



## Kinetics and Mechanistic Study of Redox Reaction of Cobalt (III) Complex with L-Ascorbic Acid in Aqueous Acid Medium

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### Authors' contributions

This work was carried out in collaboration between all authors. Author AKP designed the study and wrote the first draft of the manuscript. Author SS carried out the experimental work, computational analysis and managed the literature searches and authors SPD and PM managed the analyses of the study and finalized the manuscript. All authors read and approved the final manuscript.

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### ABSTRACT

The kinetics of the electron transfer reaction of L-ascorbic acid with a cobalt (III) complex has been studied spectrophotometrically over the range  $0.01 \leq [\text{ascorbic acid}], \text{mol dm}^{-3} \leq 0.07$ ,  $3.3 \leq \text{pH} \leq 5$ , and at  $298 \leq T, K \leq 318$  in aqueous acid medium. Kinetics measurements were run under pseudo-first order conditions. The rate of electron transfer reaction was found to be first order with respect to ascorbic acid. The results showed that the rate constant depends on size and strength of the ligand. The activation parameters favoured the electron transfer reaction. In the absence of evidence of direct coordination of ascorbic acid to Co(III) centre, an outer-sphere electron transfer mechanism was suggested. The reduction of Co(III) complex by L-ascorbic acid depends on pH and the nature of the ligand. Considering the dependence of  $k_{\text{obs}}$  with pH, it was suggested that  $\text{HA}^-$  reacts much faster than  $\text{H}_2\text{A}$  and  $\text{A}^{2-}$  is not reactive at  $\text{pH} < 5$ .  $\text{HA}^-$  is the predominant reacting species under the experimental pH of the solution.

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## 1. INTRODUCTION

The oxidation of L-Ascorbic acid is a very important redox reaction, as it has interesting biological properties and it is also a powerful reducing agent [ $E^0=0.390V$  NHE]. The reducing property of L-Ascorbic acid is due to the presence of grouping  $C(OH)=C(OH)-C=O$  containing conjugated double bonds. The complexing property is due to its 2,3-ene-diol configuration. Metal ascorbates are also important due to the developments of therapeutic agents with potential antitumor, antibacterial, antioxidant properties and it also serves as a synthetic model for metal containing biological systems.

Kinetics of oxidation of L-ascorbic acid with various oxidising agents such as nickel(IV) and nickel(III) [1], hexacyanoferrate(III) [2], Mn(III) [3], Mn(IV) [4], Cobalt(III) complexes [5], Pt(IV) [6] has been studied, but the effect of nature of the ligand on such reaction has not been thoroughly investigated. In the present work we report the kinetics of oxidation of L-ascorbic acid with Co(III) complex in aqueous perchloric acid medium. The Co(III) complex contains a ligand containing both functional group  $NH_2$  and OH group. The electron transfer rate is compared with all reported ligands and the effect of nature of ligand has been suggested.

## 2. EXPERIMENTAL

### 2.1 Materials and Methods

The details of synthesis of the complex  $[Co(en)_2(1\text{-amino-propane-2-ol})(OH_2)](ClO_4)_3$  was described in our earlier published paper [7]. Characterisation of the complex and other experimental details have also been described in our earlier paper. The pH measurements were made using a pre-standardised digital pH meter Elico(India) equipped with combined glass electrode.

### 2.2 Kinetic Measurement

The kinetics of the reaction between cobalt complex and L-ascorbic acid were studied under pseudo-first order condition by measuring the change of absorbance at fixed wavelength using a UV-Visible Spectrophotometer (CECIL7200, UK) equipped with CE 2024 thermostatic bath for

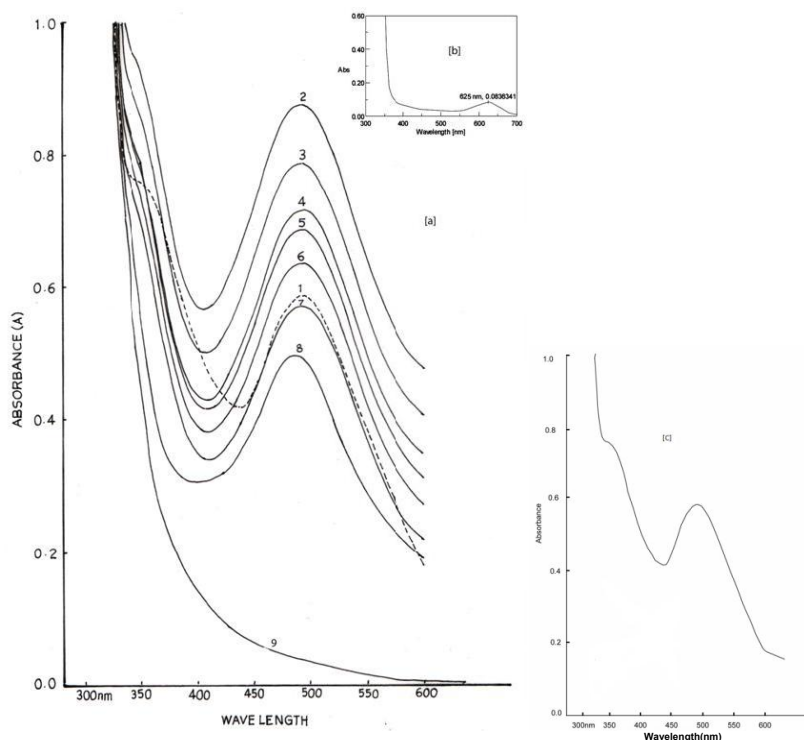
temperature control with an accuracy of  $\pm 0.1^\circ C$ . The reaction was studied under varying concentrations of L-ascorbic acid ( $0.01$  to  $0.07$  mol  $dm^{-3}$ ) and complex ( $2 \times 10^{-3}$  to  $5 \times 10^{-3}$  mol  $dm^{-3}$ ); temperature ( $298 \leq T/K \leq 318$ ) and pH (3.3 - 5.0) keeping the ionic strength (I) fixed at  $0.5$  mol  $dm^{-3}$ . The Progress of the reaction was monitored by following the decrease in absorbance at  $490$  nm with time using a conventional mixing technique shown in Fig. 1. The pseudo first order rate constants ( $k_{obs}$ ) were calculated from the slope of the plots of  $\ln(A_t - A_\infty)$  versus  $t(s)$  as per relationship presented in equation(1)

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{obs} \cdot t \quad (1)$$

where  $A_0$ ,  $A_t$  and  $A_\infty$  denote the absorbances of the reaction mixture at the beginning, at different time (t) intervals and after completion of the reaction, respectively. All the kinetic runs were made at least in duplicate and average values were reported which were reproducible to within  $\pm 3\%$ . In most cases the correlation coefficients ( $R^2$ ) of  $\ln(A_t - A_\infty)$  versus  $t(s)$  plots were found to be  $0.99$  indicating the fitting of absorbance data to first order rate equation. All calculations were made on a personal computer using linear least square program.

## 3. STOICHIOMETRY AND IDENTIFICATION OF PRODUCT

For determination of stoichiometry and products of the reactions, the reaction mixture containing L-ascorbic acid and cobalt(III) complex in the ratio 10:1 at  $303K$  and  $I = 0.5$  mol  $dm^{-3}$  was allowed to react till the completion of the reaction. The unreacted ascorbic acid was then determined iodimetrically. The oxidation products of the reaction were identified as Cobalt(II) and dehydroascorbic acid.  $Co^{II}$  as one of the final products of the reaction was confirmed by its estimation using Kitson's method [8] while dehydroascorbic acid was identified by Roe's [9] method after separating the metal ion through cation exchange resin (Dowex 50X8). The formation of dehydroascorbic acid in the reaction mixture was further confirmed by recording the FTIR spectra using FTIR spectrophotometer (PerkinElmer) and  $^1H$  NMR spectra using  $400$  MHz NMR spectrophotometer (Varian) shown in Fig. 2 and Fig. 3(b) respectively.



**Fig. 1(a).** UV-VIS spectral scans of the reaction mixture of Co(III) complex and L-ascorbic acid in aqueous acid medium,  $I = 0.5 \text{ mol dm}^{-3}$  [Co(III) complex] =  $2.31 \times 10^{-3} \text{ mol dm}^{-3}$  (1) Immediately after mixing (2),  $\Delta t = 10$  minutes, curves (3-8) and reaction mixture after 24 hrs (9).  
**(b) Inset:** Spectrum of the above reaction mixture after 24 hrs with addition of ammonium thiocyanate (Kitson method)  
**(c) UV-VIS spectrum of Co(III) complex,  $T = 303\text{K}$ , [Co(III) complex] =  $2.31 \times 10^{-3} \text{ mol dm}^{-3}$**

The overall stoichiometry was found to be 1:1 as depicted in equation [2]



FTIR Spectra of the products in Fig. 2 exhibits two broad peaks at  $3618 \text{ cm}^{-1}$  and  $3300 \text{ cm}^{-1}$ , corresponding to two hydrogen bonded OH groups. In comparison four peaks at  $3217 \text{ cm}^{-1}$ ,  $3316 \text{ cm}^{-1}$ ,  $3410.5 \text{ cm}^{-1}$  and  $3527 \text{ cm}^{-1}$  due to OH groups are observed in ascorbic acid. The peaks at  $1479 \text{ cm}^{-1}$  and  $1454 \text{ cm}^{-1}$  are attributed to C-O stretching while that observed at  $1754 \text{ cm}^{-1}$  is due to C=O stretching. Among other, the peaks at  $2995 \text{ cm}^{-1}$ ,  $2968 \text{ cm}^{-1}$ ,  $2904 \text{ cm}^{-1}$  correspond to C-H stretching in  $\text{CH}_2$  methine while peaks at  $1365 \text{ cm}^{-1}$  attributes to C-H bending. The peaks at  $1074 \text{ cm}^{-1}$  is due to C-O stretching in  $\text{CH}_2\text{OH}$  (primary alcohol). All these peaks [10] correspond to dehydroascorbic acid. The  $^1\text{H}$  NMR of ascorbic acid, presented in Fig. 3(a), shows four peaks at  $\delta 4.78, 4.81,$

$10.68$  (enol),  $16.77$  (enol) corresponding to four OH groups. The other peaks at  $\delta 5.0$  and  $\delta 3.93$  correspond to CH of furanon, and methane group, respectively.  $^1\text{H}$  NMR of product, presented in Fig. 3 (b), shows peaks at  $\delta 4.81, 4.78,$  peak at  $\delta 4.45, 4.11$  corresponding to CH group in butyrolactone while the peak at  $\delta 3.90$  corresponds to methine (CH). All peaks of  $^1\text{H}$  NMR spectra [11] of Fig. 3(b) corresponds to dehydroascorbic acid.

#### 4. RESULTS AND DISCUSSION

The time dependence spectral scan of the reaction mixture containing Co(III) complex and L-ascorbic acid at  $\text{pH} = 4.0$  is presented in Fig. 1 of our earlier published paper [7]. The absorption maxima at around  $490 \text{ nm}$  is completely vanished after a long interval of time (24 hrs). The final spectrum of the reaction mixture after a long interval of time virtually agreed with the spectrum of the mixture of Co(II) and the ligand

at the same pH, which indicates that  $\text{Co}^{\text{III}}\text{L}$  was reduced to  $\text{Co}^{\text{II}}\text{L}$  by L- ascorbic acid. It was further confirmed by testing the aged solution by Kitson method. In this method 2 cm<sup>3</sup> of the aged reaction mixture was added with 1 cm<sup>3</sup> of NH<sub>4</sub> CNS followed by addition of 5 cm<sup>3</sup> of acetone to develop a deep blue colouration. A peak at 625 nm is observed in the absorption spectra of the resulted solution shown in Fig. 1(b) [7] which is similar to that observed under identical conditions taking  $\text{Co}(\text{ClO}_4)_2$  instead of the reaction mixture. The percentage of  $\text{Co}(\text{II})$  formed in the reaction was found to be ~ 98% indicating complete reduction of  $\text{Co}(\text{III})$ .

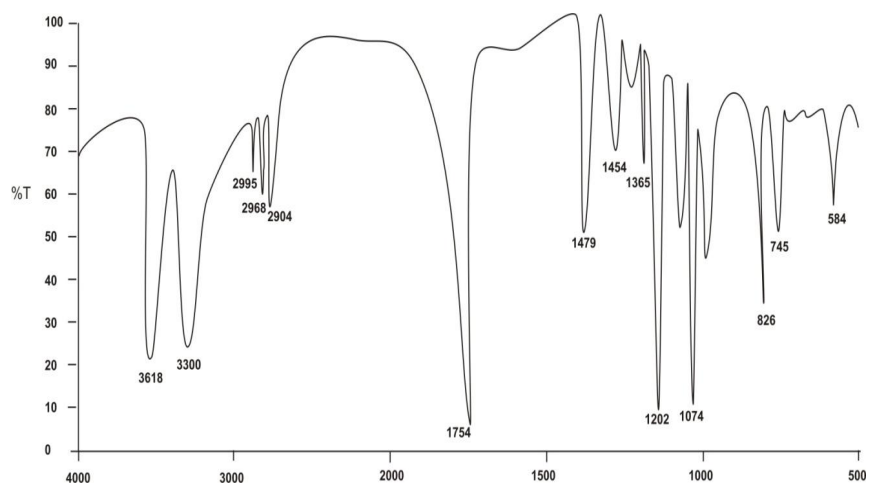
The datas of the redox reaction are collected in Table-1 which is also described in our earlier published paper [7]. Plots of  $k_{\text{obs}}$  versus  $[\text{H}_2\text{A}]$  are linear with finite positive intercepts (Fig. 4) in the temperature range 298 K- 318 K indicating first order dependence of rate with respect to  $[\text{H}_2\text{A}]$ . The pseudo-first order rate constants ( $k_{\text{obs}}$ ) are not affected by varying  $[\text{Co}(\text{III})]$  complex in the range  $2 \times 10^{-3}$  -  $5 \times 10^{-3}$  mol dm<sup>-3</sup> at pH = 3.3. In order to know the type of species that are involved in the rate determining step, the reaction was investigated at different ionic strength of the

reaction medium in the range 0.1 to 0.5 mol dm<sup>-3</sup> keeping  $[\text{Co}^{\text{III}}\text{L}]$ ,  $[\text{H}_2\text{A}]$ , pH and temperature fixed at  $2 \times 10^{-3}$  mol dm<sup>-3</sup>,  $4 \times 10^{-2}$  mol dm<sup>-3</sup>, 3.3 and 298K, respectively. It is found that the rate constants ( $k_{\text{obs}}$ ) do not vary appreciably indicating the reacting species are either uncharged ( $\text{Co}^{\text{III}}\text{L}/\text{H}_2\text{A}$ ) or one of them bears a negative charge ( $\text{HA}^-$ ) and thus supports the proposed reaction scheme 1. The variation of rate constants with pH is presented in Fig. 5 which increases with increasing pH of the reaction medium due to formation of more and more  $\text{HA}^-$  species, This clearly indicates that  $\text{H}_2\text{A}$  species is much less reactive than the  $\text{HA}^-$  species. Reduction by  $\text{A}^{2-}$  was not considered in this case as the measurement was limited to  $\text{pH} < 5.0$  ( $\text{p}K_2^{\text{H}_2\text{A}} > 11$ ) [12].

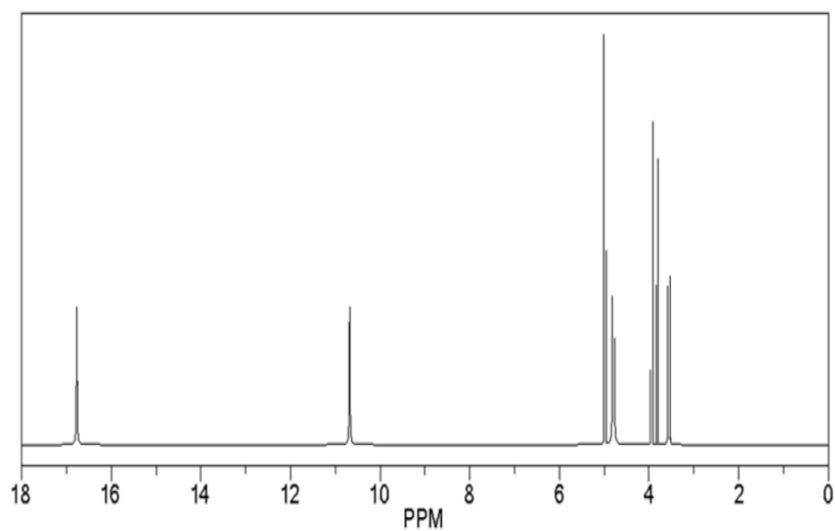
The participation of free radicals was examined by adding a known quantity of acrylonitrile to the reaction mixture and was kept for 2 h in an inert atmosphere. When the reaction mixture was diluted with methanol, no precipitate was formed indicating no intervention of free radicals in the reaction and further supported the proposed reaction scheme 1.

**Table 1. Pseudo-first order rate constants for redox reaction of  $\text{Co}(\text{III})$  complex by L-ascorbic acid,  $[\text{Complex}] = 2.31 \times 10^{-3}$  moldm<sup>-3</sup>,  $I = 0.5$ mol dm<sup>-3</sup>**

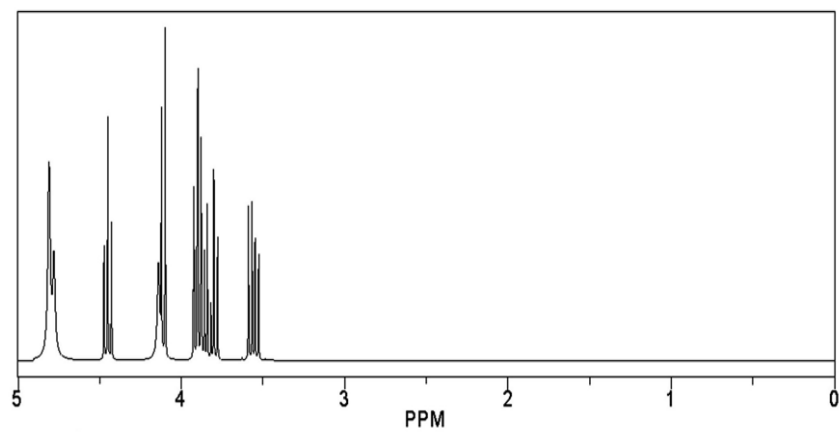
$[\text{H}_2\text{A}]$ , moldm <sup>-3</sup>	pH	$10^4 k_{\text{obs}}$ , [s <sup>-1</sup> ]				
		298K	303K	308K	313K	318K
0.01	3.3	0.260	0.800	1.056	1.400	1.879
	4	0.700	1.000	1.251	1.600	2.095
	5	0.820	1.150	1.424	1.800	2.326
0.02	3.3	0.660	1.100	1.447	2.000	2.878
	4	0.850	1.300	1.653	2.170	2.958
	5	1.014	1.380	1.900	2.500	3.348
0.03	3.3	0.760	1.400	2.050	2.600	3.500
	4	0.900	1.500	2.100	2.700	3.880
	5	1.250	1.950	2.487	3.300	4.541
0.05	3.3	1.160	1.900	2.650	3.400	4.837
	4	1.350	2.170	2.823	3.800	5.365
	5	1.450	2.620	3.469	4.900	7.353
0.07	3.3	1.330	2.600	3.496	5.100	7.993
	4	1.600	2.700	3.797	5.500	8.212
	5	1.820	3.400	4.551	6.500	9.973



**Fig. 2. FT-IR Spectra of the reaction product, dehydroascorbic acid**



**Fig. 3 (a). <sup>1</sup>H NMR spectra of ascorbic acid**



**Fig. 3 (b). <sup>1</sup>H NMR spectra of the product, dehydroascorbic acid**

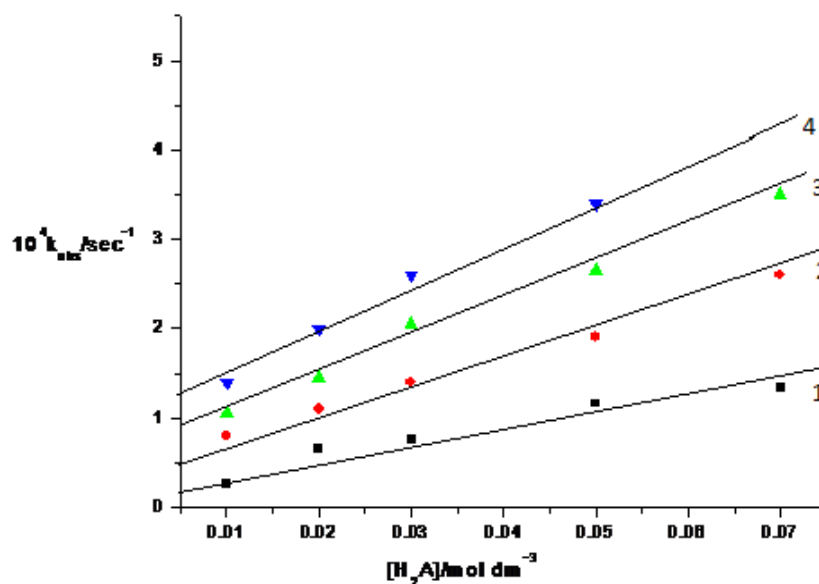


Fig. 4.  $k_{obs}$  versus  $[H_2A]$  at (1) 298K, (2) 303K, (3) 308K, (4) 313K  $[Co(III) \text{ complex}] = 2.31 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  and  $pH = 3.3$

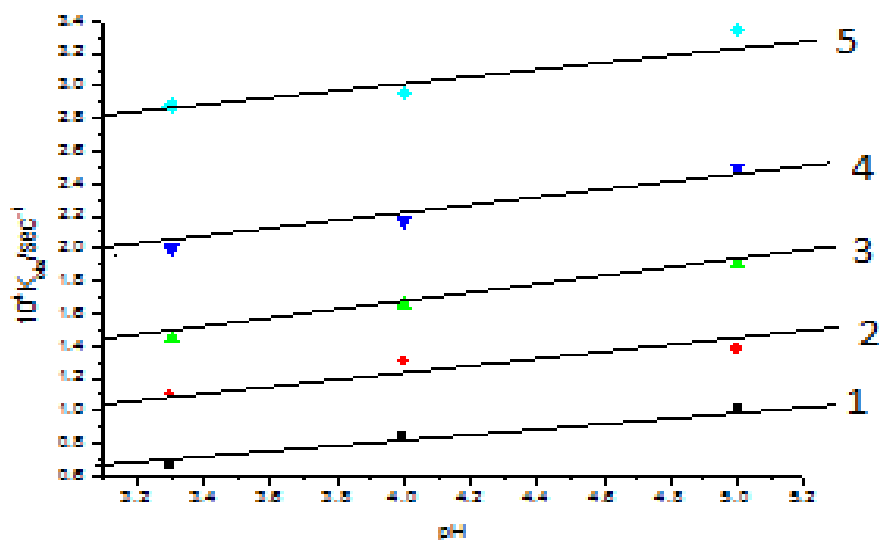
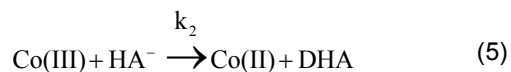
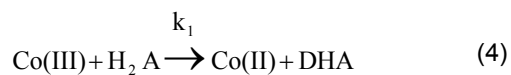
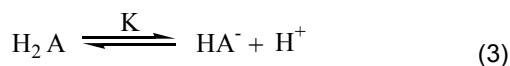


Fig. 5.  $k_{obs}$  versus  $pH$  at (1) 298K, (2) 303K, (3) 308K, (4) 313K and (5) 318K with  $[complex] = 2.31 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[H_2A] = 2 \times 10^{-2} \text{ mol dm}^{-3}$

### 5. MECHANISM OF THE REACTION

Basing on the above observations and identification of products, the probable mechanism may be delineated as in the scheme 1.



The rate law corresponding to the above mechanism is derived as:

$$\begin{aligned} \text{Rate} &= k_1[\text{Co(III)}][\text{H}_2\text{A}] + k_2[\text{Co(III)}][\text{HA}^-] \\ &= [\text{Co(III)}]\{k_1[\text{H}_2\text{A}] + k_2[\text{HA}^-]\} \\ &= [\text{Co(III)}]\left\{k_1[\text{H}_2\text{A}] + k_2 \frac{k_1[\text{H}_2\text{A}]_e}{[\text{H}^+]}\right\} \quad (6) \\ &= [\text{Co(III)}][\text{H}_2\text{A}]_e \left\{ \frac{k_1[\text{H}^+] + k_2 k_1}{[\text{H}^+]} \right\} \end{aligned}$$

$$\begin{aligned} &= \frac{[\text{Co(III)}][\text{H}_2\text{A}]_T[\text{H}^+]}{[\text{H}^+] + K} \left\{ \frac{k_1[\text{H}^+] + k_2 k_1}{[\text{H}^+]} \right\} \\ &= [\text{Co(III)}][\text{H}_2\text{A}]_T \frac{\{k_1[\text{H}^+] + k_2 k_1\}}{[\text{H}^+] + K} \quad (7) \end{aligned}$$

$$\text{Rate} = k_{\text{obs}}[\text{Co(III)}]_T$$

$$k_{\text{obs}} = [\text{H}_2\text{A}]_T \frac{\{k_1[\text{H}^+] + k_2 k_1\}}{[\text{H}^+] + K}$$

$$\frac{k_{\text{obs}}}{[\text{H}_2\text{A}]_T} = k_2 = \frac{k_1[\text{H}^+] + k_2 k_1}{[\text{H}^+] + K}$$

$$k_2\{[\text{H}^+] + K\} = k_1[\text{H}^+] + k_2 k_1 \quad (8)$$

$k_2\{[\text{H}^+] + K\}$  is plotted against  $[\text{H}^+]$  using reported value of  $K$ . From the slope and intercept, the values of  $k_1$  and  $k_2$  were calculated. It is found that the values  $k_2$  is always higher than  $k_1$ . The rate constant values at different temperatures along with activation parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ), have been derived using Eyring equation, and

presented in Table 2(a,b). Lower values of activation parameters favour the electron transfer process. The negative values of activation entropy indicates an order transition state for the electron transfer reaction.

In order to assess the effect of ligand environment of Co(III) complex on the rate of electron transfer reaction, the rate constants obtained in the present work was compared with those reported for different cobalt(III) complexes [13] given in Table 3. It is clearly seen that the rate of reaction between ascorbic acid and different cobalt complexes ( $\text{Co}^{\text{III}}\text{L} + e \rightarrow \text{Co}^{\text{II}}\text{L}$ ) is depended on the nature of the ligands. Further it is known that the ability of the electron to tunnel through the complex to reduce the metal ion is dependent on the electrode potential of the complex. The presence of different ligands in the complex causes different electrode potential for cobalt(III) reduction. The second factor that affects the reduction potential of cobalt(III) could be the size of the ligand. The rate of electron transfer reaction decreases as the size of the ligand increases. Bulky ligands like 1-amino-propane-2-ol, Phen, EDTA etc. make electro tunnelling relatively slow. The probability of an electron to tunnel through the ligand is a quantum mechanical property which can be calculated from time dependent perturbation theory.

The transition probability of an electron to pass through potential barrier between two molecules in gas phase is given in equation (9) [14]

$$P(t) = \text{Sin}^2(2\pi H_{12} t/h) \quad (9)$$

**Table 2(a). Second order rate constant ( $k_1$ ) and the calculated activation parameters**

Parameters	Temperature				
	298 K	303 K	308 K	313 K	318 K
$10^3 k_1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	2.600	4.400	6.200	8.600	12.600
$\Delta H^\ddagger [\text{kJ mol}^{-1}] (k_1)$	56.0±2.0				
$\Delta S^\ddagger [\text{J K}^{-1} \text{ mol}^{-1}] (k_1)$	-105.28±6.4				

**Table 2(b). Second order rate constants ( $k_2$ ) and the calculated activation parameters**

Parameters	Temperature				
	298 K	303 K	308 K	313 K	318 K
$10^3 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	4.587	5.882	8.497	11.111	16.149
$\Delta H^\ddagger [\text{kJ mol}^{-1}] (k_2)$	49.30±2.41				
$\Delta S^\ddagger [\text{J K}^{-1} \text{ mol}^{-1}] (k_2)$	-124.9±7.71				

**Table 3. Comparative rate constants for oxidation of L-ascorbic acid by different cobalt(III) complexes at T= 298K , I = 0.5 mol dm<sup>-3</sup>. [Ref-13]**

Complexes	Ligands	k, (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	NH <sub>3</sub>	1.9×10 <sup>2</sup>
[Co(NO <sub>2</sub> ) <sub>6</sub> ] <sup>3-</sup>	NO <sub>2</sub>	6.2×10 <sup>-1</sup>
[Co(en) <sub>3</sub> ]	en	4×10 <sup>-3</sup>
Cis- [(en) <sub>2</sub> Co(H <sub>2</sub> N-CH <sub>2</sub> -C(OH)H-CH <sub>3</sub> )OH <sub>2</sub> ] <sup>3+</sup>	Ethylenediamine- 1- amino-2 - propanol	2.94×10 <sup>-3</sup> (This work)
[Co(Phen) <sub>3</sub> ] <sup>3+</sup>	Phen	2.7×10 <sup>-3</sup>
[Co(EDTA)]	EDTA	Very slow

Where t is the time, h is planck's constants and H<sub>12</sub> is called exchange integral or interaction energy between the initial state orbital described by wave function  $\phi_1$  and final state orbital described by the wave function  $\phi_2$ . It is given in equation (10).

$$H_{12} = \int \phi_1 \hat{H} \phi_2 d\tau \quad (10)$$

Where  $\hat{H}$  is the Hamiltonian of the transferring electron. The interaction energy depends on the extent to which orbitals centered on the two interacting particles overlap with each other. In solution, the electronic transfer between two particles will be hindered by the presence of solvent molecules because such molecules prevent the extension into space of the orbitals on the exchanging particles. However the ligands of a complex ion will act as good insulating groups for electrons and orbitals of the central metal ion. The electron tunnelling theory developed by Weiss [15], Marcus & Eyring [16] gives considerable insight into the electron transfer process in the solution. The potential energy of an electron moving in coulombic field of two ions is expressed as

$$U = \frac{q_1 q_2}{Dd} - \frac{eq_1}{Dx} - \frac{eq_2}{D(d-x)} \quad (11)$$

where  $q_1$  and  $q_2$  are charges of Co(III) complex and ascorbic acid, D is the dielectric constant of the solvents, x is the distance between electron donor(ascorbic acid) to centre of electron acceptor Co(III). This distance depends on the size of the ligands around the central metal ion.

The net charge on ascorbic acid ( $q_2$ ) is zero. Therefore the equation (11) is reduced to equation (12)

$$U = - \frac{eq_1}{Dx} \quad (12)$$

The rate k(T) for electron transfer is given the transition state theory [17] as

$$k(T) = \kappa \frac{kT}{h} e^{-\Delta G^\ddagger/kT} \quad (13)$$

Where T is the reaction temperature. k is the Boltzman's constants.  $\Delta G^\ddagger$  is the free energy change of the activated complex.  $\kappa$  is the transmission coefficient is expressed by equation(14)

$$\kappa = \exp \left\{ - \left( \frac{8\pi d}{3h} \right) \left[ 2m(U - W) \right]^{\frac{1}{2}} \right\} \quad (14)$$

Where U is the height of the potential barrier, W is the kinetic energy of the electron, m is the mass of the electron, d is the width of the barrier at the height of penetration. Equations 10, 11 and 12 show that as the size of the ligand in complex increases the transmission coefficient resulting a decrease of rate constant. Accordingly lower values of rate constants have been observed for last two complexes of Table 3 along with the complex of present study. This finding is in agreement with results reported earlier [18].

It is concluded that the rate of oxidation of L-ascorbic acid by cobalt(III) complex was found to depend inversely on both the strength of the ligand in the complex and its size. The effect of size was found to be predominant. There was no evidence of direct coordination of the ascorbic acid to cobalt (III) centre indicating outer sphere ET mechanism.



## 6. CONCLUSION

The kinetics of redox reaction between  $[\text{Co}(\text{en})_2(1\text{-amino-propane-2-ol})(\text{OH}_2)](\text{ClO}_4)_3$  and L- ascorbic acid ( $\text{H}_2\text{A}$ ) under varying pH, temperature and concentrations of ascorbic acid showed a first order dependence with  $[\text{H}_2\text{A}]$ . The overall stoichiometry was found to be 1:1. Under the experimental pH (3.3 – 5.0),  $\text{HA}^-$  was the predominant species which oxidised at a much faster rate than  $\text{H}_2\text{A}$  while  $\text{A}^{2-}$  was not reactive at  $\text{pH} < 5$ . The reaction rate was dependent on the nature of ligand bound to Co(III) centre. As there was no evidence of coordination of ascorbic acid with Co(III) complex, an outer sphere electron transfer mechanism was suggested.

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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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