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Kinetics and Mechanisms of the Redox Reaction of Potassium Trisoxalatoferate(III) and Tetraoxosulphate(VI) Ion in Aqueous Hydrochloric Acid Medium

¹Boniface O. Ogori*, ²Yilkur N. Lohdip, ¹Ngamarju T. Apagu

¹Department of Chemistry, F.C.E. Pankshin, Plateau state

²Department of Chemistry, University of Jos, Jos Nigeria

* Author to whom correspondence should be addressed; E-Mail:ogorib@yahoo.com

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Abstract: The redox reaction of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and SO_4^{2-} has been investigated in aqueous acid medium. The reaction obeys the rate law:

$$\frac{-d[Fe(C_2O_4)_3^{3-}]}{dt} = \{a + b[H^+]^2\} [Fe(C_2O_4)_3^{3-}] [SO_4^{2-}]$$

where $a = 0.322 \text{ s}^{-1}$ and $b = 24.69 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}$, at $T = 27.0 \pm 1.0 \text{ }^\circ\text{C}$, $[H^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 1.2 \times 10^{-1} \text{ mol dm}^{-1}$ (NaCl), and $\lambda_{\text{max}} = 420 \text{ nm}$. Based on the kinetic data and Michaelis-Menten relationship, the outer-sphere mechanism has been proposed for the titled reaction.

Keywords: Kinetics; Trisoxalato complexes; Outer-sphere mechanism.

1. Introduction

Trisoxalato complexes of the general formula: $K_3[M(C_2O_4)_3] \cdot XH_2O$ have played a leading role in many aspects of co-ordination chemistry especially in their spectroscopic and kinetic behavior as well as, in some cases their resolution into enantiomers (Baran and Lawrence, 2002). These complexes have found useful applications in photography, medicine and in actinometry.

(Bencini *et al.*, 2000; Fenet *et al.*, 2014; Shun, 1994 and Teinkink, 1995). The redox reactions of these complexes with a variety of substrates are receiving attention. In particular, there has been detailed

investigations of the kinetics of the reduction of Tris(oxalato)cobaltate by L-ascorbic acid and oxidation of Tris(oxalato)chromate(III) ion by manganese(III) ion e.t.c.(Horacio and Nina, 2006).

Tetraoxosulphate(VI) ion, SO_4^{2-} commonly called sulphate ion is important in both the chemical and biological processes e.g. some anaerobic microorganisms such as those living near deep sea thermal vents utilize sulphates as electron acceptors, magnesium sulfate commonly known as Epsom salts is used in therapeutic baths, gypsum the natural mineral form of hydrated calcium sulfate is used to produce plaster of paris.e.t.c. The oxidation potential of sulphate ion is 2.43V and it is very reactive towards organic compounds. It can abstract H-atom, add to double bonds and oxidize by electron transfer quite rapidly. The oxidizing ability of sulphate has mostly been explored in Biological systems, (Netta and Robert, 1985). For example, the kinetics of the oxidation of Fe^{2+} has been studied in concentrated $\text{H}_2\text{SO}_4 - \text{FeSO}_4$ solutions (Ronnholm *et al.*, 1999). The results revealed that the rate of the oxidation reaction increased with increase in temperature and pressure.

It is in pursuance of more knowledge into the reactions of trisoxalato complexes with oxoanions that we report the results of the investigations into the redox reaction of potassium trisoxalatoferate(III), with a versatile inorganic oxysulphur anion, the sulphate ion.

2. Experimental

2.1. Materials and Reagents

The complex, $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ was synthesized according to a known procedure involving the direct reaction of potassium oxalate monohydrate and iron(III) chloride hexahydrate and standardized as reported in the literature (Rendel *et al.*, 1969). Sodium chloride (BDH, Analar) stock solution was prepared without further purification or standardization and used to maintain the ionic strength at $1.2 \times 10^{-1} \text{ mol dm}^{-3}$ while hydrochloric acid was used to investigate the effect of hydrogen ions on the rate of the reaction. All other chemicals were used as supplied.

2.2. Stoichiometric Studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions of fixed concentrations of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and varying concentrations of SO_4^{2-} (1.82 to 7.28) $\times 10^{-1} \text{ mol dm}^{-3}$ were reacted at $[\text{H}^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $I = 1.2 \times 10^{-1} \text{ mol dm}^{-3}$ (NaCl) and allowed to stand for 24 hours for the reaction to go to completion. The absorbance of the solutions was measured at 420nm and the stoichiometry was evaluated from the plot of absorbance versus mole ratio.

2.3. Kinetic Measurements

All kinetic runs were performed under pseudo-first order conditions with the concentration of SO_4^{2-} in at least 10 fold excess over that of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$. The rate of reaction was monitored by measuring the rate of decrease in absorbance of the mixture at 420nm using a Spectrumlab UV-Visible spectrophotometer [Model 22pc] at $27.0 \pm 1.0^\circ\text{C}$ and $[\text{H}^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-1}$ and $I = 1.2 \times 10^{-1} \text{ mol dm}^{-1}$ (NaCl) unless otherwise stated. Pseudo-first order rate constants were obtained from plots of $\log(A_t - A_\infty)$ versus time.

3. Results and Discussion

3.1. Stoichiometry

The results of the spectrophotometric titration indicated a 2:3 Stoichiometry (Figure 1) and the overall reaction is given by:



This stoichiometry however, is not in conformity with what has been reported for similar trisoxalato complexes. For example, a stoichiometry of 2:1 for complex: substrate has been reported for the redox reaction of tris(oxalato)cobaltate with L-ascorbic acid (Horacio and Nina, 2006), as well as in the reaction of the same complex with 2-methylpentane-2,4-diol (Mamman and Iyun, 2008).

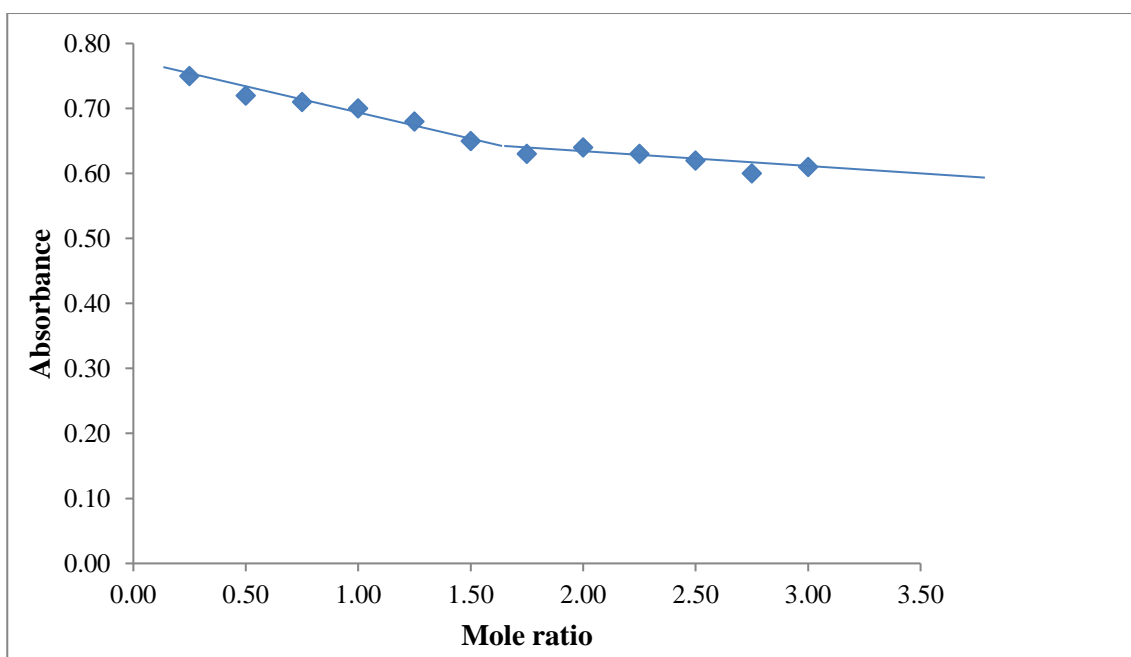


Figure 1: Plot of Absorbance vs mole ratio for the stoichiometry of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}/\text{SO}_4^{2-}$

3.2. Product Analysis

SO_3^{2-} was identified by chemical test by using BaCl_2 solution which gave a white precipitate. The precipitate was soluble in excess dilute hydrochloric acid, indicating that one of the products was SO_3^{2-} .

3.3. Determination of Order

Pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were linear for greater than 70% extent of the reaction indicating first order with respect to $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$. Values of the observed rate constants are given in Table 1.

Table 1: Second order rate constants for the reduction of SO_4^{2-} by $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$

$[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 1.52 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 1.2 \times 10^{-1} \text{ mol dm}^{-3} (\text{NaCl})$, $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda = 420 \text{ nm}$

$[\text{SO}_4^{2-}]$, mol dm^{-3}	$10^3[\text{H}^+]$, mol dm^{-3}	I , (NaCl) , mol dm^{-3}	$10^2 k_2$, $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0.182	6.0	0.12	1.56
0.273	6.0	0.12	1.42
0.364	6.0	0.12	1.53
0.455	6.0	0.12	1.72
0.546	6.0	0.12	1.73
0.637	6.0	0.12	1.74
0.455	2.0	0.12	29.90
0.455	4.0	0.12	39.90
0.455	6.0	0.12	44.80
0.455	8.0	0.12	47.30
0.455	10.0	0.12	58.20
0.455	12.0	0.12	63.60
0.455	6.0	0.12	1.56
0.455	6.0	0.20	1.66
0.455	6.0	0.28	1.68
0.455	6.0	0.36	1.76
0.455	6.0	0.44	1.81
0.455	6.0	0.52	1.92

A plot of $\log k_1$ versus $\log [\text{SO}_4^{2-}]$ was linear with a slope of 0.91 ($r = 0.982$) which signifies first order in $[\text{SO}_4^{2-}]$, as shown in Figure 2. This was also confirmed by plotting k_1 versus $[\text{SO}_4^{2-}]$ which gave a straight line passing through the origin. The second order rate constants, k_2 was obtained from $k_2 = k_1/[\text{SO}_4^{2-}]$ was found to be fairly constant (Table 1). The rate law for the reaction is therefore given by equation (2):

$$\frac{-d[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]}{dt} = k_2[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{SO}_4^{2-}] \dots\dots\dots (2)$$

$$k_2 = (1.42 \pm 0.32) \times 10^{-2} \text{ dm}^3\text{mol}^{-1} \text{ s}^{-1}$$

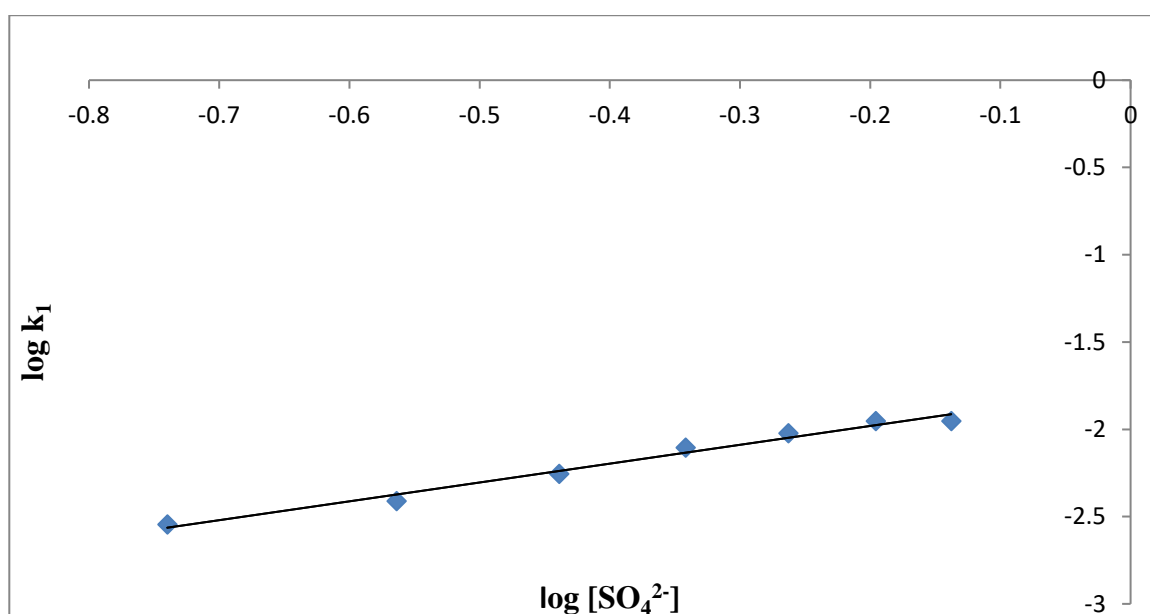


Figure 2: Plot of $\log k_1$ versus $\log [\text{SO}_4^{2-}]$ for the reduction of SO_4^{2-} by $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$

3.4. Acid Dependence

The acid dependence on the rate of this reaction was investigated at constant $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$, $[\text{SO}_4^{2-}]$ and ionic strength of $1.2 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^{-3}$ (NaCl), $[\text{H}^+] = (2.0-14.0) \times 10^{-3} \text{ mol dm}^{-3}$ at $27.0 \pm 1.0 \text{ }^\circ\text{C}$. A least square plot of k_2 versus $[\text{H}^+]$ was found to be linear ($r = 0.98$, Figure 3) and the relationship represented by:

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

$a = 0.322 \text{ s}^{-1}$ and $b = 24.69 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}$. The rate equation for the reaction can therefore be written as

$$\frac{-d[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]}{dt} = a + b\{[\text{H}^+]\}[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{SO}_4^{2-}] \dots\dots\dots (4)$$

The equation suggests that the reaction occurs via both acid dependent and acid independent pathways. It has been reported that redox reactions of many oxoanions are strongly acid dependent (Iyun, Ayoko, and Lawal, 1992). Under the present experimental conditions, therefore, it is reasonable to postulate that SO_4^{2-} is protonated in a first step to give HSO_4^- which then reacts with $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ in a slow step to give the products. Also, the intercept obtained from the plot of k_2 versus $[\text{H}^+]$ indicates that unprotonated SO_4^{2-} also reacts with the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ to form the products.

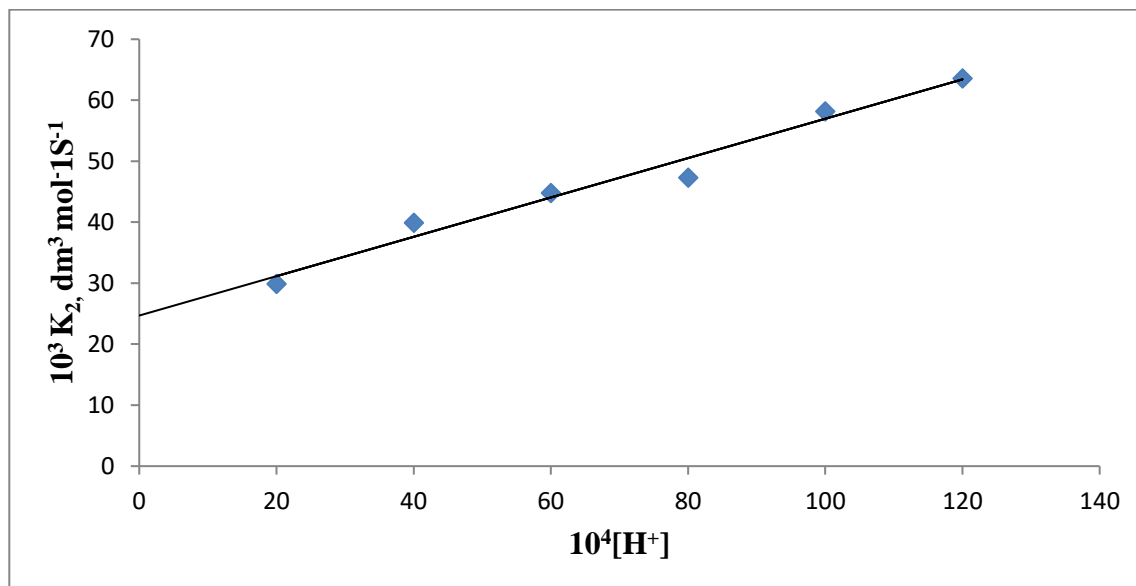


Figure 3: Plot of k_2 versus $[\text{H}^+]$ for the reduction of SO_4^{2-} by $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

3.5. Ionic Strength

The ionic strength was varied from (0.04-0.52) mol dm^{-3} using NaCl. The rate of the reaction was found to increase with increase in ionic strength of the reaction medium.

3.6. Test for Free Radicals

Addition of acrylamide to the partially reacted mixture gave a gel in the presence of excess methanol, indicating the probable presence of free radicals in the reaction medium. The polymerization of acrylamide by potassium trisoxalatoferate(III) has also been confirmed elsewhere (Sahul *et. al.*, 2003).

3.7. Effect of Added Species

The effects of added Zn^{2+} , CH_3COO^- and I^- on the rate of the reaction were studied. The values of the rate constants are shown in table 2. The rate of the reaction was found to decrease with increasing

concentration of Zn^{2+} , CH_3COO^- and I^- . This suggests that the reaction most probably occurred by an outer-sphere pathway (Iyinet *al*, 1992, Lohdipet *al*, 1998 and Shamle, *et al*, 2010).

Table 2: Effect of added species on the second order rate constants for the reduction of SO_4^{2-} by $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 1.52 \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{SO}_4^{2-}] = 4.55 \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{H}^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 1.2 \times 10^{-1} \text{ mol dm}^{-3}$, $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda = 420 \text{ nm}$.

X	$10^2[\text{x}], \text{ mol dm}^{-3}$	$10^3\text{k}_1, \text{ S}^{-1}$	$10^3\text{k}_2, \text{ dm}^{-3}\text{mol}^{-1} \text{ S}^{-1}$
Zn²⁺	4.0	13.2	28.70
	6.0	13.2	28.70
	8.0	12.7	27.60
	10.0	11.6	25.20
	12.0	11.4	24.80
	14.0	10.0	21.80
I⁻	4.0	15.2	33.10
	6.0	13.6	29.60
	8.0	11.7	25.40
	10.0	10.5	23.00
	12.0	9.4	20.3
	14.0	8.3	18.0
CH₃COO⁻	4.0	2.7	5.94
	6.0	1.95	4.30
	8.0	1.84	4.03
	10.0	1.63	3.58
	12.0	1.47	3.24
	14.0	1.32	2.90

3.8. Dielectric Constant

The effect of dielectric constant, (D) on the rate of the reaction was studied by varying acetone/water mixture, while keeping all other conditions constant. The dielectric constant (D) for the mixture was calculated as follows:

$$D_{mixt} = \frac{D_{H_2O} \times V_{H_2O} + D_{Ace} \times V_{Ace}}{V_{H_2O} \times V_{Ace}}$$

where Ace = acetone

It was observed that the reaction rate was enhanced as a function of $1/D$ (D = dielectric constant). The corresponding second order rate constants are given in Table 3. It is known that reactions involving anionic species exhibit a significant acceleration while those with neutral molecules (one or both species), will exhibit a retardation in the rate of reaction as the dielectric constant reduces from highly polar (H_2O) to less polar (acetone) solvent mixture (Ik-Hwan and Li-Ra, 2009). It is therefore, expected that the rate would increase in this reaction system.

Table 3: Effect of changes in Dielectric constant for the reduction of SO_4^{2-} by $[Fe(C_2O_4)_3^{3-}]$

D	$10^2 1/D$	$10^3 k_1 (s^{-1})$	$10^2 k_2 (dm^3 mol^{-1} s^{-1})$
7713.0	8.24	1.81	
73	13.7	9.90	2.18
69	14.5	10.3	2.27
65	15.4	10.9	2.40
61	16.4	11.5	2.53
57	17.5	13.1	2.88

3.9. Michaelis-Menten Plot

Least squares analysis of $1/k_1$ versus $1/[SO_4^{2-}]$ gave a straight line passing through the origin (Figure 4), which suggests the absence of an intermediate complex in the reaction, or if an intermediate complex is formed, it may have a small formation constant. The absence of kinetic evidence for the formation of reaction intermediates is in favour of the outer-sphere mechanism. This observation has also been reported for the reaction of di- μ -oxo-tetrakis(1,10-phenanthroline)dimanganese(III,IV) ion with SCN^- , ascorbic acid and 2-mercaptobenzoic acid (Lohdip and Iyun, 2001; Lohdip and Iyun, 2003; Lohdip and Ogara, 2004).

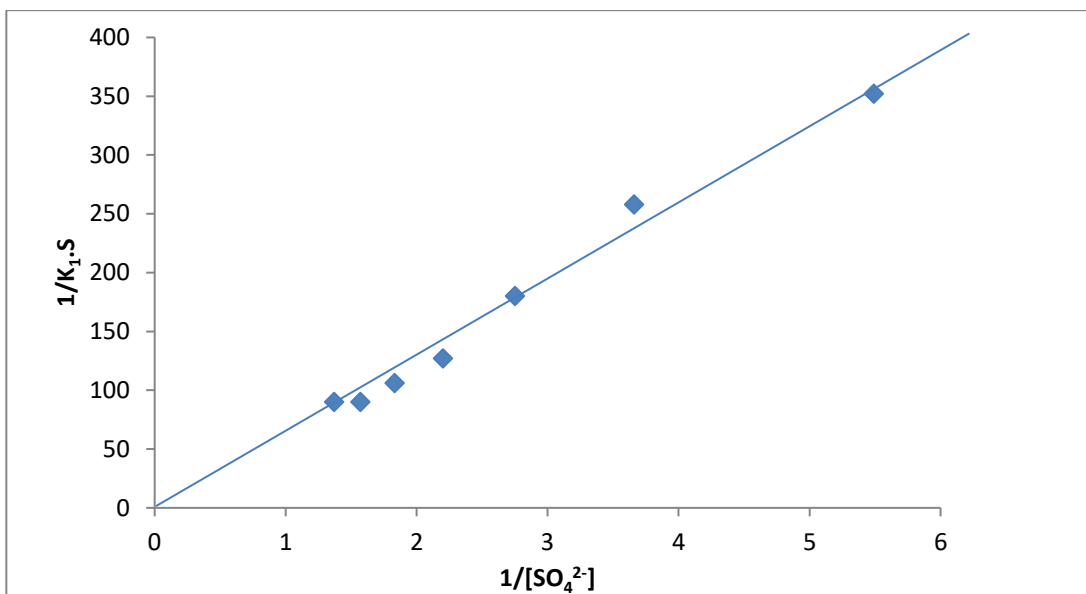
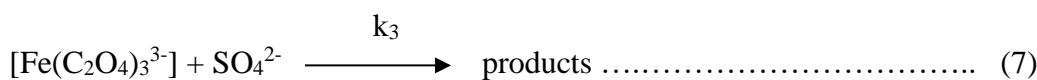
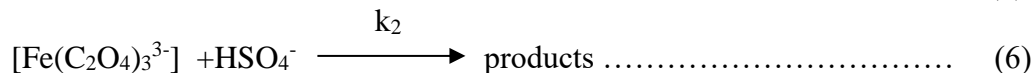


Figure 4: Plot of $1/k_1$ versus $1/[SO_4^{2-}]$ for the reduction of SO_4^{2-} by $[Fe(C_2O_4)_3^{3-}]$

3.10. Reaction Mechanism

Based on the stoichiometry, kinetic studies and other observations, the following scheme is proposed for the reaction:



$$\text{Rate} = k_2 [Fe(C_2O_4)_3^{3-}] [HSO_4^-] + k_3 [SO_4^{2-}] [Fe(C_2O_4)_3^{3-}] \dots\dots\dots (8)$$

From equation (5),

$$[HSO_4^-] = k_1 [SO_4^{2-}] [H^+] \dots\dots\dots (9)$$

Putting equation (9) into (8),

$$\text{Rate} = k_2 k_1 [Fe(C_2O_4)_3^{3-}] [SO_4^{2-}] [H^+] + k_3 [Fe(C_2O_4)_3^{3-}] [SO_4^{2-}] \dots\dots\dots (10)$$

$$\text{Rate} = (k_3 + k_2 k_1 [H^+]) [Fe(C_2O_4)_3^{3-}] [SO_4^{2-}] \dots\dots\dots (11)$$

In trying to assign a mechanistic pathway for this reaction, the following points were considered:

- (a) The alteration of the rate of the reaction by increase in ionic strength and added ions tend to suggest that the reaction occurs through an outer-sphere pathway.

- (b) Also, the Michaelis-Menten plot was linear without intercept, an indication that the reaction proceeded by outer-sphere pathway.
- (c) Furthermore, the significance of free radicals as important intermediate in this reaction is suggested by the acrylamide polymerization of the reaction mixture.

Based on the above points (a) - (c), it can be inferred that the reaction occurred through the outer-sphere pathway.

4. Conclusions

On the basis of the results of kinetic evidence for catalysis on addition of cation and anions, polymerization test, and conformity with Michaelis-Menten analysis, the redox reactions of potassium trisoxalatoferrate(III) trihydrate with tetraoxosulphate(VI) ion follows the outer-sphere mechanism.

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