Research Article

Catalytic Effect on the Electron Transfer Reactions of L-ascorbic acid with Co(III) Complex in Aqueous Acid Medium

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Abstract

The reduction Co(III) in presence of Cu(II) revealed a pseudo-first order rate behaviour. Copper (II) accelerates the rate of electron transfer between L- ascorbic acid and cobalt (III) complex which explains the catalytic effect of Cu (II). k_{obs} values depends linearly on the copper ion concentration. The kinetics of the electron transfer reaction of L-ascorbic acid with Cobalt (III) complex has been studied spectrophotometricaly over the range $0.01 \leq$ [Ascorbic acid]≤ 0.07 mol dm^{-3}, $3.3 \leq pH \leq 5$, and at 298 K $\leq$ T $\leq$318K in aqueous 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 reduction of Co(III) complex by L- ascorbic acid depends on pH and the nature of the ligand.

Keywords: Redox reaction, L-ascorbic acid, Cobalt (III) complex, Catalyst, Spectrophotometer
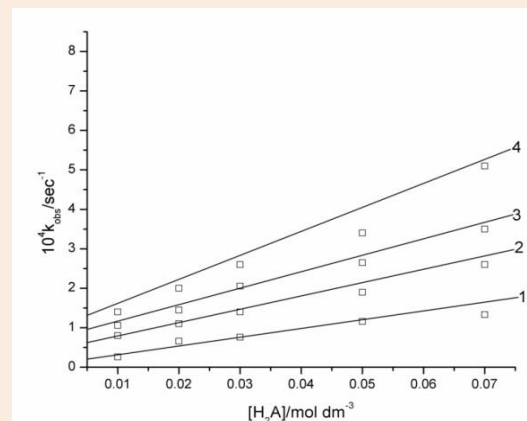
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Introduction

L-ascorbic acid (Vitamin C) is a naturally occurring organic compound with antioxidant properties. It is biosynthesised by all plants [1], algae, many vertebrates, and by few bacteria from sugar such as D-Sorbitol[2], D-Fructose and D-glucose[3]. The most important function of L-ascorbic acid is in enhancing the response of body's immune system and pulmonary function [4]. High dose of ascorbic acid [5] acts as preventive against common cold, cancer, heart disease, hypertension, AIDS etc [6]. Apart from L-ascorbic acid itself, the application of its metal complex in biology and medicine is the subject of many investigations[7, 8]. The interest in the use of metal ascorbates is mainly 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. Metal ascorbate may be considered as biometric model for enzymatic process as chromium ascorbate complex is used as a model for insulin stimulator. The present study involves interaction of Co(III) complex with L- ascorbic acid which serve as a synthetic model for biological systems.

Experimental

Materials and Methods

The complex, bis (ethylene diamine) (1-amino-propane-2-ol) cobalt (III) perchlorate was synthesised as described in the reported method [9] and characterised by elemental analysis and spectroscopic methods. Analar grade L-ascorbic acid (BDH) was used as reductant and analar grade copper sulphate (BDH) was used as catalyst. Ionic strength was

maintained at I = 0.5mol dm^{-3} using freshly prepared NaClO$_4$ (Merck). Solutions of different concentrations were prepared by proper dilution of stock solutions. Fresh solutions were prepared by using double distilled water in all quartz distillation apparatus containing KMnO$_4$ solution. The pH measurements were made using a pre-standardised Elico (India) digital pH meter equipped with glass electrode.

Kinetic Measurement

The kinetics of the reaction between cobalt complex and L-ascorbic acid was studied under pseudo-first order condition by measuring the change of absorbance in CECIL7200 (UK) UV- Visible Spectrophotometer equipped with CE 2024 thermostatic bath for temperature control with an accuracy of ±0.1^{0}C. L-ascorbic acid was varied from 0.01 to 0.07 mol dm^{-3} cobalt complex varied from 2x10^{-3} to 5x10^{-3} mol dm^{-3}, temperature range 298≤T/K≤318, 3.3≤pH≤5.0 at I=0.5 mol dm^{-3}. Progress of the electron transfer reaction was monitored by following the decrease in absorbance at 490 nm (figure 1) with time using a conventional mixing technique.

[L-ascorbic acid] was varied from 0.01 to 0.07 mol dm^{-3}, [cobalt complex] varied from 2x10^{-3} to 5x10^{-3} mol dm^{-3} , temperature range 298 ≤T /K ≤ 318 , 3.3 ≤pH ≤ 5 .0 at I = 0.5 mol dm^{-3}. The pseudo first order rate constants (k$_{obs}$) were calculated from the slope of the plot of ln(A$_t$ -A$_\infty$) versus t(s) from the relationship in equation(1)

$$\ln\left(A_t - A_\infty\right) = \ln\left(A_0 - A_\infty\right) - k_{obs}.t$$
                                                                      (1)

Where, A$_0$, A$_t$, A$_\infty$ denote absorbance of the reaction mixture at zero time, time t and infinite time respectively. A$_\infty$ was measured after the completion of the reaction. The reported rate constant data represents an average of duplicate runs which were reproducible to within ±3%. The correlation coefficients (R^2)of the plots used to determine k$_{obs}$ was found to be 0.99 in most of the cases. All calculations were made on a personal computer using linear least square program.
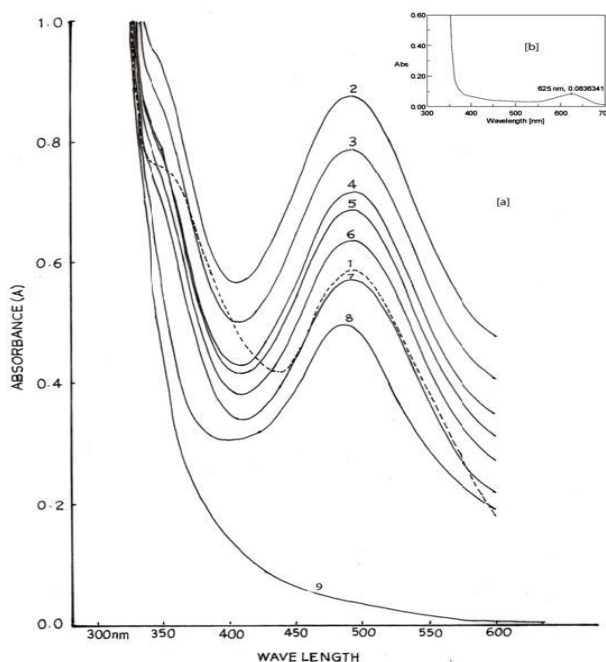
Figure 1 [a] UV-VIS Spectral scan for oxidation of ascorbic acid by co(III) complex
1. spectra of co(III) complex
2. spectra just after mixing ascorbic acid and co(III)complex curves (3-8), Δt = 10mins
9. spectra of the reaction mixture after 24 hrs
[b] Inset: Spectra of the above reaction mixture after 24 hours by Kitson method

Stoichiometry and Identification of Product

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} were allowed to react till the completion of the reaction. The unreacted ascorbic acid was then determined iodimetrically using starch indicator [10]. The iodine solution was standardised against sodium thiosulphate solution which was standardised using potassium iodate [11]. The oxidation product of the L- ascorbic acid was identified to be Cobalt(II) and dehydroascorbic acid. Dehydroascorbic acid was identified by Roe's [12] method after separating the metal ion through cation exchange resin. The overall stoichiometry was 1:1 in equation [2]

$$2Co^{III}L + H_2A = 2Co^{II}L + \text{Dehydroascoroic acid} + 2H^+ \tag{2}$$
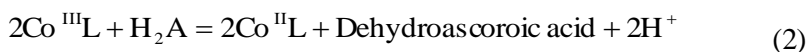
Co^{II} L was the final product of the reaction which was confirmed by Kitson method [13]. IR Spectra Figure 3 of the products shows the presence of two OH groups due to   broad peaks at 3618 cm^{-1} and 3300cm^{-1} is due two hydrogen bonded OH groups. There are four OH groups in figure 2 corresponding to peaks at 3217 cm^{-1} ,3316 cm^{-1},3410.5 cm^{-1},3527cm^{-1}.In figure 3 two peaks at 1479cm^{-1} ,1454cm^{-1} corresponds to C-O stretching and 1754 cm^{-1} due to C=O stretching frequency.2995cm^{-1},2968cm^{-1},2904cm^{-1}corresponds to C-H stretching in CH$_2$ methine. 1365cm^{-1}, and1449cm^{-1} corresponds to corresponds to C-H bending.1074cm^{-1} is due to C-O stretching in CH$_2$OH(primary alcohol)All these peaks [14,15] correspond to dehydro ascorbic acid.
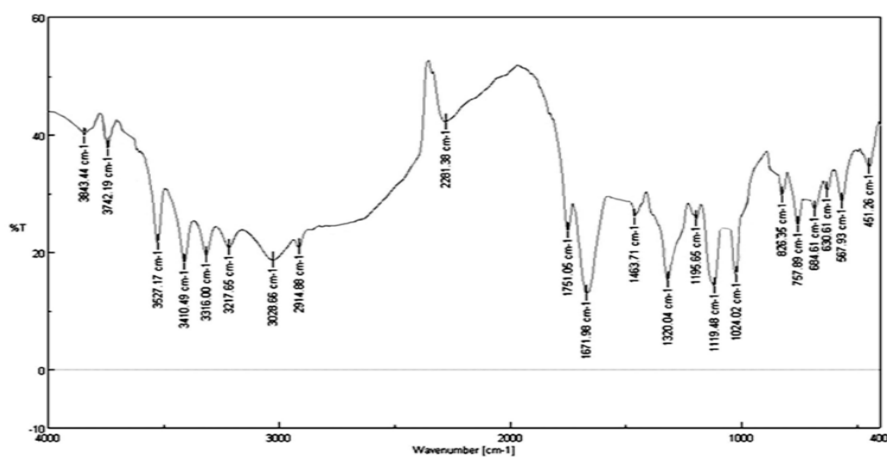

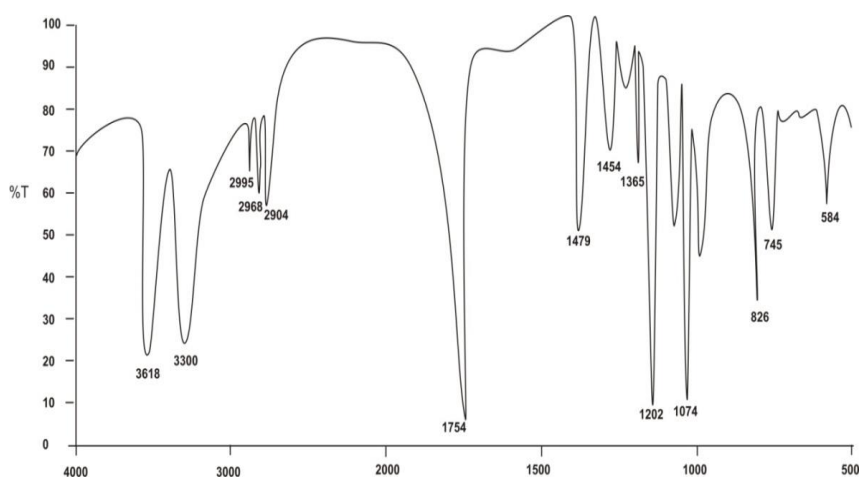**Figure 2** IR Spectra of Ascorbic Acid

Figure 3 IR Spectra of the product, Dehydroascorbic Acid

Results and Discussion

The UV-Vis spectral scan (Figure 1) of the reaction mixture of L-ascorbic acid and Co(III) complex displayed a steady decrease of absorbance with time over the range : $330 \leq \lambda(nm) \leq 600$. The absorption maxima around 490 nm completely vanished after a long interval of time (24hr) Figure 1(b) indicates complete reduction Cobalt(III) by ascorbic acid. The absence of isobestic point indicates that no stable intermediate could build up in the presence of L-ascorbic acid. 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 ligand at the same pH, which indicates that $Co^{III}L$ was reduced to $Co^{II}L$ by ascorbic acid. It was further confirmed by testing the aged solution by Kitson method. According to Kitson method 2 cm^3 of the aged reaction mixture   and 1 cm^3 of NH_4CNS were mixed followed by addition of 5 cm^3 of acetone which developed a deep blue solution. The absorption spectra of the solution showed a peak at 625 nm (Figure 1b) which is similar to the spectra of $Co(ClO_4)_2$ under identical conditions. The percentage of Co(II) was estimated by comparing calibrated curve with standard $Co(ClO_4)_2$ under identical conditions as 98%. The rate constants(k_{obs}) of above redox reaction are listed in Table 1 . Plots of k_{obs} versus L-ascorbic acid were linear with finite positive intercepts (Figure 4) in temperature range 298K- 318K indicating   first order dependence of rate with respect to $[H_2A]$. The pseudo-first order rate constants (k_{obs}) were not affected by varying $[Co(III)]$ complex in the range $2x10^{-3}$ - $5x10^{-3}$ mol dm^{-3} at pH = 3.3. In order to know what type of species are involved in the rate determining step, the reaction was investigated   by changing the ionic strength of the medium in the range 0.1 to o.5 mol dm^{-3} keeping [$Co^{III}L$] = 2 X 10^{-3} mol dm^{-3}, $[H_2A]$ = 4 X 10^{-2} mol dm^{-3},pH = 3.3 at 298K, k_{obs} did not change appreciably. This is consistent with the Coulombic concept as the reacting species are either uncharged   ($Co^{III}L/H_2A$) or one of them bears a negative Charge (HA^-) thus supporting the proposed **Scheme I**.

Table 1 Pseudo-first order rate constants for redox reaction of Co (III) Complex by L-ascorbic acid [Co-complex] = 2.31×10^{-3} mol dm^{-3}, I = 0.5mol dm^{-3}

[H$_2$A] Moldm^{-3}	pH	$10^4k_{obs}[s^{-1}]$				
		298K	303K	308K	313K	318K
0.01	3.3	0.260	0.800	1.056	1.400	1.879
	4.0	0.700	1.000	1.251	1.600	2.095
	5.0	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	0.850	1.300	1.653	2.170	2.958
	5.0	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	0.900	1.500	2.100	2.700	3.880
	5.0	1.250	1.950	2.487	3.300	4.541
0.05	3.3	1.160	1.900	2.650	3.400	4.837
	4.0	1.350	2.170	2.823	3.800	5.365
	5.0	1.450	2.620	3.469	4.900	7.353
0.07	3.3	1.330	2.600	3.496	5.100	7.993
	4.0	1.600	2.700	3.797	5.500	8.212
	5.0	1.820	3.400	4.551	6.500	9.973
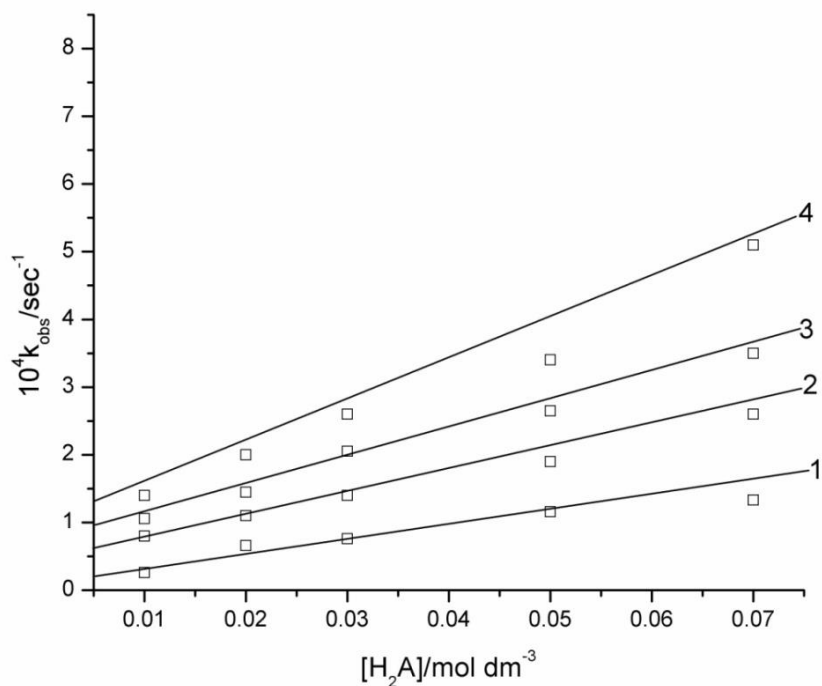
Figure 4 k_{obs} *versus* [H_2A] / mol dm^{-3} 298K [1] 303K [2] 308K [3] 313K [4] [Co-complex] = 2.31×10^{-3} moldm^{-3}, I = 0.5mol dm^{-3}, pH = 3.3

Figure 5 k_{obs} *versus* [Cu^{2+}] / mol dm^{-3} 298K [1] 303K [2] 308K [3] 313K [4] 318K [5] I = 0.5 mol dm^{-3}, [Co-complex] = 2.31×10^{-3} moldm^{-3}, pH = 4.0

The participation of free radicals was examined by adding a known quantity of Acrylonitrile to the reaction mixture and was kept for 2 hrs 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 supporting the proposed reaction scheme I.

Table 2 Second order rate constants k_1, k_2 and their activation parameters (without catalyst)

Parameters	Temperature				
	298 K	303 K	308 K	313 K	318 K
$10^3 k_1\ dm^3\ mol^{-1}s^{-1}$	2.600	4.400	6.200	8.600	12.600
$10^3 k_2\ dm^3\ mol^{-1}s^{-1}$	4.587	5.882	8.497	11.111	16.149
$\Delta H^{\ddagger}[kJ\ mol^{-1}]\ (k_1)$	56.0±2.0				
$\Delta S^{\ddagger}[JK^{-1}mol^{-1}]\ (k_1)$	-105.28±6.4				
$\Delta H^{\ddagger}[kJ\ mol^{-1}]\ (k_2)$	49.30±2.41				
$\Delta S^{\ddagger}[JK^{-1}mol^{-1}]\ (k_2)$	-124.9±7.71				

Table 3 Pseudo-first order rate constants for the redox reaction of Cobalt(III) complex by L-ascorbic acid in presence of copper I = 0.5 mol dm^{-3}, [Co-complex] =2.31× 10^{-3} moldm^{-3}, pH = 4.0

[CuSO$_4$] mol dm^{-3}	$10^4 k_{obs}[s^{-1}]$				
	298K	303K	308K	313K	318K
0.0002	1.805	2.500	3.500	4.830	6.000
0.0004	2.083	2.800	3.850	5.000	6.500
0.0005	2.280	3.000	4.000	5.200	6.500
0.0007	2.446	3.200	4.250	5.400	6.975
0.0008	2.633	3.400	4.450	5.600	7.153
0.0009	2.816	3.600	4.650	5.800	7.315
0.001	2.832	3.700	4.850	6.200	7.700
0.0015	3.409	4.400	5.820	7.300	9.352

Table 4 Second order rate constants k_1, k_2 and their activation parameters in presence of catalyst CuSO$_4$

Parameter	Temp (K)				
	298	303	308	313	318
$10^3 k_2\ dm^3\ mol^{-1}s^{-1}$	7.320	9.395	12.214	15.436	20.710
$\Delta H^{\ddagger}[kJ\ mol^{-1}]\ (k_2)$	39.10±1.39				
$\Delta S^{\ddagger}[JK^{-1}mol^{-1}]\ (k_2)$	-154.80±4.40				

Mechanism of the Reaction

Basing on the above observations and identifications of product, the probable mechanism may be delineated as in the scheme-I

$$H_2A \xrightleftharpoons{k} HA^- + H+ \tag{3}$$

$$Co(III) + H_2A \xrightarrow{k_1} Co(II) + DHA \tag{4}$$

$$Co(III) + HA \xrightarrow{k_2} Co(II) + DHA \tag{5}$$

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

$$
\begin{aligned}
Rate &= k_1[Co(III)][H_2A] + k_2[Co(III)][HA^-] \\
&= [Co(III)]\{k_1[H_2A] + k_2[HA^-]\} \\
&= [Co(III)]\left\{k_1[H_2A] + k_2\frac{k_1[H_2A]_e}{[H^+]}\right\} \\
&= [Co(III)][H_2A]_e\left\{\frac{k_1[H^+] + k_2Ka_1}{[H^+]}\right\}
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
[H_2A]_T &= [H_2A]_e + [HA^-]_e \\
&= [H_2A]_e + K_1\frac{[H_2A]_e}{[H^+]} \\
&= [H_2A]_e\left[\frac{[H^+] + K_1}{[H^+]}\right] \\
[H_2A]_e &= \frac{[H_2A]_T[H^+]}{[H^+] + K_1}
\end{aligned}
\tag{7}
$$

$$
\begin{aligned}
Rate &= [Co(III)][H_2A]_e\left[\frac{k_1[H^+] + k_2k_1}{[H^+]}\right] \\
&= [Co(III)]\frac{[H_2A]_T[H^+]}{[H^+] + K_1}\left[\frac{k_1[H^+] + k_2k_1}{[H^+]}\right] \\
&= [Co(III)][H_2A]_T\left[\frac{k_1[H^+] + k_2k_1}{[H^+ + K_1]}\right]
\end{aligned}
\tag{8}
$$

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

$$k_{obs} = [\text{H}_2\text{A}]_T \left[\frac{k_1[\text{H}^+] + k_2 k_1}{[\text{H}^+] + K_1} \right] \tag{9}$$

$$\frac{k_{obs}}{[\text{H}_2\text{A}]_T} = k_2 = \frac{k_1[\text{H}^+] + k_2 K_1}{[\text{H}^+] + K_1}$$

$$k_2[\text{H}^+] + K_1 = K_1[\text{H}^+] + k_2 K_1$$

L.H.S. expression is plotted against $[\text{H}^+]$ using reported value of K. From the slope and intercept k_1 and k_2 are calculated. The rate k_2 is faster than k_1 .These electron transfer rate constants and their activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated using Eyring equation and listed in **Table 3**. Lower values of activation parameters favour the electron transfer process. The negative values of activation entropy indicate an order transition state for the electron transfer reaction.

Mechanism of the reaction in presence of Copper

The reduction Co(III) in presence of Cu(II) also revealed a pseudo-first order rate behaviour copper (II) accelerates the rate of electron transfer between L- ascorbic acid and cobalt (III) complex which explains the catalytic effect of Cu (II). It can be also noted that at pH lower than 5.0 where H_2A and HA^- species are presents, the reaction is slower even in the presence of Cu(II), k_{obs} values depends linearly on the copper ion concentration(Fig. 5).

The mechanism can be described by the sequence of reactions in scheme II where the electron transfer reactions involving Cu(II) is much faster then the reaction of cobalt(III) with ascorbic acid.

$$\text{H}_2\text{A} + \text{Cu}^{2+} \rightleftharpoons \text{CuHA}^- + \text{H}^+ \tag{10}$$

$$\text{Co(III)} + \text{H}_2\text{A} \rightarrow \text{Co(II)} + \text{DHA} \tag{11}$$

$$\text{CuHA}^- + \text{Co(III)} \rightarrow \text{Co(II)} + \text{DHA} + \text{Cu}^{2+} \tag{12}$$
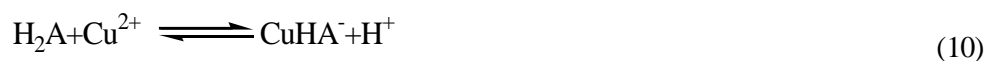
Scheme-II

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

$$\begin{aligned}
\text{Rate} &= k_1[\text{Co(III)}][\text{H}_2\text{A}]_e + k_2[\text{CuHA}^-][\text{Co(III)}] \\
&= \text{Co(III)}\big[k_1[\text{H}_2\text{A}]_e + k_2[\text{CuHA}^-]\big] \\
&= \text{Co(III)}k_1[\text{H}_2\text{A}]_e + k_2 K[\text{H}_2\text{A}]_e \frac{\text{Cu}^{2+}}{[\text{H}^+]} \\
&= [\text{Co(III)}][\text{H}_2\text{A}]_e \left\{ \frac{k_1[\text{H}^+] + k_2 K[\text{Cu}^{2+}]}{[\text{H}^+]} \right\}
\end{aligned} \tag{13}$$

$$\begin{aligned}
[\text{H}_2\text{A}]_T &= [\text{H}_2\text{A}]_e + [\text{CuHA}]_e \\
&= [\text{H}_2\text{A}]_e + K \frac{[\text{H}_2\text{A}]_e[\text{Cu}^{2+}]}{[\text{H}^+]} \\
&= [\text{H}_2\text{A}]_e \left[\frac{[\text{H}^+] + K[\text{Cu}^{2+}]}{[\text{H}^+]} \right]
\end{aligned} \tag{14}$$

$$[H_2A]_e = \frac{[H_2A]_T[H^+]}{[H^+] + K[Cu^{2+}]}$$

$$\begin{aligned}
Rate &= [H_2A]_e\left[\frac{k_1[H^+] + k_2\,K[Cu^{2+}]}{[H^+]}\right] \\
&= \frac{[H_2A]_T[H^+]}{[H^+] + K[Cu^{2+}]}\left[\frac{k_1[H^+] + k_2K[Cu^{2+}]}{[H^+]}\right]
\end{aligned}$$

(15)

$$\frac{k_{obs}}{[H_2A]_T}\big[[H^+] + K[Cu^{2+}]\big] = [H^+]\frac{k_1[H^+] + k_2K[Cu^{2+}]}{[H^+]}$$

$$k_2^*\{[H^+] + K[Cu^{2+}]\} = k_1[H^+] + k_2\,K[Cu^{2+}]$$

Left hand side expression was plotted against $[Cu^{2+}]$, a straight line was obtained with intercepts $k_1[H^+]$ and slope $= k_2\,K$ from which k_1 and k_2 were calculated using the known value of K. The value of k_2 was calculated in the temperate range of 298K―318K. From these values activation parameters were calculated by using Eyring's equation and listed in **Table 4**. The activation parameters for the electron transfer rate constant k_2 without catalyst were $\Delta H^{\neq} = 49.30 \pm 2.41$, $\Delta S^{\neq} = -124.90 \pm 7.70$ JK^{-1} mol^{-1} where as the activation parameters for the same reaction in presence of Copper were $\Delta H^{\neq} = 39.10 \pm 1.39$, $\Delta S^{\neq} = -154.80 \pm 4.40$ JK^{-1} mol^{-1} (Table-3 and 4). The difference in activation parameters for the catalysed and uncatalysed reaction explains the catalytic effect of Cu^{2+} ion on the electron transfer reaction. The catalyst cu^{2+} alters the path of reaction and produces a new path with lowering the energy barrier by lowering the activation parameters. During the experiment a red precipitate of Cu_2O was visible after 1 hr of ascorbic acid oxidation .There is no strict parallel between amount of ascorbic acid oxidised and Cu_2O formed. The amount of Cu_2O produced was too small to be determined as very low concentration of Copper ion is used.

Conclusion

The electron transfer reaction involving Copper(II) is much faster than the reaction of Cobalt(III) with ascorbic acid. The reduction of Co(III) complex by L- ascorbic acid depends on pH .Considering the dependence of k_{obs} with pH , it was suggested that HA$^-$ reacts much faster than A$^-$ and A^{2-} is not reactive at pH <5. So HA$^-$ is the predominant species in solution. As there is no direct coordination of ascorbic acid and Co(III) complex outer sphere electron transfer mechanism is suggested .

Acknowledgement

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