

KINETICS AND MECHANISM OF THE OXIDATION OF L-ASCORBIC ACID BY POTASSIUM TRISOXALATOFERRATE (III) TRIHYDRATE IN AQUEOUS HYDROCHLORIC ACID MEDIUM

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ABSTRACT

The kinetics of the oxidation of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ by L-ascorbic acid has been studied in aqueous acidic medium. The stoichiometric studies showed that 1 mole of H_2A was oxidized for every 2 moles of $Fe(C_2O_4)_3^{3-}$ reduced. Under pseudo-first order conditions of $H_2A \gg Fe(C_2O_4)_3^{3-}$, the reaction was found to have first order dependence on each of the reactants, giving second order overall.

The experimental data are consistent with the rate law:

$$-\frac{d[Fe(C_2O_4)_3^{3-}]}{dt} = (a + b[H^+])[H_2A][Fe(C_2O_4)_3^{3-}]$$

with $a = 1.8 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ $b = 0.8 \times 10^{-1} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ at 420 nm and $27.0 \pm 1.0^\circ \text{C}$

The reaction rate was found to be directly dependent on acid concentration and increased with increase in ionic strength of reaction system. It was also evident that increase in dielectric constant of the reaction medium (D) enhanced the reaction rate and addition of CH_3COO^- , $HCOO^-$, Mg^{2+} and Li^+ catalyzed the rate of the reaction. The oxidation of L-ascorbic acid by potassium trisoxalatoferate (III) trihydrate is rationalized in terms of absence of ion pair complex formation with outer-sphere reaction pathway characteristics.

Keywords: Kinetics, L-ascorbic acid, potassium trisoxalatoferate (III) trihydrate, outer-sphere mechanism

INTRODUCTION

It has been reported that H_2A , its intermediate and oxidation product may function as cycling redox couples in reactions involving electron transport and membrane electrochemical potentiation [1]. Also, ascorbic acid has attracted attention because of its major role as a redox reagent, which has resulted in a series of studies on its oxidation by transition metal complexes, especially in the trivalent state [2]. The oxidation of L-ascorbic acid by a wide range of metal ions and metal complexes has been accomplished with sufficient kinetics details [3].

Potassium trisoxalatoferate (III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ has played vital roles in many aspects of co-ordination chemistry, because of its spectroscopic and kinetic behaviors in solution and in some cases its resolution into enantiomers [4]. For example, the complex has been used in the field of photography, analytical chemistry, medicine and actinometry. The electron-transfer reaction of the complex with $S_2O_3^{2-}$, MnO_4^- and SO_4^{2-} , have been reported [4 - 6]. In this paper, we report the kinetics and mechanism of the oxidation of L-ascorbic acid by potassium trisoxalatoferate (III) trihydrate in aqueous hydrochloric acid medium as our contribution of providing additional information on the redox pattern of both the oxidant and reductant.

MATERIALS AND METHODS

Materials and Reagents

All reagents were of analytical grade and were used without further purification unless otherwise stated. Solutions of all the reagents used were dissolved in distilled water. All kinetic runs and other runs were carried out on Jenway 6300 UV-visible spectrophotometer.

Synthesis and characterization of potassium trisoxalatoferrate (III) trihydrate

The complex, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ was synthesized and characterized according to [7], involving the direct reaction of oxalic acid dihydrate, potassium hydroxide and iron (III) chloride hexahydrate.

Stoichiometric Studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing a fixed concentration of $[Fe(Ox)_3^{3-}] = (8.8 \times 10^{-3} \text{ mol dm}^{-3})$ and varying concentration H_2A $(0.88 - 4.84) \times 10^{-1} \text{ mol dm}^{-3}$ were reacted at $[H^+] = 0.2 \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$ (NaCl) and allowed to stand for 24 hours for the reaction to go to completion. The stoichiometry was evaluated from the plot of absorbance against mole ratio [8].

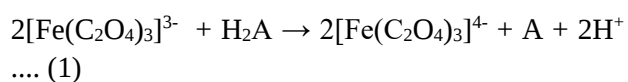
Kinetic Measurements

All kinetic runs were made under pseudo-first order conditions with the concentration of H_2A in at least 10 folds in excess over that of $[Fe(C_2O_4)_3^{3-}]$. The rate of the reaction was monitored by measuring the change in absorbance of the reaction mixture using a Jenway 6300 UV-visible spectrophotometer at $[H^+] = 0.2 \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$ (NaCl), $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 27.0 \pm 0.1^\circ\text{C}$ unless otherwise stated.

RESULTS AND DISCUSSION

Stoichiometry

The results of the spectrophotometric titration revealed a 2:1 stoichiometry and the overall reaction is given by equation (1):



Where H_2A = ascorbic acid and A = dehydroascorbic acid.

A , identified as dehydroascorbic acid in this work was also reported [2, 3, 9, and 10].

A 2:1 stoichiometry has been reported for the oxidation of L-ascorbic acid by various reducing agents [3, 9 and 10].

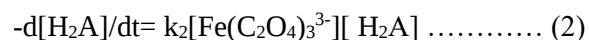
Product Analysis

Fe^{2+} was identified as one of the products by the addition of freshly prepared $K_3[Fe(CN)_6]$ with the completely reacted mixture which gave a deep blue-green solution indicating the presence of iron(II) [5]. Dehydroascorbic acid was also confirmed as the product of the oxidation of ascorbic acid on addition of 2,4-dinitrophenylhydrazine (2,4-DNP) and treatment with 85 % H_2SO_4 which formed a red coloured solution [11].

Determination of Order

Pseudo-first order plots of $\log(A_o - A_t)$ versus time were linear to greater than 85 % of the extent of the reaction indicating first order with respect to H_2A . A plot of $\log k_{\text{obs}}$ versus $\log [H_2A]$ was linear with a slope of 0.92 indicating first order in H_2A and second order overall. Values for k_{obs} and k_2 are presented in Table 1. Second order rate constants, k_2 was calculated from $k_2 = k_{\text{obs}}/[H_2A]$ were found to be fairly constant (Table 1).

Thus rate law is given by equation (2):



$$k_2 = (2.2 \pm 0.18) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Acid Dependence

The acid dependence on the rate of the reaction was monitored at constant $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$, $[\text{H}_2\text{A}]$ and $[\text{I}]$ while varying the concentration of $[\text{H}^+]$ ($17.6 - 105.6 \times 10^{-2} \text{ mol dm}^3$ at $27.0 \pm 1.0^\circ\text{C}$). Least square plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ was found to be linear with slope of 1.3 and $R^2 = 0.99$ (Fig. 1) which indicates first order in $[\text{H}^+]$ and the relationship is represented by equation (3):

$$k_2 = a + b [\text{H}^+] \dots\dots\dots (3)$$

$a = 0.68 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $b = 1.30 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}$. The rate equation for the reaction can therefore be represented by equation (4):

$$-d[\text{H}_2\text{A}]/dt = \{a + b[\text{H}^+]\}[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{H}_2\text{A}] \dots (4)$$

This suggests that the reaction occurred via acid dependent and acid independent pathways and it has

also been reported that redox reactions of L-ascorbic acid are strongly acid dependent. [4, 12 and 13].

Ionic Strength Dependence

The effect of ionic strength was studied in the range $(0.88 - 1.41) \times 10^{-2} \text{ mol dm}^{-3}$ using NaCl. The rate of the reaction was observed to increase with increase in ionic strength in the concentration range used. A plot of $\log k_2$ versus $\sqrt{I}$ was linear with a slope of 0.72, showing a positive Brønsted-Debye salt effect and suggesting the absence of intermediate complex formation and that the product of the charges at the rate determining step is positive [14 - 18]. This also indicates that the species operating at the rate determining step are of similar or like charges [19 and 20].

Table 1: Pseudo-first order and second order rate constants for the oxidation of ascorbic acid by $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 8.8 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $27.0 \pm 0.1^\circ\text{C}$ and $\lambda_{\text{max}} = 420 \text{ nm}$.

$0^2[\text{H}_2\text{A}]$, mol dm^{-3}	$10^2[\text{H}^+]$, mol dm^{-3}	10^2I , $\text{mol dm}^{-3} \text{ NaCl}$	$10^2 k_{\text{obs}}$, s^{-1}	$10^2 k_2$, $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
8.80	20	50	2.2	2.5
13.2	20	50	2.9	2.2
17.6	20	50	3.7	2.1
22.00	20	50	5.4	2.5
26.40	20	50	5.7	2.2
30.80	20	50	6.5	2.1
8.80	17.6	50	2.4	4.80
8.80	35.2	50	4.5	12.8
8.80	52.8	50	9.1	17.2
8.80	70.4	50	13.7	19.5
8.80	88.00	50	18.3	20.8
8.80	105.6	50	32.2	30.5
8.80	20	0.88	3.1	3.5
8.80	20	1.01	4.6	4.6
8.80	20	1.14	5.4	4.7
8.80	20	1.27	6.3	5.0
8.80	20	1.40	7.9	5.6

Table 2: Effect of dielectric constant on the oxidation of ascorbic acid by $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 8.8 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $[\text{H}_2\text{A}] = 0.088 \text{ mol dm}^{-3}$ and $27.0 \pm 0.1^\circ\text{C}$, $\lambda_{\text{max}} = 420 \text{ nm}$.

Dielectric Constant (D)	$10^3 I/D$	$10^2 k_{\text{obs}}, \text{S}^{-1}$	$10^3 k_2, \text{dm}^3 \text{mol}^{-1} \text{S}^{-1}$
106	9.4	2.6	3.0
130	7.7	2.9	2.9
149	6.7	3.1	2.7
215	4.7	3.3	2.6
416	2.7	3.6	2.5

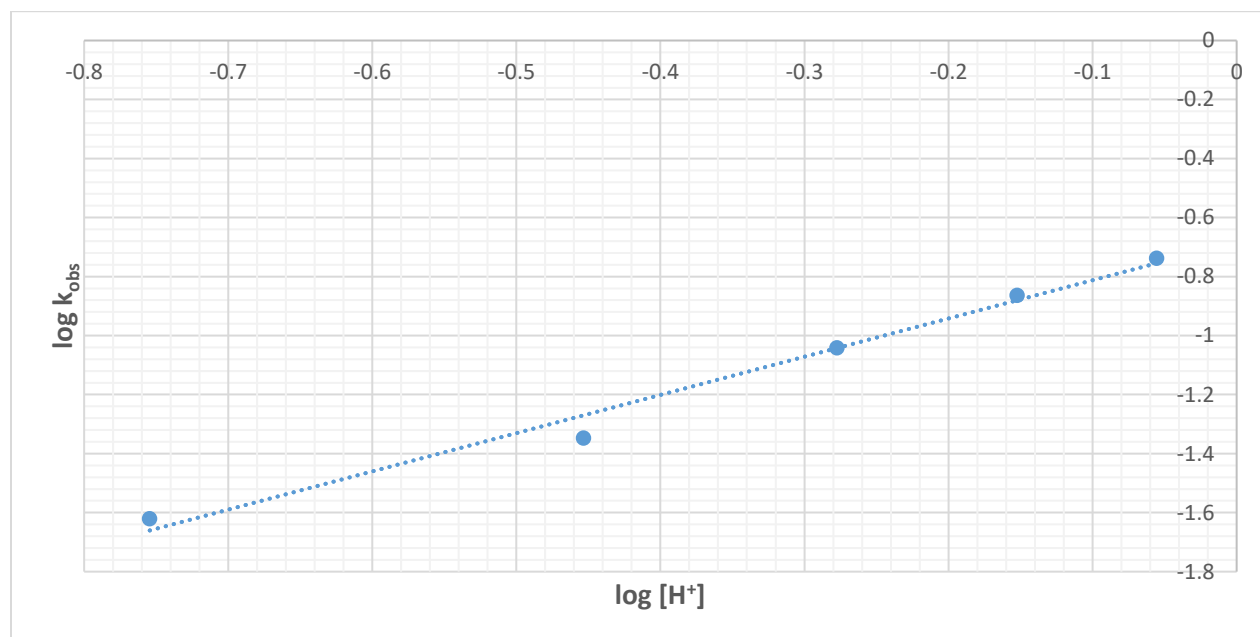


Figure 1: Plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 8.8 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}_2\text{D}] = 0.088 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 27.0 \pm 0.1^\circ\text{C}$

Dielectric Constant Dependence

The dielectric constant was studied in solution containing varying acetone/water concentrations. It was observed that the rate of the reaction was enhanced as dielectric constant, D increase. This implies that species of like charges are operating at the rate determining step [19 and 20]. Similar enhancement of dielectric constant has been reported for $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{S}_2\text{O}_3^{2-}$, MnO_4^- and SO_4^{2-} systems [4 - 6]. Relating the results of ionic strength and dielectric constant revealed that the

reaction could be pointing to more than one route [13].

Effect of Added Ions

The addition of various concentrations of CH_3COO^- , HCOO^- , Li^+ and Mg^{2+} gradually increased reaction rate. The catalysis of the reaction rate on addition of these ions is a characteristics of outer-sphere reaction [4, 13, 17, 21 and 22]. The added cations and anions catalysis by ascorbic acid is consistent with the report of [12 and 13].

Michaelis-Menten Plot

Least square analysis of the plots of $1/k_{\text{obs}}$ versus $1/[\text{H}_2\text{A}]$ (Fig. 2) gave a straight line with an insignificant intercept which is not enough to implicate inner-sphere reaction and also suggesting the absence of intermediate complex formation [5, 23 and 24]. Similar reaction pathway has been reported for the redox reaction of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} systems [4, and 5].

Test for Free Radicals

Addition of acrylamide to partially reacted mixture of oxidant and reductant in the presence of excess methanol formed a gel. This is an indication of the probable participation of free radicals in one of the reaction steps to have initiated polymerization of the acrylamide while the methanol was responsible for trapping the polymer as an insoluble precipitate. This is evidence of inner-sphere electron transfer mechanism [1]. This suggests that free radicals are important in this reaction [24 - 26]. Polymerization of acrylamide by potassium trisoxalatoferrate (III) has been confirmed elsewhere [5 and 6].

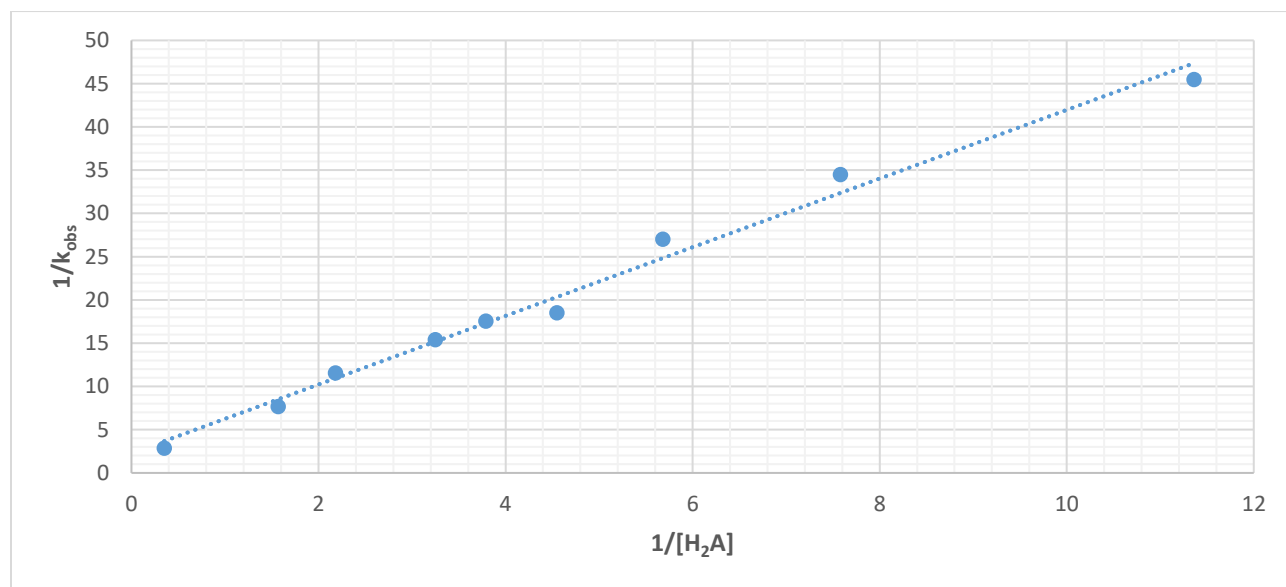
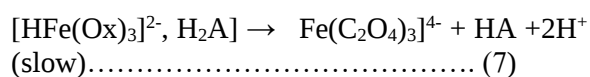
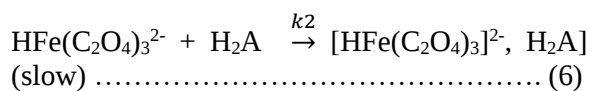
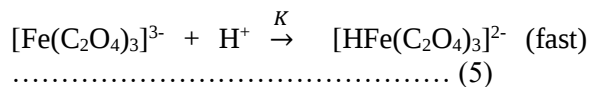
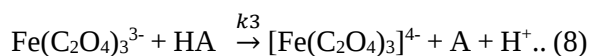


Figure 2: Plot of $1/k_{\text{obs}}$ versus $1/[\text{H}_2\text{A}]$ at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 8.8 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$, $T = 27.0 \pm 0.1^\circ\text{C}$

Mechanism of the Reaction

Based on the stoichiometry, observed positive acid and ionic strength dependence, anion and cation dependence, a plausible mechanism has been proposed to account for the kinetic data generated for L-ascorbic acid - $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ system.





From equations (6) and (7),

$$\text{Rate} = k_2 [\text{HFe}(\text{C}_2\text{O}_4)_3^{2-}] [\text{H}_2\text{A}] + k_3 [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] [\text{H}_2\text{A}] \quad (9)$$

From equation (5):

$$[\text{HFe}(\text{C}_2\text{O}_4)_3^{2-}] = k_1 [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] [\text{H}^+] \quad (10)$$

Substituting equation (10) into (9),

$$\text{Rate} = k_2 k_1 [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] [\text{H}^+] [\text{H}_2\text{A}] + k_3 [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] [\text{H}_2\text{A}] \quad (11)$$

$$\text{Rate} = (k_3 + k_2 k_1 [\text{H}^+]) [\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] [\text{H}_2\text{A}] \quad (12)$$

Equation (12) agrees with equation (4) where

$$k_3 = a = 0.68 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ and } k_1 k_2 = b = 1.30 \text{ mol}^2 \text{ dm}^6 \text{ s}^{-1}.$$

A major point of interest as to whether or not the reaction proceeded via outer sphere, inner sphere mechanism or a combination of both was resolved as follows:

- Positive cations and anions catalysis is suggestive that the reaction likely proceeded via an outer sphere electron transfer mechanism [21]. Ion catalysis and inhibition has been reported to be a characteristics of an outer sphere reaction mechanism [27].
- Probable participation of free radicals on addition of acrylamide to partially reacted mixture in the presence of excess methanol is pointing to an inner sphere electron transfer mechanism [10].
- Insignificant positive intercept for Michaelis-Menten plots of $1/k_{\text{obs}}$ versus $1/[\text{H}_2\text{A}]$ from (Fig. 5) is in support of an outer sphere reaction pathway [4].
- Positive ionic strength dependence and positive slope obtained from plots of $\log k_2$ versus $\sqrt{I}$ (Table 1) correspond reasonably with an outer sphere mechanism [17 and 18].

The evidence (a –d) is more in support of the outer sphere mechanism and is hereby proposed for the redox reaction of $\text{Fe}^{3+}/\text{H}_2\text{A}$ system.

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