

INVESTIGATIONS OF THE REDOX REACTIONS OF POTASSIUM TRISOXALATOFERRATE(III) WITH PERCHLORATE ION IN ACIDIC MEDIUM: A KINETIC APPROACH.

ABSTRACT

This study investigated the redox reactions of potassium trisoxalatoferrate(III) trihydrate with perchlorate ion in acid medium. The stoichiometry of the reaction determined by the mole ratio method were observed to be 1:2. The rate of the reaction showed two parallel pathways. The kinetic results showed first order dependence with respect to both oxidant and reductant concentrations and the experimental data are consistent with the rate law:

$$\frac{-d[Fe(C_2O_4)_3^{3-}]}{dt} = \{a + b[H^+]\}[Fe(C_2O_4)_3^{3-}][ClO_4^-] \text{ where } a = 0.07 \text{ s}^{-1} \text{ and } b = 0.74 \text{ dm}^6 \text{ mol}^{-2}.$$

The effect of added species (Zn^{2+} , Mg^{2+} , CH_3COO^- , I^- , and NO_3^-) on the rates of the reaction and other kinetic evidence suggest that the reactions occurred by the outer-sphere mechanism. The findings from the study has established baseline kinetic data for the redox reaction of potassium trisoxalatoferrate(III) trihydrate with ClO_4^- and plausible mechanisms have also been proposed for the reaction system.

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

INTRODUCTION

Potassium trisoxalatoferrate(III) trihydrate have found useful applications in photography, medicine, analytical chemistry and in actinometry. It is most abundantly used in platinum/palladium photographic

printing as a sensitizer in developing photographic prints (Beaver, 2022). The compound has been successfully used in volumetric analysis to estimate iodine in iodized salt (Humphrey, Young, Bailey, Crout, Ander, & Watts, 2018). In medicine, potassium trisoxalatoferate(III) trihydrate is used as a desensitizer in patients that exhibit a hypersensitive dental condition (Bhat & Bhat, 2019). The complex is also used in chemical actinometers because of its sensitivity over a wide range of wavelengths (Rabani, Mamane, Pousty, & Bolton, 2021).

Chemically, the term perchlorate refers to the anion consisting of a chlorine molecule in a +7 valence state combined with four oxygen molecule in a typical sp^3 tetrahedron. Perchlorate represents the highest oxidized form of chlorine and is, therefore, a strong oxidizer (Mitra, & Catalano, 2019). Despite its oxidative potential, the perchlorate anion is surprisingly stable and typically requires high activation energy in order to overcome the kinetic barrier to its reduction. These characteristics distinguish perchlorate compounds, and are responsible for their preferred use in many applications. For instance perchlorate is administered chemotherapeutically to patients with hyperthyroidism, with no side effects (Agrawal, Rangarajan, Shah, Puranik, & Purandare, 2018). Conversely, under the right circumstances, perchlorate can also act as a goitrogen in rodents and prevent thyroid hormone formation by interfering with iodide uptake (Pleus & Corey, 2018).

It is in pursuance of more knowledge into the redox reactions of potassium trisoxalatoferate(III) with oxoanions that we report the results of our investigations of its reactions with perchlorate ion.

EXPERIMENTAL

Materials and Reagents

The complex was prepared according to a known procedure as reported in the literature (Junk, Bacsa & Thomas, 2021) by dissolving 5.5g (0.03 mole) of potassium oxalate monohydrate in 100 cm^3 of water with the aid of a steam bath maintained at $25\text{ }^\circ\text{C}$ after which 2.7g (0.01mole) of iron (III) chloride hexahydrate was then added with stirring. The resulting solution was kept on an ice bath for crystallization and the

deposited green crystals were collected by Buchner filtration. The crystals were then purified by recrystallization. This was achieved by dissolving it in hot water (50 °C) and allowing it to cool gradually. The dissolved impurities were removed via filtration, leaving the pure solid. The crystals were washed with 10 cm³ portion of propanone and then dried in a dark cupboard before weighing. The complex was then characterized using IR-spectrophotometry. Sodium chloride (BDH, analar) stock solution was prepared without further purification or standardization and used to maintain the ionic strength at 0.200 mol dm⁻¹ while HCl was used to investigate the effect of hydrogen ions on the rate of the reaction. All other chemicals were used as supplied.

Stoichiometric Studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions of fixed concentrations of [Fe(C₂O₄)₃³⁻] and varying concentrations of ClO₄⁻ (0.293-0.936 mol dm⁻³) were reacted at [H⁺] = 0.200 mol dm⁻³, [Fe(C₂O₄)₃³⁻] = 0.017 mol dm⁻³ and I = 0.200 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 420 nm and the stoichiometry was evaluated from the plot of absorbance versus mole ratio.

Kinetic measurements

All kinetic runs were performed under pseudo-first order conditions with the concentration of ClO₄⁻ in at least 10 fold excess over that of [Fe(C₂O₄)₃³⁻]. The rate of reaction was monitored by measuring the rate of decrease in absorbance of the mixture at 420 nm using a Spectrumbank UV-Visible spectrophotometer [Model 22pc] at 27.0 ± 1.0 °C, [H⁺] = 0.200 mol dm⁻¹ and I = 0.200 mol dm⁻¹ (NaCl). Pseudo-first order rate constants were obtained from plots of log (A_t - A_∞) versus time.

RESULTS AND DISCUSSION

Stoichiometry

It has been observed that ClO_4^- exhibits varying stoichiometries. For example, for $\text{Ti}(\text{Hedta})/\text{ClO}_4^-$ system, the stoichiometry was 8:1, while in $\text{Ru}^{2+}/\text{ClO}_4^-$, the reaction exhibits a 2:1 stoichiometry (Lohdip, Apagu&Ogori, 2019). In this study, spectrophotometric titration using the mole ratio method gave a stoichiometry of 1:2 and the overall reaction may therefore be represented by equation (1):

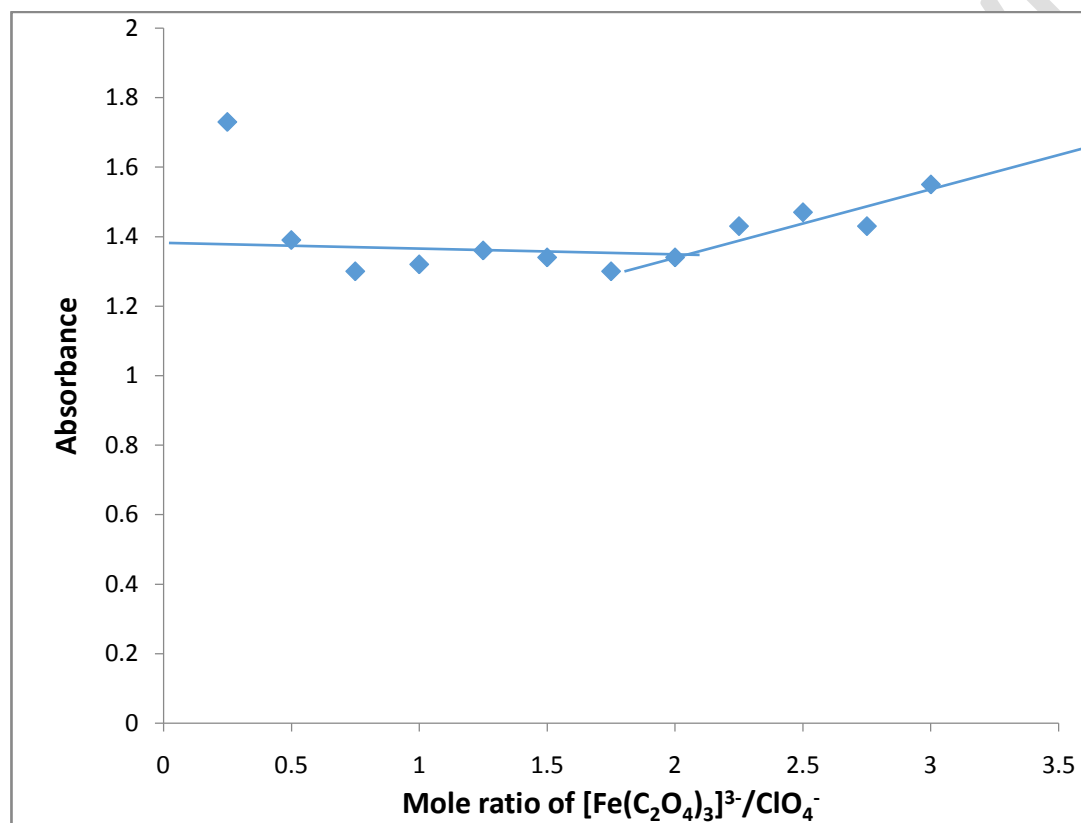
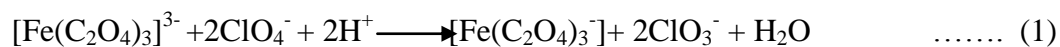


Figure 1: Plot of Absorbance vs Mole Ratio for the Reaction of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ with ClO_4^-

Determination of Order

Kinetic results for this system indicated first-order with respect to the concentration of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ as evidenced in the linearity of the pseudo-first order plot of $\log (A_t - A_\infty)$ versus time (Figure 2). The linearity was about 85% suggesting that there was no product inhibition. Values of the observed rate constants are given in Table 1.

Table 1. Second Order Rate Constants for the Oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ by ClO_4^-

$[\text{ClO}_4^-]$ mol dm^{-3}	$10[\text{H}^+]$ mol dm^{-3}	I, (NaCl) mol dm^{-3}	$10^5 k_1, \text{s}^{-1}$	$10^5 k_2$ $\text{dm}^3 \text{mol}^{-1}$	
0.585	2.0	0.20		3.02	5.16
0.644	2.0	0.20		3.43	5.32
0.702	2.0	0.20		3.56	5.07
0.761	2.0	0.20		3.93	5.17
0.819	2.0	0.20		4.19	5.12
0.878	2.0	0.20		4.41	5.02
0.936	2.0	0.20		4.96	5.30
0.995	2.0	0.20		5.32	5.35
0.878	2.4	0.20		2.47	2.81
0.878	2.8	0.20		3.50	3.98
0.878	3.2	0.20		3.82	4.36
0.878	3.6	0.20		4.59	5.22
0.878	4.0	0.20		5.44	6.20
0.878	4.4	0.20		6.87	7.83
0.878	2.0	0.20		7.75	8.83
0.878	2.0	0.24		7.50	8.55
0.878	2.0	0.28		7.58	8.63
0.878	2.0	0.32		7.38	8.40
0.878	2.0	0.36		8.59	9.78
0.878	2.0	0.40		7.09	8.15

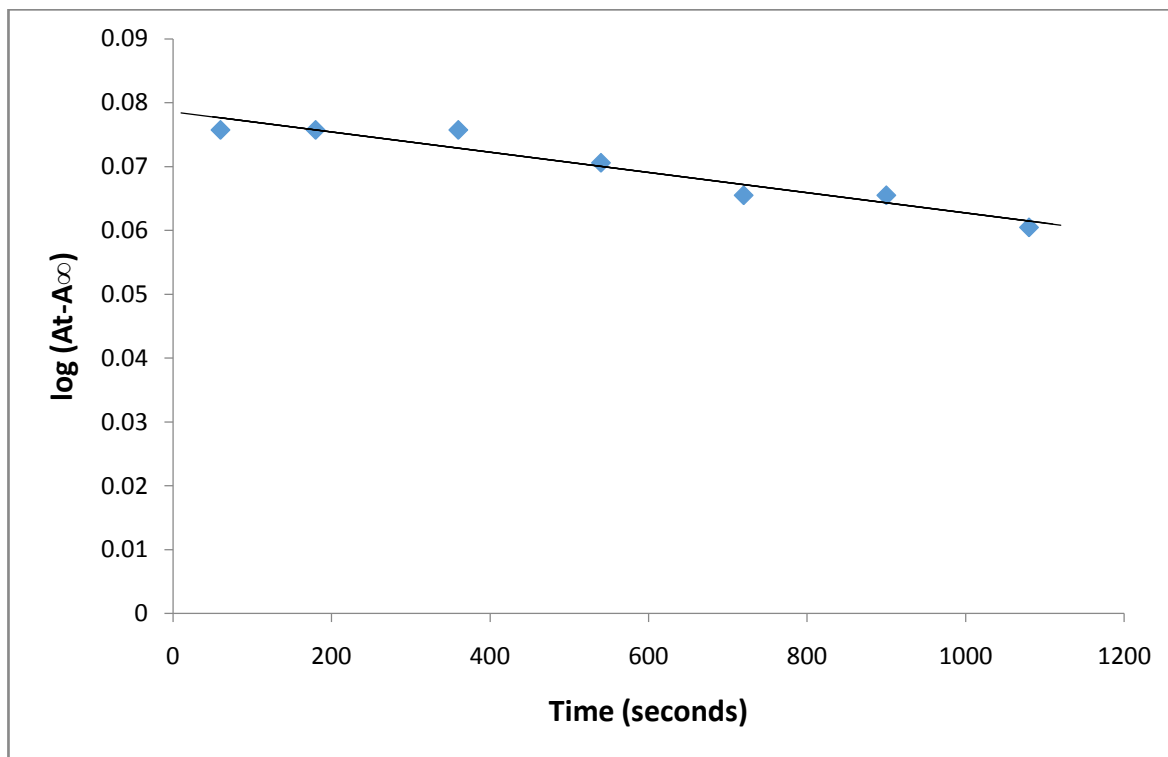


Figure 2: Pseudo-first-order Plot for the Oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by ClO_4^-

A plot of k_1 versus $\log [\text{ClO}_4^-]$ was linear with a slope of 0.992 which is approximately one, suggesting that it is also first-order in $[\text{ClO}_4^-]$ (Figure 3). The consistency of the k_2 values suggests that the reaction follows an overall second-order, therefore the experimental rate law can be described by equation (2):

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

$$k_2 = (5.02 \pm 0.33) \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

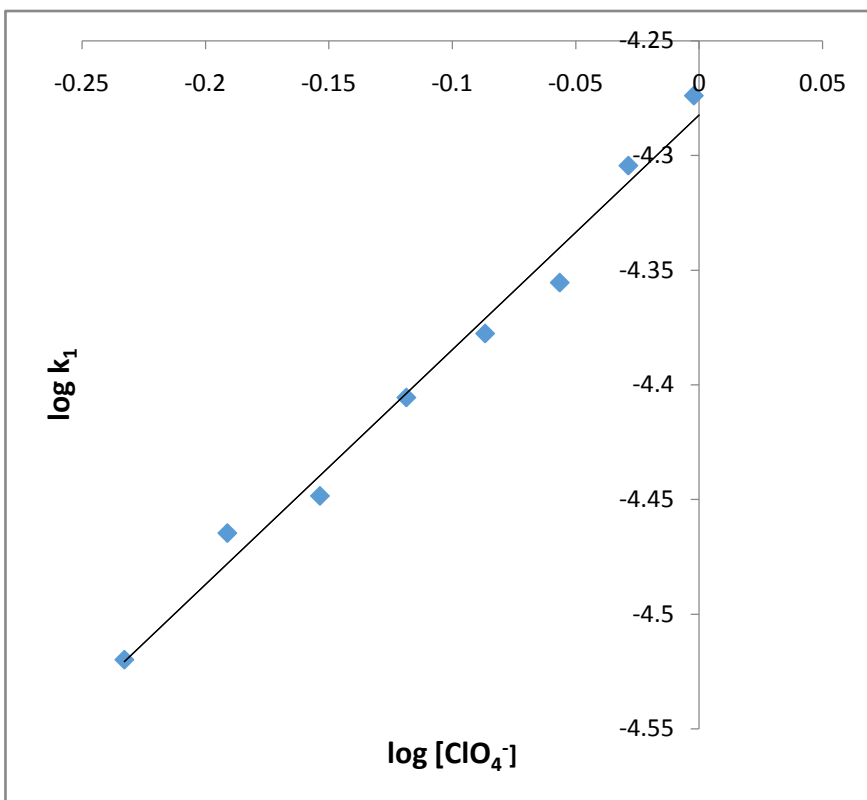


Figure 3: Plot of $\log k_1$ Versus $\log [\text{ClO}_4^-]$ for the Oxidation of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ by ClO_4^-

Acid Dependence

The reaction was found to be acid-dependent within the range of $0.2 \leq [\text{H}^+] \leq$

0.4 mol dm^{-3} (Figure 4) Plot of k_2 versus $[\text{H}^+]$ was linear with positive intercept according to the equation:

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

$$a = 0.23 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } b = 2.86 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

This suggests two pathways, one that is acid dependent and the other independent of acid. This implies that both the protonated and unprotonated species are reactive during the reaction (Hassan & Ibrahim, 2019).

Therefore, the overall rate of reaction expressed as a function of $[\text{H}^+]$ is:

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

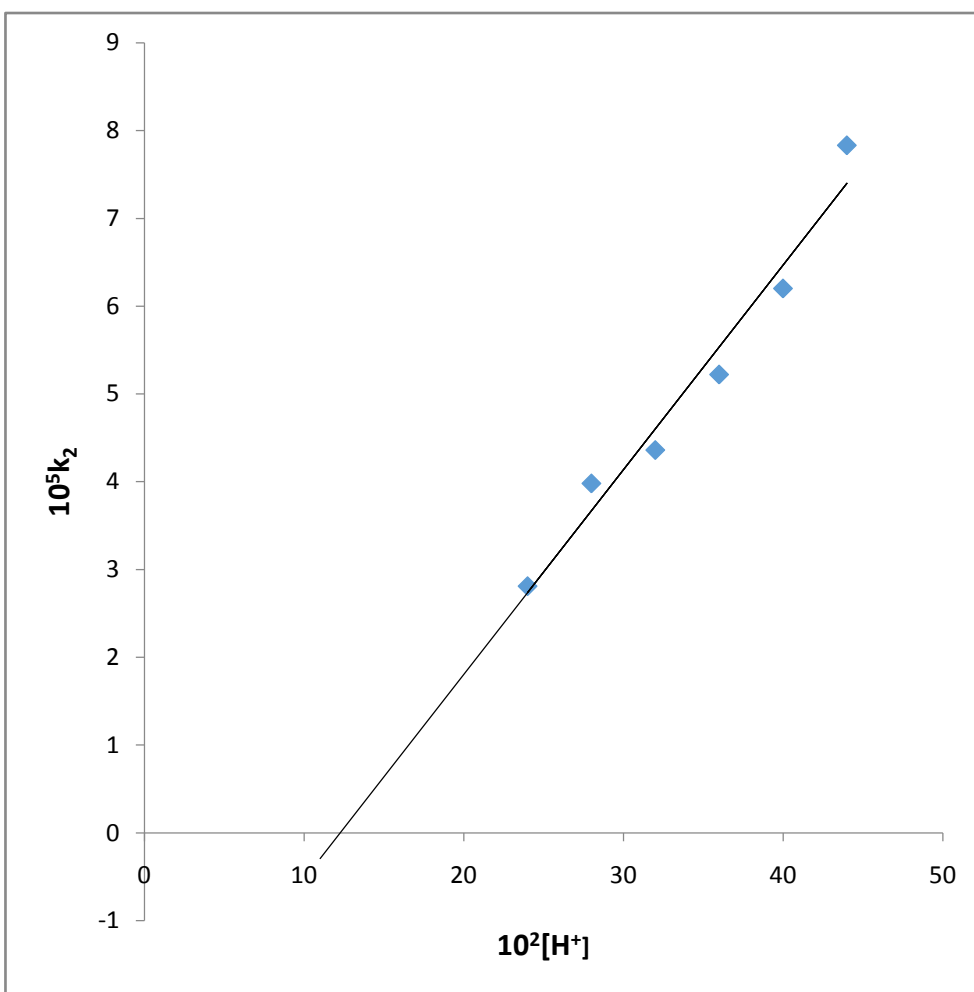


Figure 4: Plot of k_2 Versus $[H^+]$ for the Oxidation $[Fe(C_2O_4)_3]^{3-}$ by ClO_4^-

Ionic Strength and Dielectric constant

Changes in ionic strength and dielectric constant of the medium had no effect on the rate of the reaction (Tables 1). It is expected that the rate should vary with changes in these parameters since the redox species are charged (Arthur, Nkole & Osunkwo, 2021). The observed non-dependence of the rate on the dielectric constant of this reaction may be due to the fact that all the hydrogen atoms on $[H_2Fe(C_2O_4)_3]^-$ has been completely substituted with organic groups from the acetone, thereby constituting steric hindrance. Another reason may be that increase in dielectric constant of the medium decreased the polarity of the medium. As the polarity of the medium decreases, the efficiency of the electron transfer is no longer solely dependent on the rearrangement of the solvated molecules. Instead, the activation energy is a function of both

the concentration of the solvated molecules around the reactants and deformation of the encounter species (Umoru & Babatunde, 2019), hence the rate of reaction remains constant for the system.

Table 2. Effect of Changes in Dielectric Constant for the Oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by ClO_4^-

D	$10^2 1/D$	$10^5 k_1 (\text{s}^{-1})$	$10^2 k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
68.00	1.47	7.09	8.08
61.00	1.64	7.87	8.97
54.00	1.85	7.18	8.18
48.00	2.08	7.06	8.04
41.00	2.44	7.04	8.01
34.00	2.94	7.45	8.48

Effect of Added Species

The rate constant of the reaction was found to increase with increase in concentration of Zn^{2+} , Mg^{2+} , NO_3^- and CH_3COO^- (Table 3). This is suggestive of an outer sphere mechanism because outer sphere reactions are expected to be affected by presence of anions and cations, but they should have no effect on inner sphere reactions (Umoru, 2019; Adetoro, Babayo, Akiode, Iyun & Anene, 2023).

Table 3. Effect of Added Species on the Second Order Rate Constants for the Oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by ClO_4^-

X	$10^2 [\text{x}], \text{mol dm}^{-3}$	$10^5 k_1, \text{s}^{-1}$	$10^5 k_2, \text{dm}^{-3} \text{mol}^{-1} \text{S}^{-1}$
Mg^{2+}	4.00	4.91	5.60.
	6.00	5.13	5.84
	8.00	5.14	5.86
	10.0	5.19	5.91
	12.0	5.70	6.49

Zn^{2+}	4.00	6.24	7.11
	6.00	7.03	8.01
	8.00	7.38	8.41
	10.0	7.74	8.81
	12.0	8.10	9.22
NO_3^-	4.00	4.03	4.59
	6.00	4.54	5.18
	8.00	5.21	5.93
	10.0	5.70	6.49
	12.0	7.68	8.74
CH_3COO^-	4.00	8.87	10.10
	6.00	9.15	10.40
	8.00	10.40	11.80
	10.00	11.30	12.90
	12.00	12.20	13.90

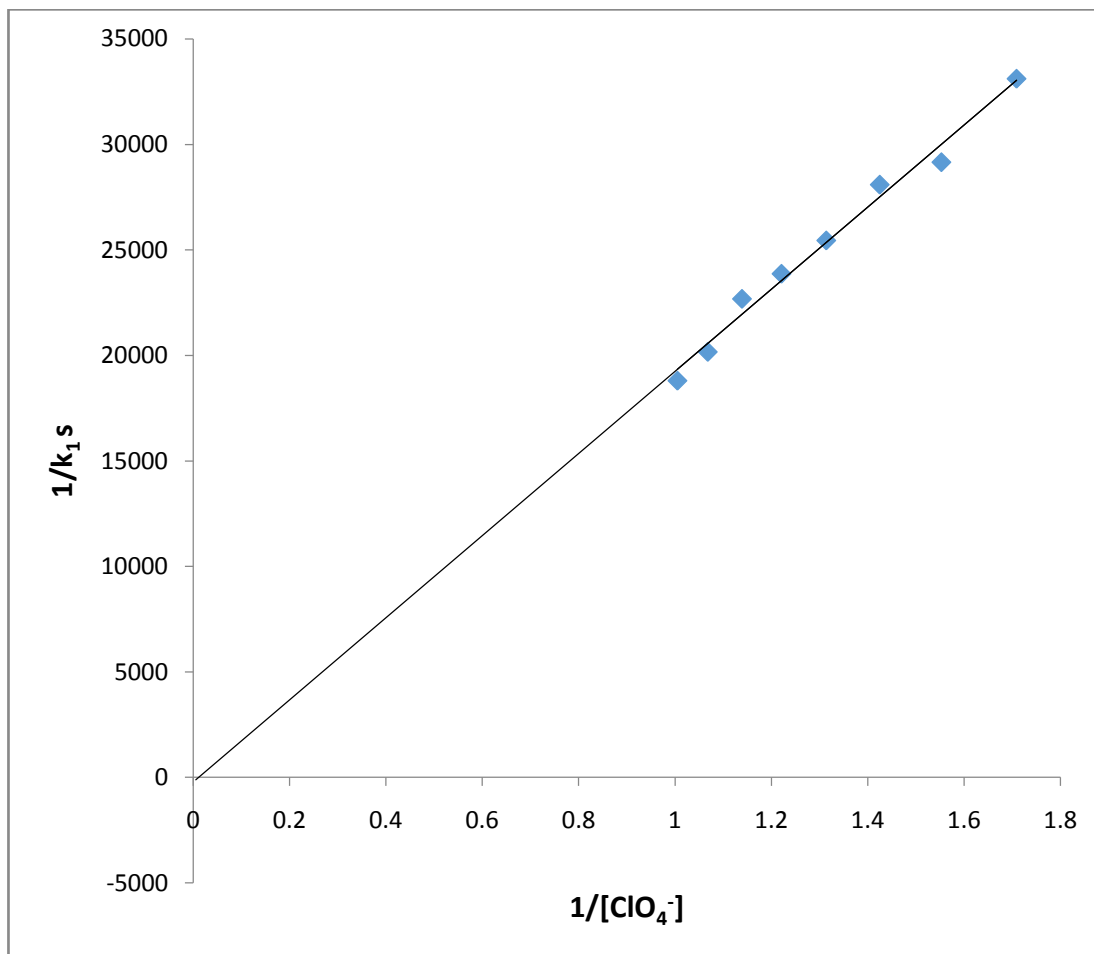


Figure 5: Michaelis-Menten Type Plot of $1/k_1$ Versus $1/[\text{ClO}_4^-]$ for the Oxidation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by ClO_4^-

Michaelis-Menten Type Plot

The Michaelis-Menten plots of $1/k_1$ versus $1/[\text{ClO}_4^-]$ (Figure 5) was linear without intercept indicating the absence of the formation of intermediates prior to electron transfer. The absence of kinetic evidence for the precursor complex is also in favour of the outer sphere mechanism.

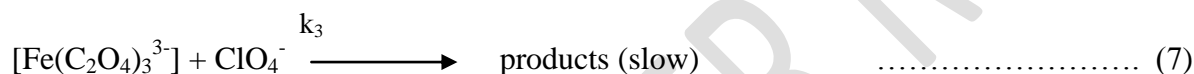
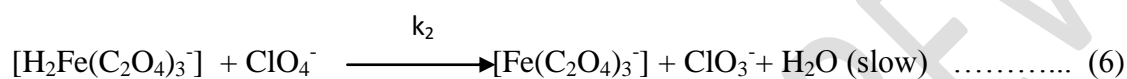
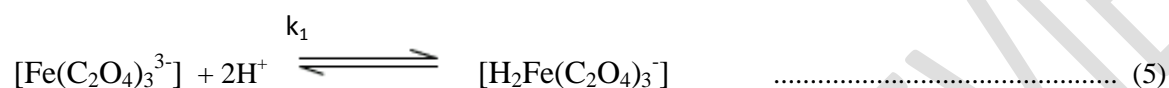
Free Radicals Formation

Addition of acrylamide to partially reacted mixture did not give a gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction medium. On the other hand, free radicals could have been formed, but reacted so quickly that this method could not detect it (Mei, Sun, Han,

Wei, An, Wang & He 2019). It is also possible that free radicals could have been formed, but with very small formation constants so that they cannot be major species in the rate determining steps of the reactions (Umoru & Babatunde, 2019).

Reaction Mechanism

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



Equations (6) and (7) are the rate determining steps.

$$\text{Rate} = k_2 [\text{H}_2\text{Fe}(\text{C}_2\text{O}_4)_3]^- [\text{ClO}_4^-] + k_3 [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} [\text{ClO}_4^-] \quad \dots\dots\dots (8)$$

From equation (5),

$$[\text{H}_2\text{Fe}(\text{C}_2\text{O}_4)_3]^- = k_1 [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} [\text{H}^+]^2 \quad \dots\dots\dots (9)$$

Substituting equation (9) into (8), gives

$$\text{Rate} = k_1 k_2 [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} [\text{H}^+]^2 [\text{ClO}_4^-] + k_3 [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} [\text{ClO}_4^-] \quad \dots\dots\dots (10)$$

$$\text{Rate} = (k_3 + k_1 k_2 [\text{H}^+]^2) [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} [\text{ClO}_4^-] \quad \dots\dots\dots (11)$$

Where $k_3 = a = 0.23 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_1 k_2 = b = 2.86 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

The pathway for the redox process is hereby proposed on the basis of the following;

- (a) Michaelis-Menten plot of $1/k_1$ versus $1/[\text{ClO}_4^-]$ was found to be linear without intercept, suggesting the absence of a pre-association step. This favours the outer-sphere mechanism.

(b) A general enhancement of the reaction rate by added cations and anions is also in support of the outer-sphere mechanism in most redox reactions that have been studied (Adetoro, Idris, Onu & Okibe, 2021).

Similar catalysis was observed in the kinetics and mechanisms of reaction of (7-amino-8-methylphenthiazine-3-ylidene)-dimethyl-ammonium chloride by perchlorate ion in acidic medium (Umoru, Al Amin, Sahabi & Babatunde, 2022) and the reaction system was proposed to occur by the outer-sphere mechanism.

(c) Addition of acrylamide to the partially oxidized reaction mixture did not give a gel even in the presence of excess methanol. This evidence is also in support of the outer-sphere pathway. From the above points (a) – (c), it can be inferred that the kinetic evidence are in support of the occurrence of the outer-sphere mechanism and is hereby proposed for this reaction.

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