



Oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium-A kinetic and mechanistic study

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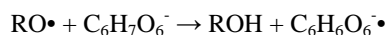
ABSTRACT

The oxidation of ascorbic acid (H_2A) by hexacyanoferrate(III)(HCF) in aqueous perchloric acid medium at a constant ionic strength of (0.6 mol dm^{-3}) was studied spectrophotometrically at 25°C . Reactions were initiated by mixing previously thermostated solutions of hexacyanoferrate(III) and ascorbic acid which also contained the required amounts of perchloric acid and sodium perchlorate. The kinetics were followed under pseudo first order conditions with ascorbic acid in excess. The reaction between hexacyanoferrate(III) and ascorbic acid in acidic medium exhibits 2:1 stoichiometry. The reaction products were identified and isolated using TLC separation techniques and characterized by IR, and GCMS spectral studies. The reaction is first order with respect to hexacyanoferrate(III) and ascorbic acid concentrations. The order with respect to acid concentration is less than unity. The effect of ionic strength and dielectric constants are also studied on the rate of reaction. A suitable mechanism is proposed based on the experimental results. The reaction constants involved in the different steps of the reaction mechanism are calculated. The activation parameters with respect to limiting step of the mechanism are computed and discussed.

Keywords: Ascorbic acid(H_2A), Hexacyanoferrate(III), Kinetics, Oxidation, Mechanism

INTRODUCTION

Ascorbic acid(H_2A) is easily oxidized and so is used as a reductant [1]. Ascorbic acid is a white naturally occurring solid organic compound with antioxidant properties. It dissolves well in water to give mildly acidic solution. It can be oxidized by one electron to a radical state or doubly oxidized to the stable form called dehydroascorbic acid. Ascorbic acid is special because it can transfer a single electron, owing to the stability of its own radical ion called "semidehydroascorbate", dehydroascorbate. The net reaction is;



However, being a good electron donor, excess ascorbate in the presence of free metal ions cannot only promote, but also initiate free radical reactions. The most important iron(III) cyanide complex is the hexacyanoferrate(III) anion, $[Fe(CN)_6]^{3-}$, a mild oxidant with the Fe^{3+} center bound in octahedral geometry to six cyanide ligands. Hexacyanoferrate(III) is a relatively poor oxidant, but a selective outer sphere reactant, applicable to the most easily oxidisable substrates and couple one of the most extensively investigated outer-sphere redox reactions. Studies involving hexacyanoferrate(III) as an oxidant in acid media are limited [2-4] by the fact that reduction potential of

the couple is small ($[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}] : 0.356\text{V}$)[5]. However, hexacyanoferrate(III) is very sensitive to the solvent and acidity. Hexacyanoferrate(III) forms different species in acidic media [6-8]. The mechanism may be quite interesting due to the formation of different intermediates of hexacyanoferrate(III). Hence, in the present study, we have investigated the kinetics and mechanism of oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium in order to understand the behavior of the active species of hexacyanoferrate(III) and to propose a suitable mechanism based on experimental results.

EXPERIMENTAL SECTION

Materials and Methods

Reagent grade chemicals and double distilled water were used throughout the work. The stock solution of the oxidant, hexacyanoferrate(III), was prepared by dissolving potassium hexacyanoferrate(III) (SISCO-CHEM) in water and the concentration was ascertained by iodometric titration [9a]. A stock solution of ascorbic acid was prepared by dissolving ascorbic acid (s.d.fine chem.) in distilled water. Perchloric acid (RANKEM) was used as the source of H^+ to vary the acid concentrations in the reaction media. The sodium perchlorate was used to maintain the ionic strength. Hexacyanoferrate(II) solution was obtained by dissolving potassium hexacyanoferrate(II) (s. d. fine-chem) in water and standardizing with cerium(IV) solution. [9b].

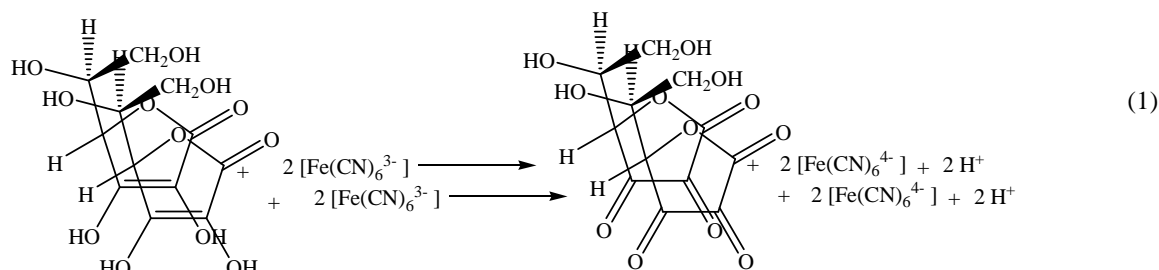
Kinetic studies

Kinetic measurements were carried out at $25 \pm 0.1^\circ\text{C}$ and at $I = 0.60 \text{ mol dm}^{-3}$. Reactions were initiated by mixing previously thermostated solutions of hexacyanoferrate(III) and ascorbic acid which also contained the required amounts of perchloric acid and sodium perchlorate. The kinetics were followed under pseudo-first order conditions with ascorbic acid in excess. Progress of the reaction was followed by measuring the absorbance of hexacyanoferrate(III) in the reaction mixture at 420 nm in a 1 cm cell placed in the thermostated compartment of a Varian Cary 50 Bio UV-Vis spectrometer. At this wave length, all other materials concerned have negligible absorbance. Application of Beer's law under the reaction conditions had been verified between 1.0×10^{-4} and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ of hexacyanoferrate(III) and ϵ was found to be $1485 \pm 25 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Fig. 1). The kinetics were followed more than 80% completion of the reaction. The first order rate constants, k_{obs} were obtained from the plot of $\log [\text{hexacyanoferrate(III)}]$ versus time. The first order plots were linear over 75% completion of the reaction (Fig. 2). The first order rate constants were reproducible within $\pm 5\%$ and the average of at least three independent kinetic runs (Table 1).

RESULTS AND DISCUSSION

Stoichiometry and product analysis

Five different sets of reaction mixtures containing excess of hexacyanoferrate(III) to ascorbic acid in presence of constant concentration of acid (0.50 mol dm^{-3}) and at constant ionic strength $I = 0.6 \text{ mol dm}^{-3}$ were kept for 8 h at 25°C in a closed container. After 5 hours, the oxidant, hexacyanoferrate(III) was analysed by measuring its absorbance at 420 nm. The product hexacyanoferrate(II) was determined with cerium(IV) solution [9b]. The stoichiometry was found to be 2:1 i.e. two moles of hexacyanoferrate(III) reacted with one mole of ascorbic acid [H_2A] as shown in Eq.(1)



After completion of the reaction, the reaction mixture was basified, concentrated and extracted with ether. The oxidation products were isolated using TLC separation techniques and characterized by physicochemical spectral studies. The reaction products were identified as hexacyanoferrate(II) and dehydroascorbic acid. The product dehydroascorbic acid was confirmed by GC-MS analysis. GC-MS data was obtained on a Shimadzu 17A gas

chromatograph with a Shimadzu QP-5050A mass spectrophotometer using EI ionization technique and the mass spectrum of product showed a molecular ion peak at 174 amu and base peak at 57 amu (Fig. 3.).

Reaction orders

The orders with respect to each of oxidant, reductant and acid were determined by the slopes of $\log k_{\text{obs}}$ versus \log (concentration) plots. The orders were obtained by varying the concentrations of oxidant, reductant and acid in turn while keeping all other concentrations and conditions constant.

Effect of [hexacyanoferrate(III)]

At constant concentration of ascorbic acid $[\text{H}_2\text{A}]$, $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, 0.50 mol dm^{-3} perchloric acid, and at constant ionic strength, 0.60 mol dm^{-3} , the hexacyanoferrate(III) concentration was varied in the range of 5.0×10^{-5} to $5.0 \times 10^{-4} \text{ mol dm}^{-3}$. The observed rate constants, k_{obs} , remain almost constant (Table 1), indicating the first order with respect to hexacyanoferrate(III) concentration. This was confirmed by the pseudo-first order rate constants which are constant at different hexacyanoferrate(III) concentrations. The pseudo-first order plots under these conditions were linear over 75% completion of the reaction at different initial concentrations of hexacyanoferrate(III) (Fig. 2) also confirming the unit order with respect to hexacyanoferrate(III) concentration.

Effect of [ascorbic acid]

The effect of ascorbic acid $[\text{H}_2\text{A}]$ concentration was varied in the range of 5.0×10^{-4} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ keeping all other conditions constant at 25°C . The k_{obs} values increased with increase in the concentration of ascorbic acid. From the slope of the plot of $\log k_{\text{obs}}$ versus $\log [\text{H}_2\text{A}]$ (Fig. 4), the order with respect to ascorbic acid concentration was found to be unity (0.98).

Effect of $[\text{HClO}_4]$

Increasing the perchloric acid concentration accelerates the rate of reaction at constant ionic strength and at other conditions constant (Table 1). The order with respect to acid ion concentration, from $\log - \log$ plot of k_{obs} versus $\log(\text{concentration})$ (Fig. 4), was found to be less than unity (0.31) in the concentration range of 0.1 to 1.0 mol dm^{-3} . Hexacyanoferrate(III) forms different protonated species in acid media as shown in equilibria (2) – (4) with the stability constants $\beta_1 (=K_1)$, $\beta_2 (=K_1K_2)$ and $\beta_3 (=K_1K_2K_3)$ belonging to the species with one, two and three protons respectively[10].



The reported equilibrium constants of the different species are $K_3 < K_2 < K_1 < 10$, the value of K_1 being nearly 10 the media under present study. While the singly protonated species is expected to form extensively in the high acid media used herein, the doubly and triply protonated species form to a lesser extent.

Effect of added product

The effect of initially added product, hexacyanoferrate(II) was studied in the 5.0×10^{-5} - $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ concentration range, keeping the ionic strength, reactant concentrations and other conditions constant. It was found that hexacyanoferrate(II) did not have any significant effect on the rate of reaction.

Effect of ionic strength and dielectric constant

At constant concentrations of reactants and with other conditions constant, the ionic strength was varied between 0.60 to 2.5 mol dm^{-3} by varying the concentrations of sodium perchlorate, and the rate was found to increase with

increasing ionic strength (Table 2). A plot of $\log k_{\text{obs}}$ versus \sqrt{I} is linear with positive slope (Fig. 5). The effect of dielectric constant (D) was studied by varying the acetic acid – water (v/v) content from 0 to 50% in the reaction mixture with all other conditions being maintained constant. Since the dielectric constants of aqueous acetic acid are not available in the literature, they were computed from the values of pure liquids [11]. It was found that as the acetic acid content of the medium increased, the rate of the reaction did not change appreciably (Table 2). No reaction of the solvent with the oxidant is occurred under the experimental conditions employed.

Test for free radicals (Polymerization study)

The intervention of free radicals was examined as follows: The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 2 hours at room temperature. When the reaction mixture was diluted with methanol, precipitate resulted, suggesting that there is participation of free radicals in the reaction.

Effect of temperature

The rate of reaction was measured at temperatures, 15, 25, 35 and 45 °C, under varying acid and ascorbic acid concentrations. The rate was found to increase with increasing temperature. The rate constants of the slow step of the Scheme 1 were obtained from the intercepts and slopes of the plots of $[H_2A]/k_{\text{obs}}$ versus $1/[H^+]$ (Table 3) and the values of k and K_1 as $1.55 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $13.8 \pm 0.4 \text{ dm}^3 \text{ mol}^{-1}$ respectively at 25 °C. The energy of activation was calculated from the slope of the plot of $\log k$ vs $1/T$ and the value is $24 \pm 2 \text{ kJ mol}^{-1}$. The enthalpy of activation, ΔH^\ddagger and entropy of activation, ΔS^\ddagger , were obtained by Eyring equation [12, 13].

$$k = \frac{k_B T}{h} e^{(-\Delta G^\ddagger/RT)} = \frac{k_B T}{h} e^{-(\Delta H^\ddagger + T\Delta S^\ddagger)/RT} \quad (5)$$

k is the second-order rate constant, k_B is the Boltzmann's constant, R is the gas constant, T is the absolute temperature and ΔG^\ddagger is the free energy of activation. The linear form of (Eq. 5) is

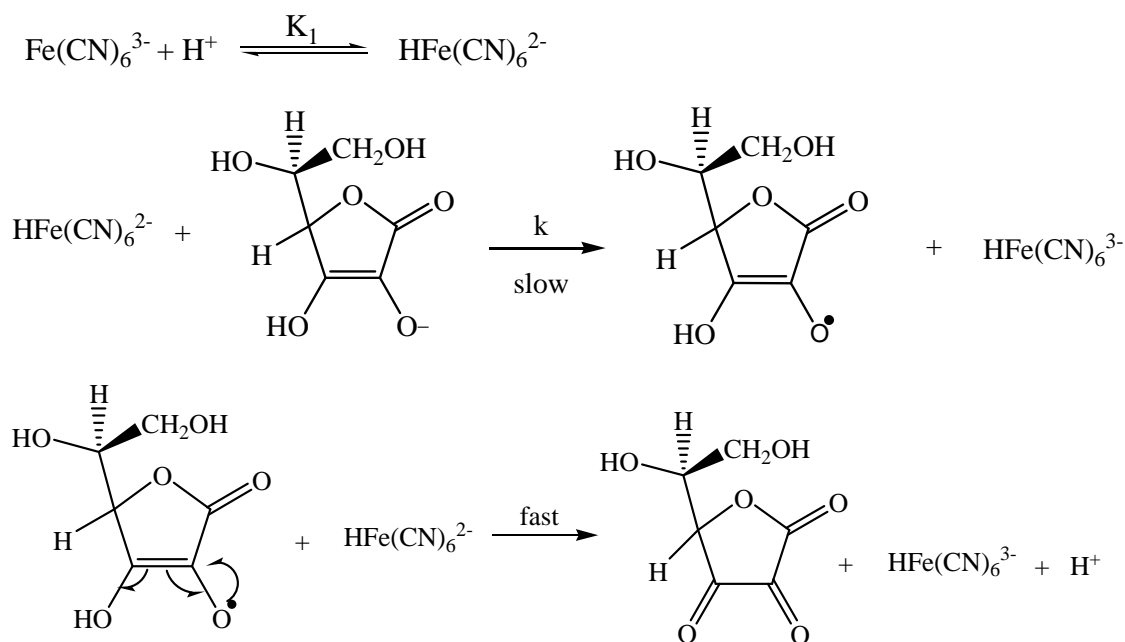
$$\ln \frac{k}{T} = - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h}$$

The slope of the plot of k/T vs $1/T$ gives the value of enthalpy of activation, ($\Delta H^\ddagger = 21 \pm 2 \text{ kJ mol}^{-1}$) (Table 3). By using this value of ΔH^\ddagger , and the rate constant at a particular temperature T , the value of ΔS^\ddagger was obtained by simple rearrangement of Eq. 5 ($\Delta S^\ddagger = -168 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$) (Table 3). Using these values of ΔH^\ddagger and ΔS^\ddagger , the obtained free energy of activation, ΔG^\ddagger_{298} , is given in Table 3.

The hexacyanoferrate(III) oxidation of ascorbic acid $[H_2A]$ occurs in a measurable quantities in presence of 0.50 mol dm^{-3} perchloric acid at 25 °C and has a stoichiometry of 2:1, i.e., two moles of hexacyanoferrate(III) requires one mole of ascorbic acid. The order with respect to hexacyanoferrate(III) and ascorbic acid concentrations were found to be unity. No effect of added products was observed. As the perchloric acid concentration increases the rate of the reaction also increases. The effect of acid on the reaction rate is to accelerate the reaction at constant reactant concentration and at constant ionic strength, this suggest the involvement of one or more protonated species [14]. The less than unit order in acid concentration is due to its involvement in the formation of different hexacyanoferrate(III) species. As discussed above, hexacyanoferrate(III) forms different protonated species in acid media [10]. Among different protonated species the active form of oxidant was found to be $HFe(CN)_6^{2-}$. In most of the oxidation reactions, hexacyanoferrate(III) resembles copper(II), which involves free radical formation and rapidly oxidizes it [15-18]. Hexacyanoferrate(III)- hexacyanoferrate(II) system, which has higher redox potential than copper(II) - copper(I) system, substantiates a better possibility for the rapid oxidation of the free radical with hexacyanoferrate(III) and the rapid oxidation of free radicals might completely mask the polymerization.

The mechanism (Scheme 1) involves the formation of the active species, $HFe(CN)_6^{2-}$, in a prior equilibrium, which reacts in a slow step with ascorbic ion to form the product, hexacyanoferrate(II) and an intermediate ascorbate free radical. The formed intermediate ascorbate free radical reacts with another mole of $HFe(CN)_6^{2-}$ species in a later

fast step to give the final product dehydroascorbate. The experimental results are accommodated in the form of following mechanism (Scheme 1).



Scheme 1

From the above mechanism the rate law (11) can be derived as follows:

$$\begin{aligned} \text{Rate} &= \frac{-d [\text{Fe(CN)}_6^{3-}]}{dt} = k [\text{Fe(CN)}_6^{3-}] [\text{HA}^-] \\ &= k K_1 [\text{Fe(CN)}_6^{3-}] [\text{HA}^-] [\text{H}^+] \end{aligned} \quad (7)$$

But, the total concentration of hexacyanoferrate(III) is given by,

$$\begin{aligned} [\text{Fe(CN)}_6^{3-}]_t &= [\text{Fe(CN)}_6^{3-}]_f + [\text{HFe(CN)}_6^{2-}] \\ &= [\text{Fe(CN)}_6^{3-}]_f + K_1 [\text{Fe(CN)}_6^{3-}] [\text{H}^+] \\ &= [\text{Fe(CN)}_6^{3-}]_f \{ 1 + K_1 [\text{H}^+] \} \end{aligned}$$

$$[\text{Fe(CN)}_6^{3-}]_f = \frac{[\text{Fe(CN)}_6^{3-}]_t}{1 + K_1 [\text{H}^+]}$$

where 't' and 'f' refers to total and free (8)

Similarly,

$$\begin{aligned} [\text{H}^+]_t &= [\text{H}^+]_f + K_1 [\text{Fe(CN)}_6^{3-}] [\text{H}^+] \\ [\text{H}^+]_t &= [\text{H}^+]_f \{ 1 + K_1 [\text{Fe(CN)}_6^{3-}] \} \\ [\text{H}^+]_f &= \frac{[\text{H}^+]_t}{1 + K_1 [\text{Fe(CN)}_6^{3-}]} \end{aligned} \quad (9)$$

In view of the low concentration of hexacyanoferrate(III) used in the experiment, the term $K_1[\text{Fe}(\text{CN})_6^{3-}]$ is neglected (Eq. 9) in comparison with unity.

Hence,

$$[\text{H}^+]_f = [\text{H}^+]_t \quad (10)$$

Substituting (Eq. 8) and (Eq. 10) in (Eq. 7) and omitting subscripts we obtain equation (11).

$$\text{Rate} = \frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{k K_1 [\text{Fe}(\text{CN})_6^{3-}] [\text{HA}^-] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (11)$$

Or

$$\frac{\text{Rate}}{[\text{Fe}(\text{CN})_6^{3-}]} = k_{\text{obs}} = \frac{k K_1 [\text{HA}^-] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (11)$$

The rate law (11) explains the observed orders with respect to oxidant, reductant and acid concentrations. The rate law (11) can be rearranged to (Eq. 12) which is suitable for verification.

$$\frac{[\text{HA}^-]}{k_{\text{obs}}} = \frac{1}{k K_1 [\text{H}^+]} + \frac{1}{k} \quad (12)$$

According to (Eq. 12), other conditions being constant, the plot of $[\text{HA}^-]/k_{\text{obs}}$ versus $1/[\text{H}^+]$ should be linear and are found to be so in Fig. 5. The rate constant with respect to slow step and equilibrium constant of the first step of Scheme 1 are determined by varying the ascorbic acid and HClO_4 concentrations at four different temperatures. From the slopes and intercepts, the values of K_1 and k are calculated at four different temperatures and the values are given in Table 3. For example at 25 °C, k and K_1 values are calculated as follows:

(i) The intercept of the plot of $[\text{HA}^-]/k_{\text{obs}}$ versus $1/[\text{H}^+]$ gives the value of k .

$$\text{Intercept} = \frac{1}{k}$$

$$k = \frac{1}{\text{Intercept}}$$

$$= 1.55 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = \frac{1}{0.645}$$

(ii) The slope of the plot of $[\text{HA}^-]/k_{\text{obs}}$ versus $1/[\text{H}^+]$ gives the value of K_1 .

Therefore

$$\text{Slope} = \frac{1}{k K_1}$$

$$K_1 = \frac{1}{\text{slope} \times k}$$

$$K_1 = \frac{1}{0.047 \times 1.55} = 13.80 \text{ dm}^3 \text{ mol}^{-1}$$

Using these values of $k(=1.55 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ and $K_1(=13.80 \text{ dm}^3 \text{ mol}^{-1})$, rates under different experimental conditions are calculated and are found to be in good agreement with experimental values (Table 1). Similarly the

values of k and K_1 are calculated at 15, 35 and 45°C and are given in Table 3. The van't Hoff plots are drawn for variation of K_1 with temperature ($\log K_1$ versus $1/T$) and the values of enthalpy of reaction ΔH , entropy of reaction ΔS and free energy of reaction ΔG , are calculated and the values are listed in Table 3.

The effect of ionic strength and dielectric constant on the rate qualitatively explains the reaction between two negatively charged ions as in Scheme 1. The moderate values of ΔH^\ddagger and ΔS^\ddagger were both favorable for electron transfer processes. The observed modest enthalpy of activation and relatively low entropy of activation and higher rate constant of slow step indicate that oxidation presumably occurs by an inner – sphere mechanism[19].

Table 1 Effect of variation of hexacyanoferrate(III), ascorbic acid and perchloric acid concentrations on the oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C, I = 0.6 mol dm⁻³

[Fe(CN) ₆ ³⁻] x 10 ⁴ (mol dm ⁻³)	[H ₂ A] x 10 ³ (mol dm ⁻³)	[HClO ₄] (mol dm ⁻³)	k _{obs} x 10 ³ (s ⁻¹) Exptl	k _{obs} x 10 ³ (s ⁻¹) Calc
0.5	5.0	0.5	7.75	7.76
1.0	5.0	0.5	7.70	7.76
2.0	5.0	0.5	7.78	7.76
3.0	5.0	0.5	7.79	7.76
4.0	5.0	0.5	7.70	7.76
5.0	5.0	0.5	7.73	7.76
2.0	0.5	0.5	0.45	0.68
2.0	1.0	0.5	1.24	1.35
2.0	2.0	0.5	2.67	2.70
2.0	3.0	0.5	4.20	4.05
2.0	4.0	0.5	5.76	5.40
2.0	5.0	0.5	7.78	7.76
2.0	5.0	0.1	4.88	4.49
2.0	5.0	0.3	7.02	6.98
2.0	5.0	0.5	7.78	7.76
2.0	5.0	0.7	9.03	9.00
2.0	5.0	0.9	9.54	9.61
2.0	5.0	1.0	10.0	9.97

Table 2 Effect of variation of ionic strength and dielectric constant on the oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C.

I (mol dm ⁻³)	k _{obs} × 10 ³ (s ⁻¹)	% of CH ₃ COOH (v/v)	D	k _{obs} × 10 ³ (s ⁻¹)
0.6	7.78	0	78.5	7.78
1.1	8.76	10	71.2	7.71
1.5	9.57	20	64.0	7.73
2.0	10.28	30	56.8	7.75
2.5	11.27	40	49.6	7.76
		50	42.4	7.80

Table 3 (a) Effect of temperature on the oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium.

Temperature (K)	1/T x 10 ³	k (s ⁻¹)	log k (Y)	log k (Y* _{calc.})
288	3.477	1.15	0.059	0.0542
298	3.355	1.55	0.189	0.201
308	3.247	2.22	0.347	0.338
318	3.145	2.92	0.466	0.467

(b) Activation parameters with respect to slow step of Scheme 1

Activation Parameters	Values
E_a (kJ mol ⁻¹)	24 ± 2
ΔH^\ddagger (kJ mol ⁻¹)	21 ± 2
ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	-168 ± 3
ΔG^\ddagger (kJ mol ⁻¹)	71 ± 2
log A	4.4 ± 0.4

(c) Thermodynamic quantities with respect to equilibrium step of Scheme 1

Temperature (K)	K_1 (mol dm ⁻³)	Quantities	Using K_1 values
288	16.26	ΔH (kJ mol ⁻¹)	-15 ± 2
298	13.80	ΔS (J K ⁻¹ mol ⁻¹)	-28 ± 1
308	10.64	ΔG (kJ mol ⁻¹)	-6 ± 0.3
318	9.21		

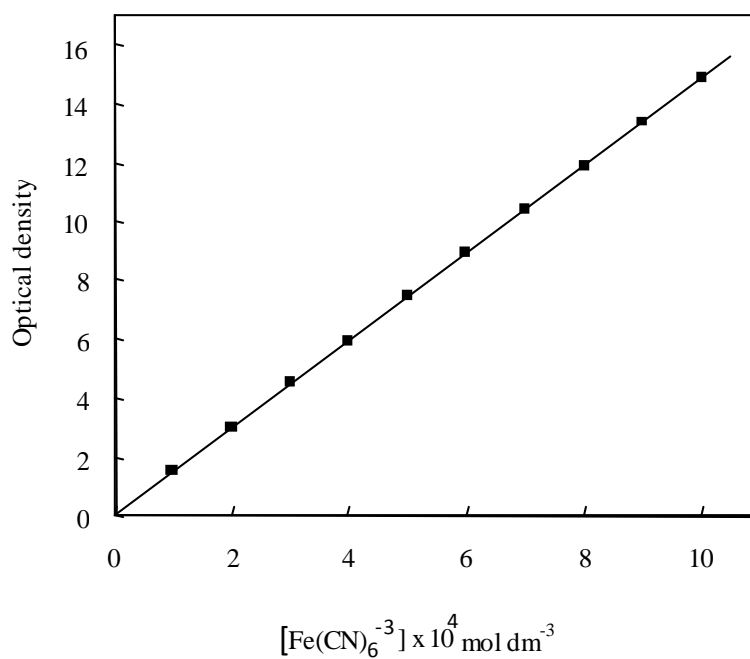


Fig: 1 Verification of Beer's law for hexacyanoferrate(III) concentrations at 420 nm in 0.50 mol dm⁻³ perchloric acid at 25 °C.

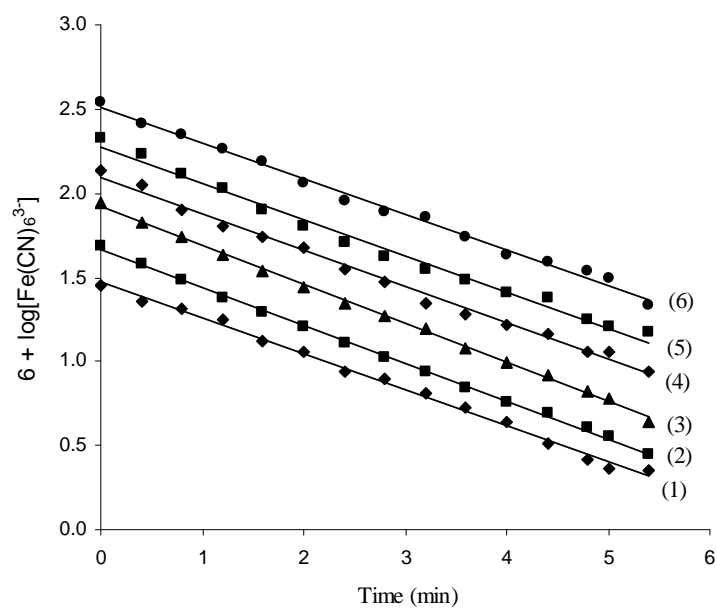


Fig: 2 First order plots of the oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium at 25°C. [Hexacyanoferrate(III)] $\times 10^{-4}$ mol dm^{-3} = 1) 0.5; 2) 1.0; 3) 2.0; 4) 3.0; 5) 4.0; 6) 5.0.

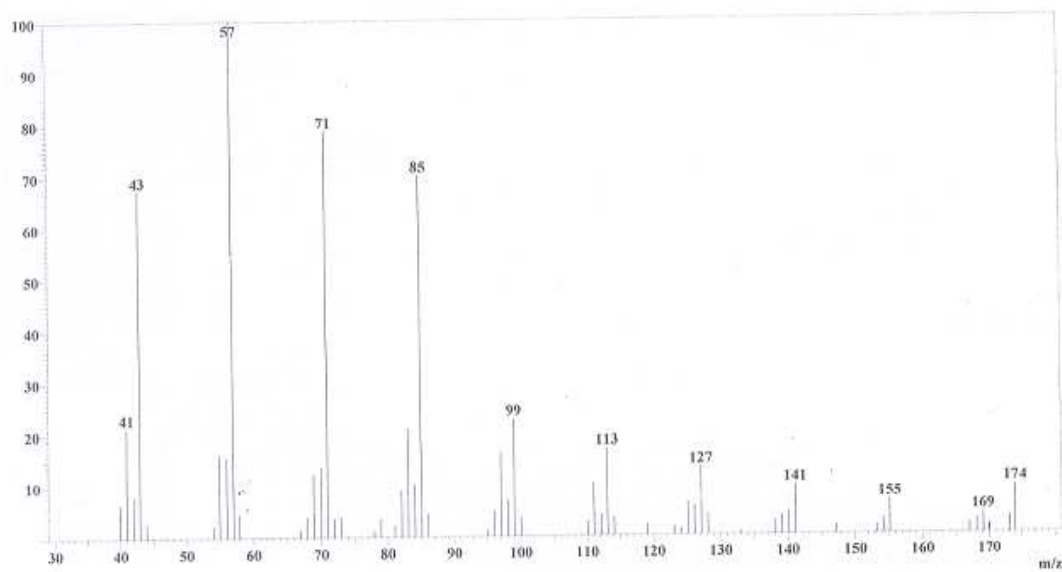


Fig: 3 GC – MS spectrum of the product dehydroascorbic acid.

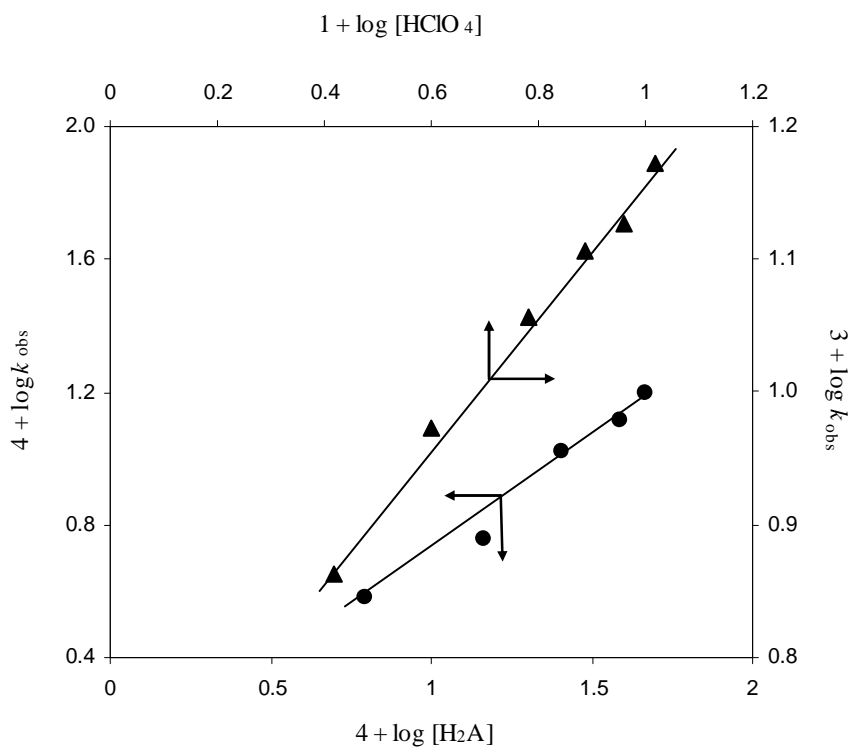


Fig: 4 Order with respect to ascorbic acid and perchloric acid concentrations.

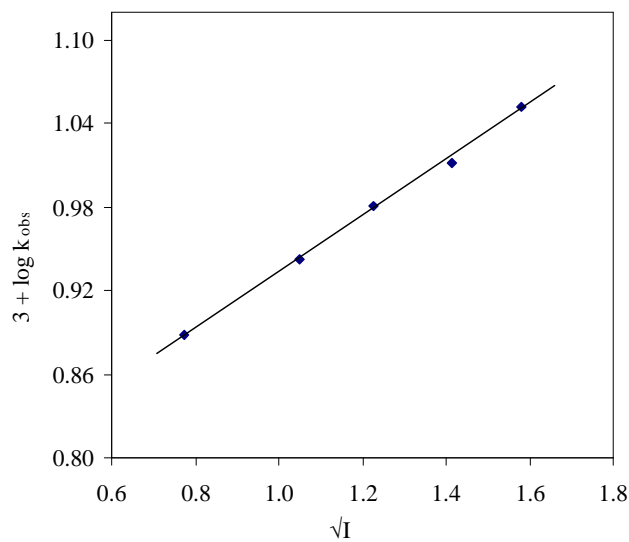


Fig:5 Effect of ionic strength on the oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium at 25 °C.

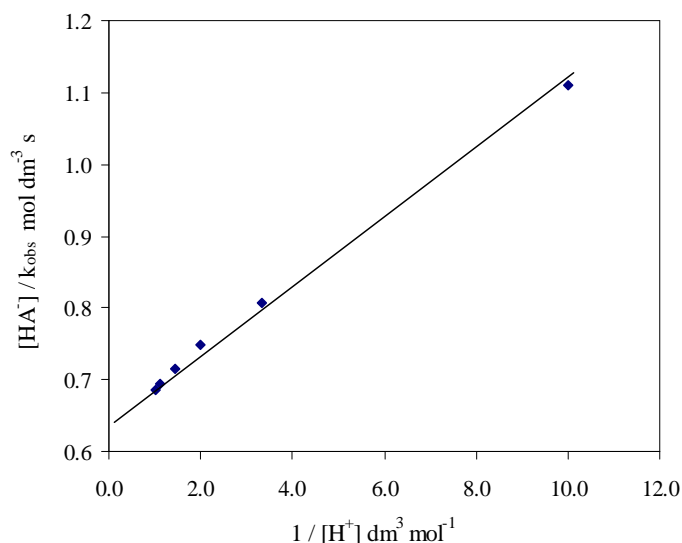


Fig: 6 Verification of rate law (11) in the form of (12)

CONCLUSION

The reaction between hexacyanoferrate(III) and ascorbic acid occurs with measurable velocity in perchloric acid media. The role of hydrogen ion is crucial to the reaction. Among various species of hexacyanoferrate(III) in acidic medium, $\text{HFe}(\text{CN})_6^{2-}$ is considered as active species for the title reaction. Rate constant with respect to slow step and equilibrium constant involved in the mechanism are evaluated. The activation parameters with respect to the slow step and thermodynamic quantities are calculated and discussed.

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