



KINETICS AND MECHANISM OF THE REDUCTION OF POTASSIUM TRISOXALATOFERRATE (III) BY THIOPHENOL IN AQUEOUS HYDROCHLORIC ACID MEDIUM



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Abstract: The kinetics and mechanism of the reduction of potassium trisoxalatoferrate (III) by thiophenol was investigated spectrophotometrically in aqueous hydrochloric acid medium at $[H^+] = 0.2 \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}$ (NaCl), $29 \pm 0.1^\circ\text{C}$ and 420 nm. Spectrophotometric titration following the mole ratio method gave a point of inflexion at the mole ratio of 1:1, inferring that one mole of the oxidant consumed one mole of the reductant. Kinetic decays indicated first order dependence of the reaction on both oxidant and reductant which gave an overall order of second order. Reaction rates increased with increase in $[H^+]$ but decreased as ionic strength was increased. Increase in the concentration of added ions had positive effect on the reaction rate and free radicals probably did not participate in the reaction. The reaction was rationalized in terms of the outer-sphere pathway.

Keywords: Kinetics, potassium trisoxalatoferrate (III), thiophenol, outer-sphere mechanism

Introduction

Potassium trisoxalatoferrate (III), $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ 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 (Ogori and Lohdip, 2017). 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 (Ogori and Lohdip, 2017; Ogori *et al.*, 2016; 2021). Sulfhydryl compounds (thiols) play many significant biological roles. Their redox couple, RSH/RSSR play a major role in mediating cell potentials at biological sites. Biological and biomimetic iron-sulphur clusters like ferredoxin and rubredoxins are complexes of cysteine where various thiol fragments are ligated to metal centres (Ukoha *et al.*, 2018a). These Fe-S cluster plays very important physiological roles in electron transfer, enzymatic transformation, storage and regulation of gene expression. However, a clear understanding of the Fe^{3+} interaction with thiols at cellular sites has received little attention. Many thiols have been tried in these biomimetic processes but thiophenol has rarely been used, not just for Fe^{3+} reduction but also for other metal centres. This might be due to the foul odour of thiophenol, its relative toxicity and low solubility (Ukoha *et al.*, 2017; 2018a).

This present study is an effort to investigate the redox kinetics of potassium trisoxalatoferrate (III) using thiophenol, a relatively uninvestigated thiol. It is our hope that the kinetic data generated will give a clearer understanding of the interaction of Fe^{3+} with thiophenol at cellular sites.

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 as described by Ogori and Lohdip, (2017) 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. The concentration of $Fe(C_2O_4)_3^{3-}$ was kept constant at $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ while that of thiophenol was varied between $(0.05 - 0.175) \text{ mol dm}^{-3}$ at $[H^+] = 0.2 \text{ mol dm}^{-3}$ and constant ionic strength of 0.6 mol dm^{-3} (NaCl) at $29.0 \pm 1.0^\circ\text{C}$. At the completion of the reaction, absorbances of the reaction solutions were obtained at $\lambda_{\text{max}} = 420 \text{ nm}$. The stoichiometry was then determined from the plot of absorbance versus mole ratio of $Fe(C_2O_4)_3^{3-} : \text{PhSH}$.

Product Analysis

At the completion of the reaction, the reaction mixture was analyzed for the type of organic and inorganic products formed. Addition of 20 cm^3 of ethanol and 5 cm^3 of concentrated HCl were added to the reaction mixture which resulted in the formation of white crystals of formamide disulphide.

Kinetic Studies

Kinetic runs were made under pseudo-first order conditions with $[\text{PhSH}]$ in at least 10-fold excess over $[Fe(C_2O_4)_3^{3-}]$ at the stated conditions by monitoring the change in the absorbance of the complex at 420 nm using Jenway 6300 spectrophotometer. Pseudo-first order rate constants, k_{obs} were obtained from the gradient of the plot of $\log(A_t - A_\infty)$ against time (A_t and A_∞ are absorbances at time 't' and infinity respectively). Plots of kinetic decays were linear for at least 90 % extent of the reaction. Second order rate constants, k_2 , were determined as the ratio of $k_{\text{obs}}/[\text{PhSH}]$.

Acid Dependence

The effect of $[H^+]$ on the reaction rate was investigated by keeping the concentration of the other reactants constant while varying the hydrogen ion concentration in the range of 0.075 – 0.45 mol dm⁻³ using HCl.

Effect of Ionic Strength

The effect of ionic strength on the rate of the reaction was studied over the range of (0.3 – 1.05) mol dm⁻³ using NaCl, while other reaction conditions were kept constant.

Effect of Dielectric Constant

The effect of medium dielectric constant, D, on the reaction rate was investigated by carrying out the reaction in medium of varying dielectric constants using acetone. The medium dielectric constants were varied by using a binary solvent mixture of water and acetone while keeping all other conditions constant.

Effect of Added Ions

The influence of the presence of added CH₃COO⁻, NO₃⁻, K⁺, and Mg²⁺ on the rate of the reaction were investigated by varying the concentration of these ions while keeping the concentration of other reactants and other conditions constant.

Test for Participation of Free Radicals

The test for free radicals was done by adding about 2 g of acrylamide to partially reacted mixture containing various concentrations of the other reactants. Excess methanol was also added to the reaction mixture.

Test for the Formation of Intermediate Complex

The test for the presence of stable and detectable intermediate complex formed in the course of the reaction was done by the Michaelis-Menten plot of $1/k_{obs}$ versus $1/[reductant]$. Identification or otherwise of intercepts from this plot would give an idea of the presence or otherwise of intermediate complex formation.

Results and Discussion

Stoichiometry and Product Analysis

The results of the stoichiometric studies for the oxidation of thiophenol by Fe(C₂O₄)₃³⁻ revealed that one mole of the reductant was consumed by one mole of the oxidant as shown in Fig. 1. The stoichiometric equation can be represented by equation 1.



A similar stoichiometry has been reported for the oxidation of thiophenol by Cr(IV) (Ukoha *et al.*, 2018a) and V(V) (Ukoha *et al.*, 2017). The formation of disulphides was confirmed by the formation of a white crystalline solid after ether has been extracted from the organic extract. The same observation was reported for the reaction of V(V) with PhSH while the formation of a sulphoxide was reported for the reaction of Cr(IV) and PhSH ((Ukoha *et al.*, 2017; Ukoha *et al.*, 2018a). The formation of Fe²⁺ is a major feature of the oxidation of Fe³⁺ by thiols (Nkole *et al.*, 2018) which was confirmed by the formation of a bluish colouration on addition of K₃[Fe(CN)₆] to the completely reacted mixture (Ogori *et al.*, 2016).

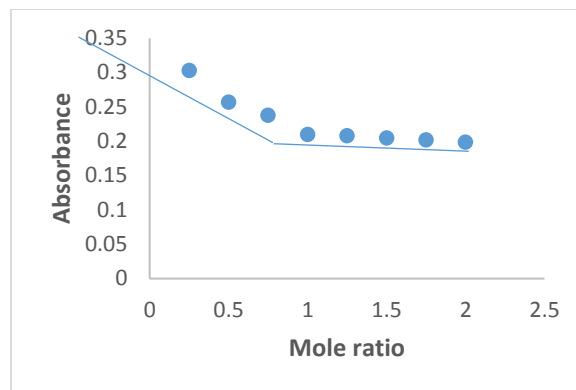
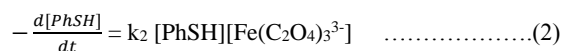


Fig. 1: Plot of absorbance against mole ratio for the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiophenol at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm⁻³, $I = 0.6$ mol dm⁻³ (NaCl), $[H^+] = 0.2$ mol dm⁻³, $\lambda_{max} = 420$ nm and $T = 29 \pm 0.1$ °C.

Order of Reaction

Pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were linear up to 90 % extent of the reaction, indicating first order on $[Fe(C_2O_4)_3^{3-}]$ (Fig 2). Pseudo-first and second order rate constants are presented in Table 1. Least square fits ($R^2 = 0.99$) of the plot of $\log k_{obs}$ versus $\log [PhSH]$ (Fig. 3) was linear with a slope of 1, indicating first order on $[PhSH]$. This implies that the reaction is first order with respect to the concentration of each reactant and second order overall. k_{obs} increased with increase in $[PhSH]$ and k_2 values were invariant with values within $(3.8 \pm 0.1) \times 10^{-2}$ dm³ mol⁻¹ s⁻¹. The fairly constancy of the k_2 values is a proof that the reaction is indeed first order with respect to $[PhSH]$. Therefore, the rate of the reaction can be illustrated in equation 2.



Most reactions of thiols with metal complexes also displayed first order dependence on both $[oxidant]$ and $[reductant]$ and were found to be second order overall (Ukoha *et al.*, 2017, 2018).

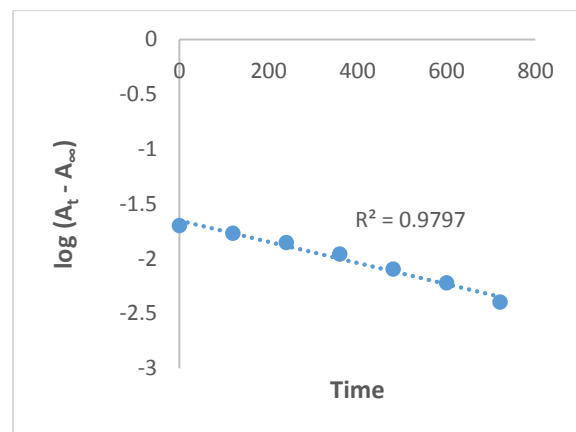


Fig. 2: Plot of $\log k_{obs}$ against $\log [PhSH]$ for the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiophenol at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm⁻³, $I = 0.6$ mol dm⁻³ (NaCl), $[H^+] = 0.2$ mol dm⁻³, $\lambda_{max} = 420$ nm and $T = 29 \pm 0.1$ °C.

Table 1: Pseudo-first and second order rate constants for the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ by thiophenol in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}$ (NaCl), $[\text{H}] = 0.20 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$.

10^2 [PhSH] mol dm^{-3}	10^1 [H ⁺] mol dm^{-3}	I, 10^1 mol dm^{-3} (NaCl)	10^3 k_{obs} s^{-1}	10^2 k_2 , $\text{dm}^3 \text{mol}^{-1}$ s^{-1}
5.00	2.0	6.0	1.85	3.9
7.50	2.0	6.0	2.92	3.9
10.00	2.0	6.0	3.75	3.8
12.50	2.0	6.0	4.50	3.6
15.00	2.0	6.0	5.68	3.8
17.50	2.0	6.0	6.58	3.8
5.00	0.75	6.0	0.48	0.64
5.00	1.50	6.0	1.21	0.81
5.00	2.25	6.0	2.22	0.99
5.00	3.00	6.0	3.43	1.14
5.00	3.75	6.0	5.28	1.41
5.00	4.50	6.0	9.55	2.12
5.00	2.0	3.0	8.15	2.72
5.00	2.0	4.5	4.75	1.06
5.00	2.0	6.0	3.25	0.54
5.00	2.0	7.5	2.04	0.27
5.00	2.0	9.0	1.83	0.18
5.00	2.0	10.5	1.52	0.15

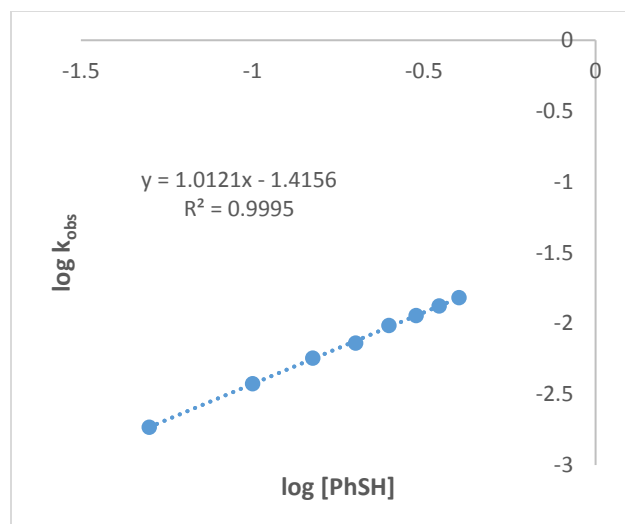


Fig. 3: Plot of $\log k_{\text{obs}}$ against $\log [\text{PhSH}]$ for the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ by thiophenol at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}$ (NaCl), $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$.

Acid Dependence

The effect of $[\text{H}^+]$ on the rate of reaction was investigated within the range $0.075 - 0.45 \text{ mol dm}^{-3}$ with the concentration of the oxidant, reductant and ionic strength maintained constant. Increase in $[\text{H}^+]$ resulted in the rate of the reaction as shown in Table 1. A plot of k_2 versus $[\text{H}^+]$ was linear with an intercept which conforms to equation (3).

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

Although, enhancement of reaction rate with increase in $[\text{H}^+]$ is not popular with oxidation of thiols by metal ions (Ukoha *et al.*, 2017), enhancement of reaction rate with increase in $[\text{H}^+]$ was reported for the oxidation of thiophenol with Cr (IV) and V (V) (Ukoha *et al.*, 2017, 2018a).

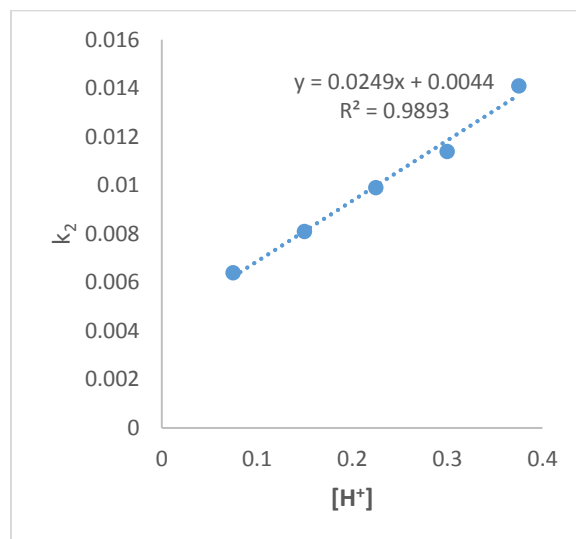


Fig. 4: Plot of k_2 against $[\text{H}^+]$ for the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ by thiophenol at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{PhSH}] = 0.05 \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}$ (NaCl), $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$.

Ionic Strength Dependence

The effect of ionic strength on the rate of the reaction was studied by varying the ionic strength from 0.3 to 1.05 mol dm^{-3} using NaCl. The results shown in Table 1 indicate that within this prevailing ionic strength, the rate of the reaction decreased. This negative salt effect is supported with the plot of $\log k_2$ versus \sqrt{I} as shown in Fig. 5. This is in accord with a reaction where the redox partners interact with positive charges or negative charges at the rate determining step and an outer-sphere mechanistic pathway (Ukoha *et al.*, 2017). A similar salt effect has been documented for the oxidation of thiophenol with Cr (IV) and V (V) (Ukoha *et al.*, 2017, 2018a).

Effect of Medium Dielectric Constant

Dielectric constant (D) was varied from 70.5 to 48.5 by varying the water/acetone mixture while keeping the concentration of other reactants constant. The results displayed in Table 2 indicate a slight increase in rate constant as D decreases. This observation infers interaction of anions and cations at the rate determining step (Oladunni *et al.*, 2021). Increase in rate constant with decrease D has been reported for the oxidation of thiophenol with Cr (IV) and V (V) (Ukoha *et al.*, 2017, 2018a).

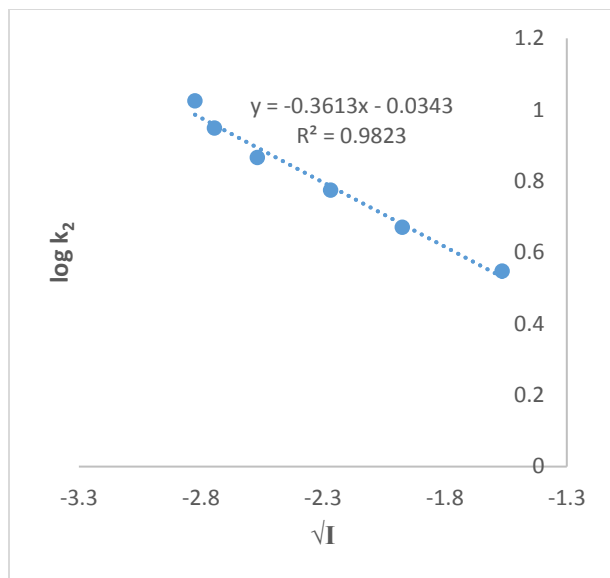


Fig. 5: Plot of $\log k_2$ against \sqrt{I} for the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by thiophenol at $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{PhSH}] = 0.05 \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$.

Table 2: Effect of dielectric constant on the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by thiophenol in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{PhSH}] = 0.05 \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$

D	$10^2 I/D$	$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10^2 k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
70.50	1.42	1.25	1.05
65.22	1.53	1.86	1.66
61.78	1.62	2.75	2.47
57.16	1.75	3.45	3.54
53.97	1.85	4.98	4.76
48.25	2.07	6.22	5.55

Effect of Added Ions

The catalytic effect of added ions was investigated by adding various amounts of K^+ , Mg^{2+} , NO_3^- and CH_3COO^- in the range 0.05 to 0.25 mol dm^{-3} while keeping the concentration of the other reactants constant. The result in Table 3 indicate that rate of the reaction increased in the presence of these added ions. This observation shows a positive catalysis and points to absence of precursor complex formation with outer-sphere characteristics (Myek *et al.*, 2014). Retardation of reaction rates on addition of added ions was reported for the oxidation of thiophenol by Cr(IV) while reaction rates were unaffected on addition of added ions for the oxidation of thiophenol by V (V) (Ukoha *et al.*, 2017; 2018a).

Table 3: Effect of added ions on the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ by thiophenol in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{PhSH}] = 0.05 \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$.

X	$10^1 [\text{X}], \text{ mol dm}^{-3}$	$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10^2 k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
CH_3COO^-	0.50	1.03	2.05
	1.00	2.76	2.76
	1.50	4.55	3.03
	2.00	9.10	4.55
	2.50	14.50	5.80
NO_3^-	0.50	0.71	1.43
	1.00	1.87	1.87
	1.50	2.85	1.90
	2.00	5.12	2.56
	2.45	7.05	2.82
Mg^{2+}	0.50	0.78	1.55
	1.00	1.58	1.58
	1.50	3.60	2.40
	2.00	5.63	2.82
	2.45	8.80	3.52
K^+	0.50	0.68	1.35
	1.00	1.93	1.93
	1.50	4.15	2.77
	2.00	6.60	3.30
	2.45	10.90	4.36

Test for Free Radicals

The formation of free radicals of the form PhS^\bullet is a common feature of the redox reaction of thiols and was confirmed by the positive free radicals scavenging by acrylamide in the reaction mixture in excess methanol (Ukoha *et al.*, 2017; 2018a). This is an indication that the reaction most probably followed the inner-sphere reaction path (Ogori *et al.*, 2021). Negative free radicals scavenging by acrylamide was reported for the oxidation of thiophenol by V (V) (Ukoha *et al.*, 2017).

Test for Intermediate Complex Formation

Michaelis-Menten type of plot of $1/k_{\text{obs}}$ versus $1/[\text{PhSH}]$ (Fig. 6) was linear without an appreciable intercept. This corroborates operation of outer-sphere electron transfer reaction. Inner-sphere electron transfer reaction mechanism was reported for the oxidation of thiophenol by V (V) and the oxidation of thiophenol by Cr (IV) (Ukoha *et al.*, 2017, 2018a).

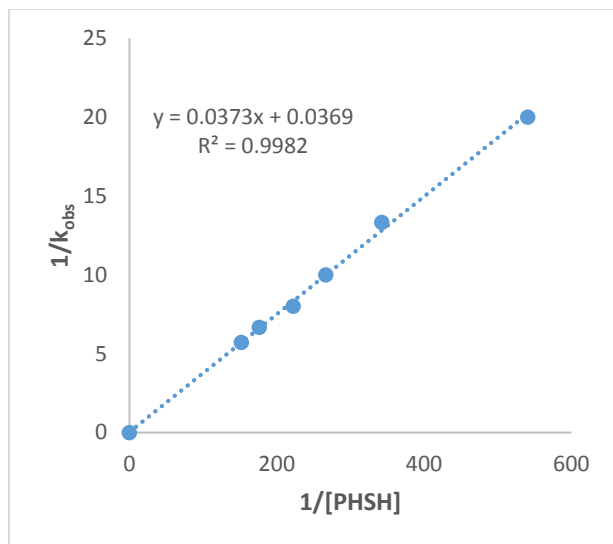
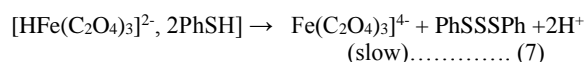
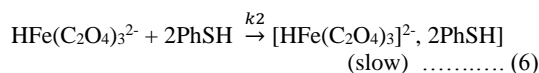
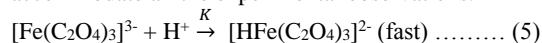


Fig. 6: Plot of $1/k_{\text{obs}}$ against $1/[\text{PhSH}]$ for the reduction of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ by thiophenol at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.6 \text{ mol dm}^{-3}$ (NaCl), $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 29 \pm 0.1 \text{ }^\circ\text{C}$.

Reaction Mechanism

The following reaction mechanism is hereby proposed to accommodate all the experimental observations.



From equations (6) and (7),

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

From equation (5):

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

Substituting equation (10) into (9),

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

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

Equation (12) agrees with equation (4) where $k_3 = a$ and $k_1 k_2 = b$

Conclusion

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 (Oladuninni *et al.*, 2021). Ion catalysis and inhibition has been reported to be a characteristics of an outer sphere reaction mechanism (Ukoha *et al.*, 2023).
- 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 (Ogori and Lohdip, 2017).
- Insignificant positive intercept for Michaelis-Menten plots of $1/k_{\text{obs}}$ versus $1/[\text{PhSH}]$ from (Fig. 4) is in support of an outer sphere reaction pathway (Ogori and Lohdip, 2017).
- Negative 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 (Anweting *et al.*, 2023).

The observations (a –d) is more in support of the outer sphere mechanism and is hereby proposed for the redox reaction of $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]/\text{PhSH}$ system.

References

- Anweting, I. B., Idris, S. O., and Onu, A. D. (2017). Kinetics and mechanism of the oxidation of thiourea by tetrakis (2,2-bipyridine)- μ -oxodiiron (III) complex in aqueous acidic medium. *FUW Trends in Science and Technology Journal*, 2856 – 860.
- Anweting I. B., Okon, I. E. and Jones, I. (2023). Kinetics and Mechanism of the Oxidation of Theophylline by Permanganate Ion in Aqueous Sulphuric Acid Medium. *The Pacific Journal of Science and Technology*, 24, 103 – 109.
- Busari, A., Idris, S. O., Onu, A. D. and Abdulkadir, I. (2019). Kinetics of the oxidation of thiourea by tris(1,10-phenanthroline) iron(III) complex iron in aqueous perchloric acid media. *ATBU Journal of Science, Technology and Education*, 7, 120-129.
- Myek, B., Iyun, J. F. and Idris, S. O. (2014). Preliminary study on the kinetics and mechanism of the oxidation of naphthol greenB by dichromate ion in aqueous hydrochloric acid medium. *Aceh International Journal of Science and Technology*, 3(1): 37 - 42.
- Nkole, I. U. and Osunkwo, C. R. (2019). Kinetics approach To the reduction of ethylenediaminetetraacetatoferrate(III) complex by iodide ion in aqueous acidic medium. *Asian Journal of Physical and Chemical Sciences*, 7(2): 1-8.
- Ogori, B. O. and Lohdip, Y. N. (2017). Kinetics and mechanism of the oxidation of thiosulphate by potassium trisoxalatoferrate(III) in aqueous hydrochloric acid medium. *Chemistry Research Journal*, 2(4): 78-83.

- Ogori, B. O., Lohdip, Y. N. and Apagu, N. T. (2021). Kinetics and mechanisms of the redox reaction of potassium trioxalatoferrate(III) and tetraoxosulphate(VI) ions in aqueous hydrochloric acid medium. *International Journal of Modern Chemistry*, 13(1): 1-11.
- Ogori, B. O., Lohdip, Y. N. and Egila, J. N. (2016). Kinetics and Mechanism of the Oxidation of Potassium trioxalatoferrate(III) trihydrate by Permanganate ion in Aqueous Hydrochloric Acid Medium, *Academic Journal Conference Proceedings*, Article No. D940687.
- Oladunni, N., Idris, S. O., Onu, A. D., & Shallangwa, G. A. (2021) Kinetics and Mechanism of the Oxidation of Catechol by Oxygenated $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]^{5+}$ Complex. *Science Frontiers*, 2, 1-7.
- Ukoha, P. O., Anibodu, C. O., Obeta, U. R., & Oruma, U. S. (2023). Reactions of 2,5-pyridine Dicarboxylic Acid (dicarpy)-bridged Iron (III) Dimer, $[\text{Fe}(\text{saloph})_2-\mu\text{-dicarpy}]$, with β -Mercaptoacetic Acid and β -mercaptoethylamine in Aqueous Perchloric Acid. *Discovery*, e88d1284.
- Ukoha, P. O., Okonkwo, S. O. and Ujam, O. T. (2017). Kinetic and Mechanism of Reduction of Vanadium (V) by Thiophenol in Aqueous Perchloric Acid Medium. *J. Chem. Soc. Nigeria*, 42, 47 – 52.
- Ukoha, P. O., Oruna, U. S., Ukwueze, N. N. and Ujam, O. T. (2018a). Kinetic and Mechanism of Reduction of Tetraoxochromate (VI) by Thiophenol in Aqueous Perchloric Acid Medium. *J. Chem. Soc. Nigeria*, 42, 47 – 52.
- Ukoha, P. O., Ugwanyi, K. O., & Obeta, U. R. (2018b). Reduction of the Adipato-Bridged Binuclear Iron (III) Complex, $[(\text{Fesalen})_2\text{adi}]$ by Thioglycolic Acid: Kinetic and Mechanistic Study. *Communications in Physical Chemistry*, 3, 49-60.