2.52	
323	7.74	5.28	$\Delta H^\ddagger = 61.85 \text{ KJ mol}^{-1}$
333	22.52	15.36	



**Fig 4: The plot of  $k_2$  versus  $[\text{Cu}^{2+}]$  for the catalysed reduction of  $[\text{Co(III)EDTA}]^-$  by  $\text{H}_2\text{A}$  at  $[\text{Co(III)EDTA}]^- = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{A}] = 21.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Cu}^{2+}] = (0.3 - 1.3) \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{I} = 0.4 \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1 \text{ K}$ ,  $\lambda_{\text{max}} = 535 \text{ nm}$**

Although the negative value of activation entropy might suggest a more ordered activated complex occasioned by possible bridging of the reactant partners, the Michaelis – Menten plot of  $1/k_{\text{obs}}$  versus  $1/[\text{H}_2\text{A}]$  (Fig. 5) however was

linear with zero intercept, thus a strong indication of the absence of intermediate(s), hence suggesting an outer – sphere mechanism for this reaction. Ascorbic acid undergoing an outer – sphere mechanism with other forms of  $\text{Co(III)}$  complexes have been known to give similar activation entropy (Sadhana *et al.*, 2014, 2015).



**Fig 5: Michaelis-Menten plot for the reaction of  $[\text{Co(III)EDTA}]^-$  and  $\text{H}_2\text{A}$  at  $[\text{Co(III)EDTA}]^- = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{A}] = (3.0 - 21.0) \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Cu}^{2+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{I} = 0.4 \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1 \text{ K}$ ,  $\lambda_{\text{max}} = 535 \text{ nm}$**

Conclusion

The stoichiometry of the reaction between  $\text{H}_2\text{A}$  and  $[\text{Co(III)EDTA}]^-$  was found to be in the ratio of 1:2 for  $\text{H}_2\text{A} : [\text{Co(III)EDTA}]^-$ , an equation of this reaction was given in Equation 1. The kinetic study revealed a first order dependent on  $[\text{H}_2\text{A}]$ , and catalyst, but the reaction was independent of  $[\text{H}^+]$ . Ionic strength variation indicated a negative salt effect, attributed to two unlike charges at the rate determining step. The effect of added anions inhibition and absence of intermediate as seen from the Michaelis-Menten Plot led to the suggestion that the reaction follows an outer – sphere mechanistic path. The proposed mechanism for the  $\text{Cu}^{2+}$  catalysed reduction of ethylenediaminetetraacetatocobaltate(III) ion is given in the scheme below:



$$\text{Rate} = k_1 [\text{CuH}_2\text{A}^{2+}] [\text{Co}(\text{EDTA})^-] \quad (6)$$

$[\text{CuH}_2\text{A}^{2+}]$  is an intermediate that is produced in an equilibrium step (Equation 2), thus:

$$K_{eq} = \frac{[\text{CuH}_2\text{A}^{2+}]}{[\text{H}_2\text{A}][\text{Cu}^{2+}]} \quad (7)$$

$$[\text{CuH}_2\text{A}^{2+}] = K_{eq} [\text{H}_2\text{A}] [\text{Cu}^{2+}] \quad (8)$$

substituting Equation 8 into 6 gives:

$$\text{Rate} = K_{eq}k_1 [\text{Cu}^{2+}] [\text{H}_2\text{A}] [\text{Co}(\text{EDTA})^-] \quad (9)$$

The rate law in Equation 9 can thus be written as;

$$\text{Rate} = a[\text{Cu}^{2+}] [\text{H}_2\text{A}] [\text{Co}(\text{EDTA})^-] \quad (10)$$

Equation 10 corresponds to the experimental rate law where  $a = K_{eq}k_1 = 3.9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

### Conflicts of Interest

There are no conflicts to declare.

### References

- Abdur-Rashid K, Dasgupta TP & Burgess J 1996. Kinetics and mechanism of the oxidation of L-ascorbic acid by *cis*-diaqua cobalt(III) amine complexes. *J. Chem. Soc.: Dalton Transactions*, 7: 1385 – 1391.
- Arunachalam P, Sudhir KS, Sathyaseelan VS & Toleti SR 2015. A Spectrophotometric Method for the Determination Co-EDTA Complexes. *Int. J. Appl. Sci. and Biotechn.* 3(4): 584 – 587.
- Bengt N 1970. The diminished inertness of the Tris(ethylenediamine)-cobalt(III) ion when irradiated with ultraviolet light in the presence of ethylenediaminetetraacetate. *Acta Chemica Scandinavica*, 24: 1703 – 1712.
- Bitziou E, Snowden ME, Joseph MB, Leigh SJ, Covington JA, Macpherson JV & Unwin, PR 2013. Dual electrode micro – channel flow cell for redox titrations: Kinetics and analysis of homogeneous ascorbic acid oxidation. *Journal of Electroanalytical Chemistry*, 692: 72 – 79.
- Carlos BG, Pastori GM & Foyer CH 2000. Ascorbate biosynthesis in mitochondria is linked to the electron transport Chain between complexes III and IV. *American Society of Plant Physiologists*. 123(1): 335 – 344.
- Chatterjee IB, Kar NC, Ghosh NC & Guha BC 1961. Aspect of ascorbic acid biosynthesis in animals. *Annals of the New York Academy of Sciences*, 92: 36 – 56.
- Davis BM 1992. Reactions of L-ascorbic acid with transition metal complexes. *Polyhedron*, 11(3): 285 – 321.
- Gromov VF, Matveyeva AV, Khomikovskii PM & Abkin AD 1966. The effect of methanol on the polymerization of acrylamide in aqueous solution. *Polymer Science U.S.S.R*, 9(7): 1616 – 1623.
- Hacisevki A 2009. An overview of ascorbic acid biochemistry. *Journal of the Faculty of Pharmacy of Ankara University*, 38(3): 233 – 255.
- Hahn RB & Welcher FJ 1963. Inorganic qualitative analysis: A short course for introductory chemistry. *J. Chem. Educ.*, 40(8): 442.
- Hamzeh MA 2001. Kinetics of oxidation of L-ascorbic acid by cobalt(III) complexes. *J. Chem. Soc. Pak.*, 23(2): 69 – 73.
- Idris SO, Suleman JO, Iyun JF & Osunlaja AA 2015. Reduction of 3,7-Bis(dimethylamino)phenazothionium chloride by benzenethiol in aqueous nitric acid medium: A mechanistic approach. *Am. Chem. Sci. J.*, 5(4): 313 – 321.
- Isherwood FA, Chen YT & Mapson LW 1954. Synthesis of L-ascorbic acid in plants and animals. *Biochemistry Journal*, 56(1): 1 – 15.
- Khan Z, Kumar P & Din K 2005. Kinetics of the Reaction of Water Soluble Colloidal MnO<sub>2</sub> by Ascorbic Acid. *J. Colloid Interface Sci.*, 200: 184 – 189.
- Khan Z, Singh T, Hussian JI & Hashmi AA 2013. Au(III) – CTAB reduction by ascorbic acid: Preparation and characterization of gold nanoparticles. *Colloid and Surfaces B: Biointerfaces*, 104: 11 – 17.
- Lappin AG, Laranjeira MCM & Youde-Owei L 1981. *J. Chem. Soc., Dalton Transaction*, 721.
- Lawrence MAW, Maragh PT & Dasgupta TP 2012. Mechanistic studies on the intra-molecular electron transfer in the adduct species of some oxo-centered trinuclear iron(III)/chromium(III) cations and L-ascorbic acid in aqueous acetate buffer. *Inorganica Chimica Acta*, 388: 88 – 97.
- Lemma K, House DA, Retta N & Elding LI 2002. Kinetics and mechanism of reduction of halo and haloam(m)ineplatinum(IV) complexes by L-ascorbate. *Inorganica Chimica Acta*, 331: 98 – 108.
- Leal JM, Domingo PL, Garcia B & Ibeas S 1993. Alkali-metal ion catalysis of then oxidation of L-ascorbic acid by hexacyanoferrate(III) in strongly acidic media. *J. Chem. Soc., Faraday Transactions*, 89(19): 3571- 3577.
- Luty-Blocho M, Paclawski K, Wojnicki M & Fitzner K 2013. The kinetics of redox reaction of gold(III) chloride complex ions with L-ascorbic acid. *Inorganica Chimica Acta*, 395: 189 – 196.
- Maity D, Mijanuddin M, Drew MGB, Marek J, Mondal PC, Pahari B & Ali M 2007. Oxovanadium(V) complexes of Bis(phenolate) ligands with acetylacetone as co-ligand: Synthesis, crystal structure, electrochemical and kinetics studies on the oxidation of ascorbic acid. *Polyhedron*, 26: 4494 – 4502.
- Majumdar T, Pahari S, Mandal HK & Mohapatra A 2010. Kinetic studies on the reaction between  $[\text{Co}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$  and ascorbic acid: Effect of surfactant, polymer and their mixture. *Journal of Molecular Liquids*, 153(2-3): 101 – 106.
- Mamman S & Iyun JF 2007. Kinetics and mechanisms of the reactions of benzenediols with binuclear oxalatocobaltate(III) Complex. *Int. J. Pure and Appl. Chem.*, 2: 407 – 413.
- Mondal A, De P, Mukhopadhyay S, Banerjee R, Kar P, Jose AD & Das A 2009. Kinetics of oxidation of quinol and ascorbic acid with the phensubstituted semiquinone ligand, (5,6-dioxlene-1,10-phenanthroline-O,O) Bound to the Ru(bipy)<sub>2</sub> moiety. *Polyhedron*, 28: 2655 – 2660.
- Onu AD, Iyun JF & Idris SO 2009. The kinetics of the reduction of tetroxiodate(VII) by N-(2-hydroxyethyl)ethylenediaminetriacetatocobaltate(II) Ion in aqueous perchloric acid. *Transition Metal Chemistry*, 34: 849 – 853.
- Perveen A, Nezamoleslam T & Iftikhar IN 2013. Preparation of cobalt(III) complexes with trans-1,2-iaminocyclohexane-N,N,N',N'-tetraacetate acid (CDTA) and ethylenediaminetetraacetic acid (EDTA). *Afri. J. Pure and Appl. Chem.*, 7(6): 218-2224.
- Sadhana S, Patnaik AK, Das SP & Mohanty P 2014. Kinetics and mechanistic study of redox reaction of cobalt (III) Complex with L-ascorbic acid in aqueous acid medium. *Chem. Sci. Rev. and Letters*, 3(12): 774 – 783.
- Sadhana S, Patnaik AK, Das SP & Mohanty P 2015. Kinetics and mechanistic study of redox reaction of cobalt (III)

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- complex with L-ascorbic acid in aqueous acid medium. *Am. Chem. Sci. J.*, 9(2): 1 – 10.
- Saha B, Gangopadhyay S, Ali M & Banarjee P 1995. Kinetic studies on the reduction of nickel(IV) and nickel(III) oxime-imine complexes by ascorbic acid. *American Chemical Society, Dalton Transactions*, 7: 1083-1088.
- Sailani R, Dubey S, Khandelwal CL, Sharma PD & Khan P 2011. Kinetics and mechanism of oxidation of L-ascorbic acid by peroxomonosulphate in acid perchlorate medium. Role of copper(II) as a trace metal-ion catalyst. *Rendus Chimie*, 14: 1088 – 1094.
- Sharpe AG 1981. *Inorganic Chemistry, 1st edition*. Longman, London, p. 518.
- Singh B, Das RS, Banerjee R & Mukhopadhyay S 2014. Uncatalyzed and copper(II) catalyzed oxidation of glutathione by Co(III)<sub>2</sub> bound superoxide complex. *Inorganica Chimica Acta*, 418: 51 – 58.
- Szabolcs S, Gyorgy P & Laszlo W 2005. Cobalt(III) EDTA complex removal from aqueous alkaline borate solution by nanofiltration. *Desalination*, 175: 179 – 185.
- Taqi KMM & Ram SS 1988. Inner sphere oxidation of L-ascorbic acid by Ru(III) ion and its complexes in aqueous acidic medium. *Inorganica Chimica Acta.*, 149(1): 89–94.
- Tipson RS 1945. A qualitative test for dehydroascorbic acid. *J. Am. Pharmac. Ass.*, 34(7): 190 – 192.