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Kinetic Approach to the Mechanism of the Reduction of Permanganate Ion by Thioglycolic Acid in Aqueous Hydrochloric Acid Medium

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ABSTRACT
The kinetics and mechanism of the electron transfer reaction between permanganate ion (hereafter MnO_4^-) and thioglycolic acid (hereafter TSH) was studied spectrophotometrically under pseudo-first-order conditions of [TSH] >> [MnO_4^-] at T = 25 ± 0.1 °C, [H^+] = 0.15 mol dm^{-3}, I = 0.75 mol dm^{-3} (NaCl) and λ_{max} = 530 nm. Spectrophotometric titration using the mole ratio method revealed that one mole of the permanganate ion reacted with five moles of the thioglycolic acid. The reaction followed first order kinetics with respect to the concentration of each reactant, giving an overall order of two. Reaction rates increased with increasing hydrogen ion concentration, ionic strength, dielectric constant and added ions. The Michaelis-Menten plot of $1/k_{obs}$ versus 1/[TSH] was linear with a small positive intercept (5.46 s) relative to the range of $1/k_{obs}$ values. Although a positive free radical test indicated the formation of transient radical intermediates, the combined kinetic evidence was consistent with a predominantly outer-sphere electron transfer mechanism. The reaction obeys the following rate law:
$\frac{-[TSH]}{dt}$ = (a + b[H^+]) [TSH][MnO_4^-]
The findings contribute to the mechanistic understanding of TSH oxidation in aqueous media and provide a basis for future studies of related sulphur-containing redox systems.

Keywords: Kinetics, Mechanism, Electron Transfer, Pseudo-First-Order, Thiol

INTRODUCTION

Electron transfer reactions play a central role in environmental remediation, biological and industrial systems, pollutant degradation and nutrient cycling (Anweting et al., 2023a & 2023b). Despite the numerous studies on sulphur-containing organic compounds, kinetic and mechanistic investigations on oxidation of TSH ($HSCH_2COOH$) remain limited. This study aims to advance understanding of the redox behaviour of TSH because of its widespread applications in cosmetics (as depilatory agent), metal recovery, leather processing, wheel cleaning formulations, industrial wastewater treatment, environmental remediation and the broader chemistry of sulphur-containing compounds (Nkole et al., 2018a & 2018b). The acid is widely used because it contains both the thiol group (-SH) and carboxylic acid group (-COOH) which accounts for its strong reducing ability (Nkole et al., 2025).

Permanganate ion (MnO_4^-) is a powerful oxidizing and hydroxylating agent that has vast applications as reported in literature because of its versatility (Myek et al., 2018; Anweting et al., 2023a; Mohammed et al., 2009). The extent of oxidation by MnO_4^- is dependent on the pH of the medium and the nature of the reductant. Studies on the redox chemistry of permanganate ion are important for understanding manganese cycling in natural systems.

Previous investigations on the reduction of hexachloroiridate (IV) (Sun & Stanbury, 2002) and an iron (III) complex (Nkole et al., 2018a) by TSH revealed kinetic evidence consistent with radical intermediate formation and electron transfer originating at the sulphur donor atom. A structurally related bifunctional ligand, thiodiglycolic acid, has similarly shown Michaelis-Menten type kinetics in its reduction of an iron (III)-salen complex (Subramaniam et al., 2014). Kinetic investigations of MnO_4^-reduction have primarily involved reductants containing a single redox-active functional group such as aldehydes, alcohols, amino acids and monofunctional thiols. In contrast, TSH is a bifunctional reductant possessing both thiol and carboxylic functional groups, whose combined influence on the kinetics and mechanism of MnO_4^- reduction have received little attention. This knowledge gap motivated the present study.

Therefore, the study was undertaken to elucidate the kinetics and mechanism of the reduction of MnO_4^- by TSH in aqueous acidic medium. Particular emphasis was placed on determining the reaction stoichiometry, order and product(s), evaluating the effects of hydrogen ion concentration, ionic strength, added ions, medium dielectric constant and using these kinetic data to propose a plausible reaction mechanism.

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.

Stoichiometric Studies

The stoichiometry of the reactions was determined by spectrophotometric titration using the mole ratio method. The concentration of MnO_4^- was kept constant at 1.0×10^{-3} mol dm^{-3} while that of TSH was varied between (0.01 – 0.06) mol dm^{-3} at [H^+] = 0.15 mol dm^{-3} and constant ionic strength of 0.75 mol dm^{-3} (NaCl) at 25.0 ± 0.1 ºC. After the completion of the reaction, absorbances of the reaction solutions were obtained at λ_{max} = 530 nm. The stoichiometry was then

determined from the plot of absorbance versus mole ratio of MnO_4^-: TSH (Oladunni et al., 2021).

Product Analysis

Spectroscopic confirmation of the disulphide product was not undertaken in the present study. The organic product identification relied on the established qualitative method of McAuley and Gomwalk (Ukoha et al., 2018), consistent with the approach used in prior kinetic studies of thiol oxidation (Nkole et al., 2018; Nkole et al., 2018b). Spectroscopic verification of the product was considered beyond the scope of this work. For the inorganic product, addition of sodium hydroxide solution to the completely reacted mixture gave a white precipitate which was insoluble in excess and turned brown on exposure to air due to oxidation by atmospheric oxygen to hydrated MnO_2 (Myek et al., 2018). This confirmed Mn^{2+} as the inorganic product of the reaction.

Kinetic Studies

Kinetic runs were done under pseudo-first order conditions with [TSH] in at least 10-fold excess over [MnO_4^-] at the stated conditions of [TSH] = 0.01 – 0.06 mol dm^{-3}, [MnO_4^-] = 0.001 mol dm^{-3}, [I] = 0.75 mol dm^{-3}, [H^+] = 0.15 mol dm^{-3}, T = 25 ± 0.1 ºC and λ_{max} = 530 nm by monitoring the change in the absorbance of the complex 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). The kinetic plots remained linear over at least 90 % extent of the reaction. Second order rate constants, k_2 (with respect to [TSH]), were determined as the ratio of k_{obs}/[TSH] (Babatunde & Ajayi, 2013).

Effect of Hydrogen Ion Concentration on Reaction Rate

The effect of varying hydrogen ion concentration on the reaction rate was investigated by keeping the concentration of the other reactants constant ([TSH] = 0.01 mol dm^{-3}, [MnO_4^-] = 0.001 mol dm^{-3}, [I] = 0.75 mol dm^{-3}) (NaCl) while varying the hydrogen ion concentration in the range of 0.03 – 0.14 mol dm^{-3} using hydrochloric acid (Anweting et al., 2023a).

Effect of Ionic Strength on the Reaction Rate

The effect of ionic strength on the rate of the reaction was studied over the range of (0.225 – 0.6) mol dm^{-3} using NaCl, while other reaction conditions were kept constant ([TSH] = 0.01 mol dm^{-3}, [MnO_4^-] = 0.001 mol dm^{-3}, [H^+] = 0.15 mol dm^{-3}) (Nkole et al., 2025).

Effect of Dielectric Constant

The effect of medium dielectric constant, D, on the reaction rate was investigated by carrying out the reaction in media of varying dielectric constants using acetone/water mixture, while keeping all other conditions constant (Abiti et al., 2018).

Effect of Added Ions on the Reaction Rate

The influence of added ions (CH_3COO^-, $HCOO^-$, K^+, and Mg^{2+}) on the rates of the reaction was investigated by varying the concentration of these ions while keeping the concentration of other reactants constant ([TSH] = 0.01 mol dm^{-3}, [MnO_4^-] = 0.001 mol dm^{-3}, [I] = 0.75 mol dm^{-3}, [H^+] = 0.15 mol dm^{-3}, T = 25 ± 0.1 ºC and λ_{max} = 530 nm (Babatunde & Ajayi, 2013). These ions were selected to distinguish between cationic and anionic catalytic effects.

Test for the Participation of Free Radicals in the Course of the Reaction

The test for free radicals was done by adding 2 g of acrylamide to partially reacted mixture containing various concentrations of the solution of MnO_4^-, TSH, NaCl and hydrogen ion followed by excess methanol. The acrylamide was also added to a separate mixture of MnO_4^- and TSH to serve as control (Anweting et al., 2023b).

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]. The presence or absence of an intercept from this plot would give an idea of the presence or otherwise of intermediate complex formation (Ibrahim et al., 2022).

RESULTS AND DISCUSSION

Stoichiometry

It was observed that one mole of MnO_4^- consumed five moles of TSH as illustrated in Figure 1 and equation 1. A 2:1 stoichiometry has been reported for the oxidation of mercaptoethanolic acid by 2-hydroxyethylethylenediaminetriacetatoiron(III) [Fe(III)HEDTAOH$_2$] (Nkole et al., 2025), 1:1 stoichiometry for the oxidation of TSH by [Fe(III)EDTA] (Nkole et al., 2018a), for the oxidation of TSH by [(Fesalen)$_2$adi] (Ukoha et al., 2018), the oxidation of TSH by [Fe(III)HEDTAOH$_2$] (Nkole et al., 2018b), oxidation of TSH by Mn(salphen)$^+$ (Ibrahim et al., 2022) and the reduction of permanganate ion by malachite green (Mohammed et al., 2009). Differences in stoichiometry likely arise from oxidant structure, oxidant state, reaction medium and reaction conditions.

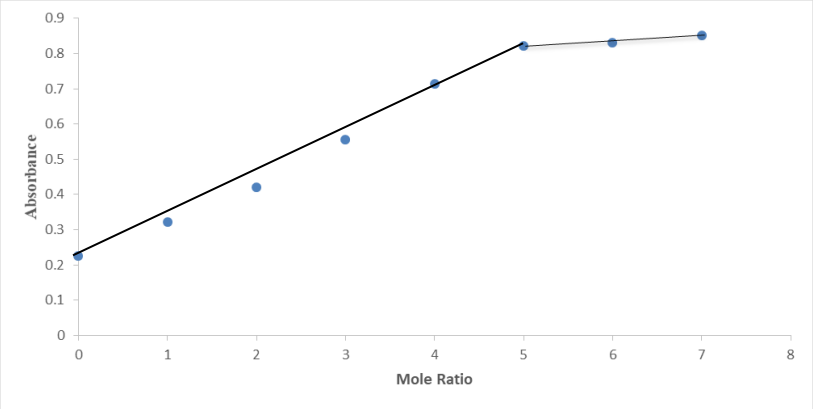

Figure 1: Plot of absorbance versus mole ratio for the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.75 mol dm^{-3} (NaCl), $[H^+] = 0.15$ mol dm^{-3}, $\lambda_{max} = 530$ nm and T = 25 ± 0.1 ºC

$$MnO_4^- + 5HSCH_2COOH + 3H^+ \rightarrow^{5}/_{2} HOOCCH_2SSCH_2COOH + Mn^{2+} + 4H_2O \quad (1)$$

Product Analysis

Subjecting the completely reacted mixture of oxidant and reductant to qualitative analysis showed that a disulphide bond was formed as the organic product and Mn^{2+} as the inorganic product of the reaction. Formation of disulphide (TSST) is consistent with the oxidation of thiols (Nkole et al., 2025; Nkole et al., 2018a; Ukoha et al., 2018; Ibrahim et al., 2022). However, the formation of sulfenic acid (RSOH) was reported for the oxidation of TSH by $[Fe(III)HEDTAOH_2]$ (Nkole et al., 2018b). Earlier researchers have documented Mn^{2+} as the product of the reduction of MnO_4^- by theobromine (Anweting et al., 2023a), the reduction of MnO_4^- by orange II dye (Myek et al., 2018) and the reduction of MnO_4^- by safranin-o (Bugaje et al., 2021).

Order of Reaction

Pseudo-first order plots of log (A_t-A_∞) versus time were linear to more than 90 % extent of the reaction, a suggestion that the reaction is first order with respect to $[MnO_4^-]$ (Figure 2). Plot of log k_{obs} versus log [TSH] was done in order to determine the order of the reaction with respect to [TSH] as shown in Figure 3. The slope of 0.99 indicates that the order of the reaction with respect to [TSH] is first order. The relative uniformity of the values of the second order rate constant, k_2, as shown in Table 1, further supports that the order of the reaction with respect to [TSH] is first order and second order overall (Mohammed et al., 2009; Abdulsalam et al., 2024) and this conforms to the rate equation in equation 2.

$$\frac{-[TSH]}{dt} = k_2 [TSH] [MnO_4^-] \quad (2)$$

Earlier researchers have reported a similar order of reaction (first order) for the reduction of $[(Fesalen)_2adi]$ by TSH (Ukoha et al., 2018), the reduction of [Fe(III)EDTA] by TSH, reduction of $Mn(salphen)^+$ by TSH (Ibrahim et al., 2022), reduction of $[Co(salophen)^+]$ by TSH (Abdulsalam et al., 2024), the reduction of $[Fe(III)HEDTAOH_2]$ by mercaptoethanolic acid (Nkole et al., 2025) and the reduction of permanganate ion by malachite green.

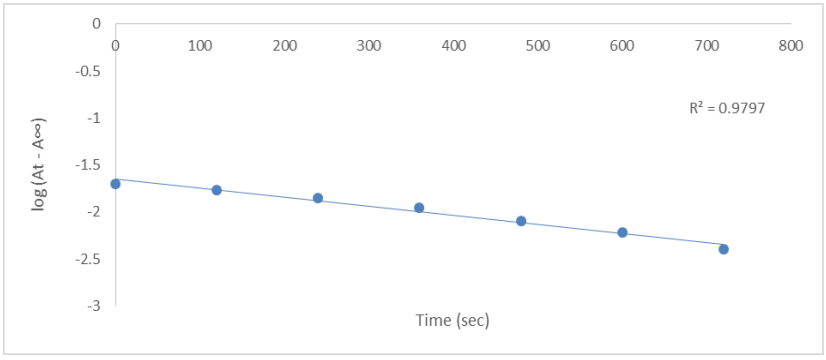

Figure 2: Plot of log (A_t-A_∞) versus time for the reduction of MnO_4^- by TSH at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.75 mol dm^{-3} (NaCl), $[H^+] = 0.15$ mol dm^{-3}, $\lambda_{max} = 530$ nm and T = 25 ± 0.1 ºC

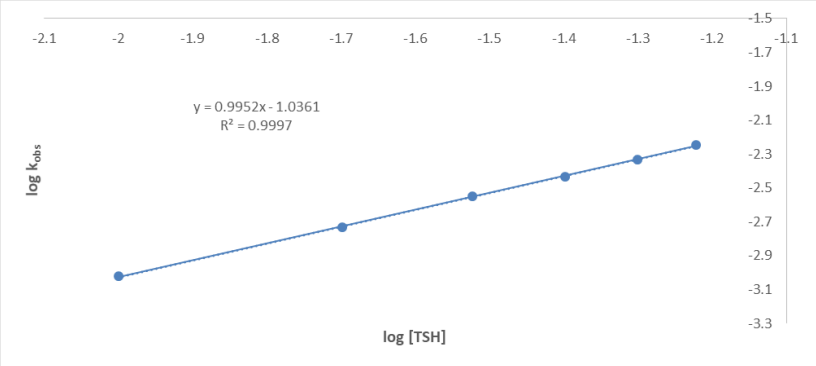

Figure 3: Plot of log k_{obs} versus log [TSH] for the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.75 mol dm^{-3} (NaCl), $[H^+] = 0.15$ mol dm^{-3}, $\lambda_{max} = 530$ nm and T = 25 ± 0.1 ºC

Table 1: **Pseudo-first and second order rate constants for the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.75 mol dm^{-3}(NaCl), $[H^+] = 0.15$ mol dm^{-3}, $\lambda_{max} = 530$ nm and T = 25 ± 0.1 ºC**

10^2 [TSH]mol dm^{-3}	$[H^+]$ mol dm^{-3}	I, mol dm^{-3} (NaCl)	$10^3 k_{obs}$ s^{-1}	$10^2 k_2 dm^3$ mol^{-1} s^{-1}
1.00	0.15	0.75	0.95	9.50
2.00	0.15	0.75	1.85	9.30
3.00	0.15	0.75	2.82	9.40
4.00	0.15	0.75	3.70	9.30
5.00	0.15	0.75	4.65	9.30
6.00	0.15	0.75	5.68	9.40
1.00	0.03	0.75	0.04	0.13
1.00	0.06	0.75	0.11	0.18
1.00	0.08	0.75	0.27	0.34
1.00	0.09	0.75	0.36	0.40
1.00	0.12	0.75	0.68	0.57
1.00	0.14	0.75	0.95	0.68
1.00	0.15	0.225	0.02	0.04
1.00	0.15	0.300	0.21	0.07
1.00	0.15	0.375	0.32	0.09
1.00	0.15	0.450	0.55	0.12
1.00	0.15	0.525	0.78	0.15
1.00	0.15	0.600	1.12	0.19

Effect of Hydrogen Ion Concentration on Reaction Rate

From Table 1, it can be seen that reaction rate increased with increasing hydrogen ion concentration in the concentration range investigated (0.03-0.14) mol dm^{-3}. Protonation of permanganate ion increases its oxidizing ability, facilitating electron transfer. Plot of k_2 versus $[H^+]$ was linear with a positive intercept as shown in Figure 4. The acid dependent rate equation conforms to equation 3 and the overall rate equation is given in equation (4).

$$k_2 = a + b\,[H^+] \quad (3)$$

$$\frac{-[TSH]}{dt} = (a + b\,[H^+])\,[TSH][MnO_4^-] \quad (4)$$

Where $a = 4.0 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} (intercept) and b = 0.0504 dm^6 mol^{-2} s^{-1} (slope)

The rate of the reaction in this case showed parallel pathways: one involving the protonated and the other, the unprotonated species both reacting to give a product (Myek et al., 2018). The acid-independent rate constant obtained for this study is smaller than the values reported for the MnO_4^- oxidation of theophylline, theobromine and malachite green (Anweting et al., 2023a,b; Mohammed et al., 2009), indicating a marked slower reactivity of unprotonated MnO_4^- toward TSH.

Similar results were reported for the oxidation of TSH by [(Fesalen)$_2$adi] (Ukoha et al., 2018), the reduction of [Fe(III)EDTA] by TSH, the reduction of [Fe(III)HEDTAOH$_2$] by mercaptoethanolic acid (Nkole et al., 2025) and the reduction of permanganate ion by malachite green (Mohammed et al., 2009). However, reaction rates were invariant with increase in hydrogen ion concentration for the reduction of $Mn(salphen)^+$ (Ibrahim et al., 2022) and the reduction of $[Co(salophen)^+]$ by TSH (Abdulsalam et al., 2024).

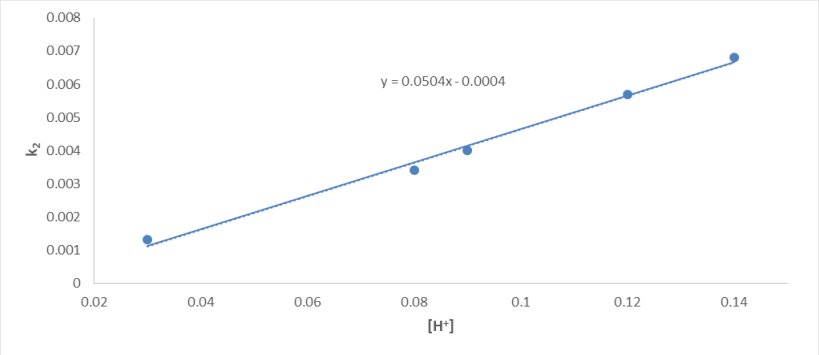

Figure 4: Plot of k_2 versus $[H^+]$ for the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.75 mol dm^{-3} (NaCl), λ_{max} = 530 nm and T = 25 ± 0.1 ºC

Effect of Ionic Strength on the Reaction Rate

The increase in ionic strength of the reaction medium resulted in an increase in the reaction rate within the concentration range studied. This observed positive salt effect suggests that ions of like charges are interacting in the activated complex (Babatunde & Ajayi, 2013). A plot of log k_2 versus $\sqrt{I}$ gave a straight line with a positive slope of 2.17 (Figure 5), indicating the magnitude of charges on the redox species. This observation is consistent with an outer-sphere reaction mechanism (Ibrahim et al., 2022). It has been established that for species of like charges, the rate increases with an increase in ionic strength, while for species of opposite charges, rate decreases as the ionic strength increases (Holder et al., 2000). Results analogous to this were reported by earlier researchers for the oxidation of theophylline by MnO_4^- (Anweting et al., 2023b), the reduction of [Fe(III)EDTA] by TSH and the reduction of [Fe(III)HEDTAOH$_2$] by mercaptoethanolic acid (Nkole et al., 2025). However, lack of primary kinetic salt effect was reported for the reduction of [(Fesalen)$_2$adi] by TSH (Ukoha et al., 2018), reduction of $Mn(salphen)^+$ by TSH (Ibrahim et al., 2022), and reaction rate was observed to decrease with increase in ionic strength for the reduction of permanganate ion by malachite green (Mohammed et al., 2009) and for the reduction of $[Co(salophen)^+]$ by TSH (Abdulsalam et al., 2024).

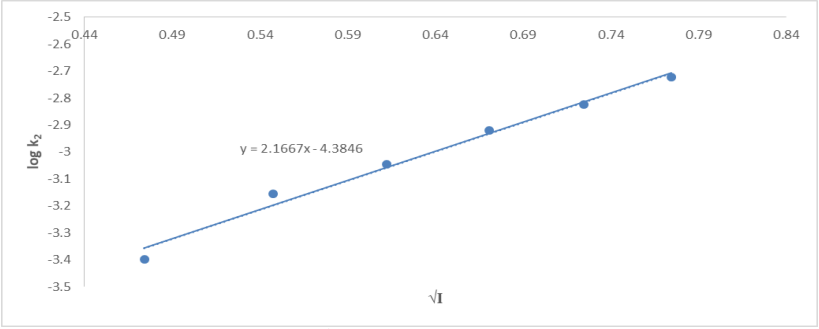

Figure 5: Plot of log k_2 versus $\sqrt{I}$ for the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H^+]$ = 0.15 mol dm^{-3}, λ_{max} = 530 nm and T = 25 ± 0.1 ºC

Effect of Medium Dielectric Constant

The rate of the reaction decreased as the dielectric constant of the reaction medium, D, decreased from 77.10 to 51.10 as shown in Table 2. Changes in dielectric constant could alter the rate or course of a reaction because as dielectric constant decreases, degree of ion paring increases due to increase in the magnitude of electrostatic attraction (Ukoha et al., 2018). For reactions operating by the formation of ion-pair precursor complexes, decrease in D will accelerate the reaction where ions of opposite charges are involved. A decrease in D increases the rate of reaction where like-charged ions are involved and decrease in D will not affect the reaction rate when one of the participating species is neutral (Ukoha et al., 2018). Reaction rate was observed to decrease with decrease in D as reported for the reduction of [Fe(III)HEDTAOH$_2$] by mercaptoethanolic acid (Nkole et al., 2025) and increase with increase in D for the reduction of [Fe(III)HEDTAOH$_2$] by TSH (Nkole et al., 2018b). However, lack of dependence of the reaction on dielectric constant was reported for the reduction of [(Fesalen) $_{2adi}$] by TSH (Ukoha et al., 2018).

Table 2 Effect of dielectric constant on the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at [MnO_4^-] = 1.0 × 10^{-3} mol dm^{-3}, [TSH] = 0.01 mol dm^{-3}, I = 0.75 mol dm^{-3}(NaCl), [H^+] = 0.15 mol dm^{-3}, λ_{max} = 530 nm and T = 25 ± 0.1 ºC

D	$10^2$1/D	10^3k_{obs}, s^{-1}	10^2k_2, dm^3 mol^{-1} s^{-1}
77.10	1.30	12.20	4.07
72.20	1.38	9.28	3.71
67.05	1.49	6.95	3.48
61.92	1.61	4.86	3.24
56.25	1.78	2.88	2.88
51.10	1.96	2.22	2.44

Effect of Added Ions on Reaction Rate

It was observed that reaction rate increased with increase in the concentration of added ions (K^+, Mg^{2+}, $HCOO^-$ and CH_3COO^-) within the concentration range investigated as shown in Table 3. This implies that the reaction proceeded through the outer-sphere mechanistic pathway in which the reactant ions maintain their coordination integrity in the activated complex prior to and during the electron transfer process (Abdulsalam et al., 2024). These observations suggest that the reactant species at the activated complex are like-charged and the solvent molecules close to the complex are subject to strong electrostatic forces (Nkole et al., 2018a). Earlier researchers have reported the catalysis of added ions for the reduction of [Fe (III) EDTA] by TSH (Nkole et al., 2018a) and the reduction of [Fe (III) HEDTAOH2] by mercaptoethanolic acid (Nkole et al., 2025). However, lack of anion or cation catalysis was reported for the reduction of [$(Fesalen)_{2adi}$] by TSH (Ukoha et al., 2018) and inhibition of reaction rate was reported for the reduction of permanganate ion by safranin-O (Bugaje et al., 2021). Together with the ionic strength and dielectric constant studies, the added ions effect provides complementary evidence for the proposed reaction pathway.

Test for Free Radicals

Polymerization test to detect the presence of free radicals on the reaction was done and confirmed by the positive free radicals scavenging by acrylamide in the reaction mixture in excess methanol by the formation of gelatinous precipitate (Abiti et al., 2018). This observation is often taken as evidence for an inner-sphere reaction pathway (Babatunde & Ajayi, 2013). This agrees with a work earlier reported for the reduction of [Fe(III)EDTA] by TSH (Nkole et al., 2018a), reduction of [$Fe(III)HEDTAOH_2$] by TSH (Nkole et al., 2018b), the reduction of [$Fe(III)HEDTAOH_2$] by mercaptoethanolic acid (Nkole et al., 2025) and the reduction of safranin-o by permanganate ion (Bugaje et al., 2021). Although radical intermediates are often associated with inner-sphere pathways, they may also arise following the initial electron transfer steps in outer-sphere reactions. Consequently, the free radical test alone is not sufficient to distinguish between the two mechanisms.

Table 3: Effect of added ions on the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at [MnO_4^-] = 1.0 × 10^{-3} mol dm^{-3}, [TSH] = 0.01 mol dm^{-3}, I = 0.75 mol dm^{-3}(NaCl), [H^+] = 0.15 mol dm^{-3}, λ_{max} = 530 nm and T = 25 ± 0.1 ºC

X	[X], 10^1 mol dm^{-3}	10^3 k_{obs}, s^{-1}	10^2 k_2, dm^3 mol^{-1} s^{-1}
CH_3COO^-	0.75	0.13	0.17
	1.50	0.35	0.23
	2.25	0.62	0.28
	3.00	0.99	0.33
	3.75	1.38	0.37
$HCOO^-$	0.75	0.22	0.29
	1.50	0.52	0.35
	2.25	0.89	0.40
	3.00	1.34	0.45
	3.75	1.85	0.50
Mg^{2+}	0.75	1.01	1.35
	1.50	2.18	1.45
	2.25	3.46	1.54
	3.00	6.55	2.18
	3.75	8.51	2.27
K^+	0.75	0.55	0.73
	1.50	1.18	0.79
	2.25	1.95	0.86
	3.00	2.83	0.94
	3.75	3.88	1.04

Test for Intermediate Complex Formation

Michaelis-Menten type of plot of $1/k_{obs}$ versus 1/[TSH] was linear with a small positive intercept (5.46 s, relative to the range of $1/k_{obs}$ values) (Figure 6). The small intercept indicates that any complex formed is either weakly associated or present at concentrations too low to significantly influence the overall reaction rate. This suggests the absence of a kinetically significant intermediate complex and is consistent with a predominantly outer-sphere electron transfer mechanism (Myek et al., 2018). Similar reports have been documented by earlier researchers for the reduction of [Fe(III)EDTA] (Nkole et al., 2018a), $[Co(salophen)^+]$, (Abdulsalam et al., 2024) and $Mn(salphen)^+$ (Ibrahim et al., 2022), by TSH, the reduction of $[Fe(III)HEDTAOH_2]$ by mercaptoethanolic acid (Nkole et al., 2025) and the reduction of permanganate ion by methylene blue (Osunlaja et al., 2012) and methyl orange (Myek et al., 2026). However, the likely formation of intermediate complex was reported for the reduction of $[(Fesalen)_{2adi}]$ by TSH (Ukoha et al., 2018).

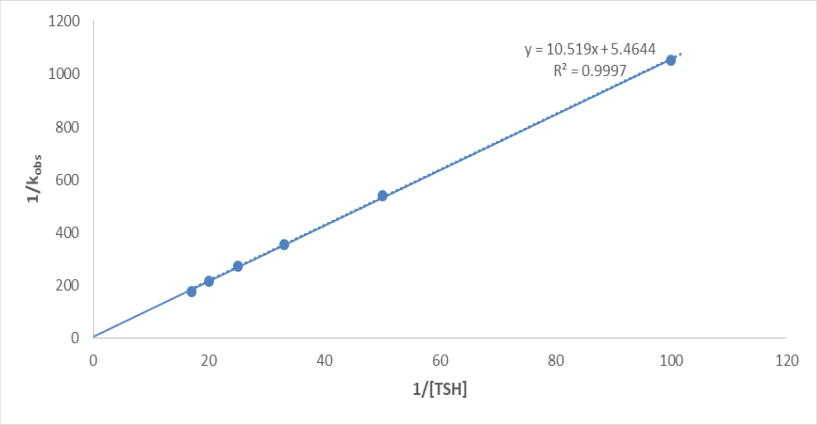

Figure 6: Plot of $1/k_{obs}$ versus 1/[TSH] for the reduction of MnO_4^- by TSH in aqueous hydrochloric acid medium at $[MnO_4^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 0.15$ mol dm^{-3}, I = 0.75 mol dm^{-3} (NaCl), $\lambda_{max} = 530$ nm and T = 25 ± 0.1 ºC

Mechanism of the Reaction

$MnO_4^- + H^+ \rightleftharpoons [HMnO_4]$ (fast) k_1 (5)

$HMnO_4 + TSH \rightleftharpoons [HMnO_4, TSH]$ (fast) (6)

$[HMnO_4, TSH] \rightarrow MnO_4^{2-} + TS^{\bullet} + 2H^+$ (slow) k_2 (7)

$MnO_4^- + TSH \rightarrow MnO42^- + TS^{\bullet} + H^+$ (slow) k_3 (8)

$2TS^{\bullet} \rightarrow TSST$ (9)

$MnO_4^{2-} + 4TSH + 4H^+ \rightarrow Mn^{2+} + 4TS^{\bullet} + 4H_2O$ (10)

From equations (6), (7) and (8),

$Rate = k_2 [HMnO_4] [TSH] + k_3 [MnO_4^-] [TSH]$ (11)

From equation (5):

$[HMnO_4] = k_1 [MnO_4^-] [H^+]$ (12)

Substituting equation (12) into (11),

$Rate = k_2k_1 [MnO_4^-] [H^+] [TSH] + k_3 [MnO_4^-] [TSH]$ (13)

$Rate = (k_3 + k_2k_1 [H^+]) [MnO_4^-] [TSH]$ (14)

Equation (14) agrees with equation (4) where $k_3 = a = 4.0 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} and $k_1k_2 = b = 5.04 \times 10^{-2}$ dm^6 mol^{-2} s^{-1}.

It should be noted that the mechanism above rests on kinetic diagnostics such as salt effects, dielectric-constant dependence, added ion catalysis and the Michaelis-Menten intercept rather than direct spectroscopic detection of the proposed $[HMnO_4\text{-}TSH]$ precursor complex or the $TS^{\bullet}$ radical. Also, no activation parameters were determined as kinetic runs were carried out at a single temperature.

CONCLUSION

The electron transfer reaction for the reduction of MnO_4^- by TSH showed that the reaction followed first-order kinetics with respect to each reactant and second-order overall, and a 1:5 stoichiometry. Increase in $[H^+]$, ionic strength and added ions caused a corresponding increase in reaction rate. However, decrease in medium dielectric constant resulted in a decrease in reaction rate. Plot of $1/k_{obs}$ versus 1/[TSH] was linear with a small intercept (5.46 s) relative to the range of $1/k_{obs}$ values while gel formation was observed on addition of acrylamide to partially reacted mixture.

Although the free radical test suggested the formation of transient radical intermediates, the overall collective kinetic evidence more strongly supports a predominantly outer-sphere electron transfer mechanism for the reduction of MnO_4^- by TSH. These findings contribute to the mechanistic understanding of TSH oxidation in aqueous media and provide a basis for future studies of related sulphur-containing redox systems.

The absence of activation parameters and direct spectroscopic evidence for intermediates limits a definitive mechanistic assignment. Future studies involving temperature-dependent kinetics and spectroscopic or computational investigations are recommended to further elucidate the reaction mechanism.

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