FULafia Journal of Science & Technology
ISSN (print) 2449-0954 \ ISSN (online) 2636-4972
https://lafiascijournals.org.ng/index.php/fjst
Sponsored By TERTIARY EDUCATION TRUST FUND
Manuscript => Received: Dec., 2025; Accepted: April, 2026; Published: May, 2026 https://doi.org/10.62050/fjst2026.v10n2.678

SPECTROPHOTOMETRIC INVESTIGATION OF REDOX REACTION BETWEEN METHYL ORANGE AND TETRAOXOMANGANATE(VII) ION IN AQUEOUS ACID: KINETICS AND MECHANISTIC APPROACH

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ABSTRACT

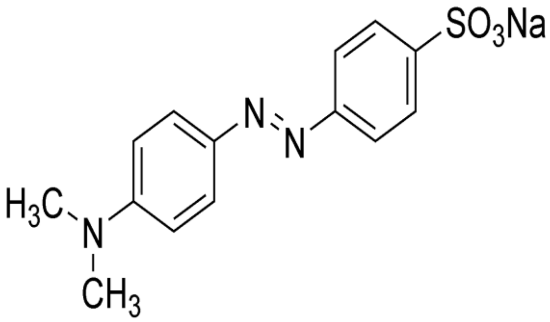
The spectrophotometric investigation of the redox reaction between methyl orange (here after referred to as MO) and tetraoxomanganate(VII) has been studied in aqueous acid using sodium chloride (NaCl) as an ionic strength I = 0.50 Cmol dm^{-3}, hydrogen ion concentration = 1.0 × 10^{-3} mol/dm^{3} (H_2SO_4) and Temperature = 24±1 °C. The redox reaction showed a stoichiometry of 2:1 and the overall reaction conforms to the rate law: $\frac{-d[MO]}{dt} = k_2[MO][MnO_4^-]$. The reaction is first order with respect to both the oxidant and reductant concentrations. Lack of polymerization from this reaction suggests probable absence of free radical formation during the course of the reaction. The rate of reaction showed lack of hydrogen ion concentration dependence. The result of ionic strength showed zero effect on the rate of the reaction. Added ions catalyzed the rate of the reaction. Outersphere mechanism is proposed for this reaction.

Keywords: Mechanism, Methyl orange, Redox, Polymerization

INTRODUCTION

The first generally accepted theory of electron was developed by Marcus (2006) to address outer-sphere electron transfer and was based on a transition-state theory approach. The theory of electron transfer was then extended to include inner-sphere electron transfer by Noel Hush and Marcus (Reimers *et al.*, 2015). The resultant theory, called Marcus-Hush theory (Reimers *et al.*, 2015), has guided most discussions on electron transfer ever since. Both theories are, however, semi-classical in nature, although they have been extended following earlier work in non-radiative transitions (Susan *et al.*, 1978). It is well established in inorganic electron transfer reactions that electron transfer processes must be preceded by the reorganization of the solvation (also called hydration) shells surrounding reactants (Reynolds & Lumry, 1966). It was Libby (1952) who accounted for this phenomenon based on the Franck-Condon principle, suggesting that, before the fast electron transfer can occur, the slower nuclear rearrangements of water molecules in the hydration shells must take place, the proton being 1,836 times as massive as the electron (Ji, 2012).

Methyl orange is an azobenzene derivative that can be formed from dimethylaniline and sulfanilic acid, first through a diazonium salt formation with the sulfanilic acid, followed by a nucleophilic attack from the dimethylaniline and rearomatization (Liu & Shi, 2005). Methyl orange is a synthetic pH indicator widely used in analytical chemistry, especially for acid-base titration. Known for its vivid and distinct color change, methyl orange helps chemists accurately identify pH changes within a specific range. In the UV/Visible range, absorption of methyl orange is occurred between 350 – 550 nm. This explained the green-purple visible light range that established the orange colour of methyl orange (Ayed *et al.*, 2010). Despite the uses of this dye (Scheme 1), the knowledge of its redox reaction has not received much attention, which prompted the research in this area.



Scheme 1: Structure of the dye

Permanganate generally called tetraoxomanganate(VII) ion, (MnO_4^-) has +7 oxidation state and is therefore a strong oxidising agent. It is a tetrahedral geometry compound (Dash *et al.*, 2009). The solution which is slightly stablein neutral or alkaline medium is purple in colour. Trichloroethane ($C_2H_3Cl_3$) is oxidised by permanganate to form CO_2, MnO_2, sodium ion, chloride ions and hydronium ion. Thisreport present findings on the redox reaction of methyl orange with tetraoxomanganate(VII) ion in aqueous medium with the aim to underpin and publicized the knowledge of the kinetic data that characterize this reaction.

MATERIALS AND METHODS

A 1×10^{-3} mol dm^{-3} stock solution of MO was prepared by dissolving 0.082 g in 250 ml volumetric flask using distilled water. A 0.1 mol dm^{-3} $KMnO_4$ was prepared by dissolving 0.395 g in 25 ml distilled water. H_2SO_4 furnishes H^+ in the medium. Calcium chloride and sodium nitrate solution were prepared using a known volume of distilled water. Spectrophotometer UV-2500PC series between wavelength range 400–600 nm was used to determine the absorption maxima of MO (λ_{max} = 465 nm)

Stoichiometry

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method by keeping the concentration of the dye constant at 4.8×10^{-5} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ_{max} = 465 nm, T = 24 ± 1 °C, and [MO] = $(0.200 - 2.00) \times 10^{-4})$ mol dm^{-3}. The stoichiometry was determined from the plot of absorbance versus [reductant]/[oxidant] after the reaction had reached completion by the observation of a steady zero absorbance value over a period of two days (Adetoro *et al.*, 2023).

Kinetic Studies

The kinetic experiments were conducted under pseudo – first order conditions with $[MnO_4^-]$ in at least 90 - fold excess over methyl orange [MO] at temperature 24± 1 °C and ionic strength, I = 0.50 mol dm^3 (NaCl). The pseudo-first order plots of log $(A_t - A_\infty)$ versus time, were made (where A_t and A_∞ are the absorbance at time t and at the end of the reaction respectively). From the slope of the plots, the pseudo-first order rate constant (k_1) was determined (Myek *et al.*, 2018).

Ionic Strength of the Reaction Rate and Free Radical Test

The effect of ionic strength on the rate of the reaction was studied in the range of 0.3 - 1.0 mol dm^{-3} (NaCl) while the concentrations of other reagents were kept constant temperature of 24 ± 1 °C. Free radical test was carried out by addition of acrylonitrile to the reaction mixture, with an excess methanol.

Changes in Hydrogen Ion on the Reaction Rate and Added Ions

Tetraoxosulphate(VI) acid concentration range $(1.0 - 25.0) \times 10^{-3}$ mol dm^{-3} was used to elucidate the influence of hydrogen ions on the reaction rate while the [MO] and $[MnO_4^-]$ were kept constant at 24± 1 °C and I = 0.50 mol dm^{-3} (NaCl). Ca^{2+} and NO_3^- on the reaction rates were investigated by varying the concentrations of the substrates in the range $(40–100) \times 10^{-3}$ mol dm^{-3}, while keeping all other conditions constant.

RESULTS AND DISCUSSION

The stoichiometric study showed that two moles of MO was oxidised by one mole of MnO_4^-. The overall stoichiometry equation is represented in equation (1).

$$2MO + MnO_4^- \rightarrow Mn^{2+} + O_2^{2-} + 2MO^- + O_2 \qquad (1)$$

A similar report of 2:1 can be found in the oxidation of orange II with permanganate ion (Myek *et al.*, 2018). Plot of $Logk_1$ against log $[MnO_4^-]$ was linear with a slope of 1.0 (Fig. 1) indicating that the reaction is first order with respect to the oxidant $[MnO_4^-]$. This result agreed with the literature by Anweting *et al.* (2023). Constancy of k_2 values obtained in this work further clarified the first order dependence on $[MnO_4^-]$ as can be similarly seen in Adetoro *et al.* (2023). With this, equation (2) is similar to the rate law:

$$\frac{-d[MO]}{dt} = k_2[MO]\left[MnO_4^-\right] \qquad (2)$$

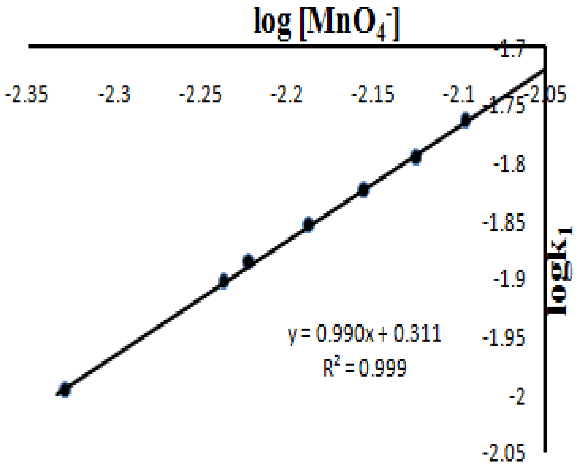


Figure 1: Michaelis-Menten sketch of $1/k_1$ against $1/[MnO_4^-]$ for the redox reaction between Methyl Orange and MnO_4^- at [MO] = 4.8×10^{-5} mol dm^{-3}, $[MnO_4^-] = (4.7 – 8.0) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 465 nm and T= 24 ± 1 °C

Table 1: First order and second order rate constants for the reaction of MO and MnO_4^- at [MO] = 4.8 × 10^{-5} mol dm^{-3}, λ = 465 nm and T = 24 ± 1 °C

$10^3[MnO_4^-]$, mol/dm^3	$10^3[H^+]$, mol/dm^3	10^1[I], mol/dm^3	10^2k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
4.7	1.0	5.0	1.01	2.15
5.8	1.0	5.0	1.25	2.16
6.0	1.0	5.0	1.30	2.17
6.5	1.0	5.0	1.40	2.15
7.0	1.0	5.0	1.50	2.14
7.5	1.0	5.0	1.60	2.13
8.0	1.0	5.0	1.72	2.15
6.5	1.0	3.0	1.39	2.14
6.5	1.0	5.0	1.40	2.15
6.5	1.0	6.0	1.41	2.17
6.5	1.0	7.0	1.40	2.16
6.5	1.0	8.0	1.39	2.14
6.5	1.0	9.0	1.40	2.15
6.5	1.0	10.0	1.41	2.17
6.5	1.0	5.0	1.40	2.15
6.5	3.0	5.0	1.42	2.18
6.5	10.0	5.0	1.48	2.28
6.5	15.0	5.0	1.40	2.15
6.5	25.0	5.0	1.39	2.14

The result obtained for the effect of changes in ionic strength (Table 1) showed that the rate of reaction did not affect the rate of the reaction medium. This obeys a zero BrØnsted-Debye salt effect, implying that the rate determining step is composed of reactants of charge and neutral species in the activated complex (Bensen, 1969; Birk, 1978; Jones *et al.*, 2023). Lack of changes in the rate of reaction when hydrogen ion concentration was varied in the range (1.0 - 25) ×10^{-3} mol dm^{-3} as showed in Table 1, indicate that neither the oxidant nor the reductant undergoes significant protonation under the reaction conditions (Rao *et al.*, 1987).

Table 2: Added Ca^{2+} and NO_3^- on the rate of reaction of MO with MnO_4^- at [MO] = 4.8 × 10^{-5} mol dm^{-3}, $[MnO_4^-]$ = 6.5 × 10^{-3} mol dm^{-3}, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, I = 0.50 mol dm^{-3}, T = 24 ± 1 °C and λ = 465 nm

Ion	10^3[ion], Mol dm^{-3}	10^2k_1, s^{-1}	k_2, dm^{-3} $mol^{-1}s^{-1}$
Ca^{2+}	0.0	1.40	2.15
	40.0	1.50	2.31
	60.0	1.63	2.51
	80.0	1.88	2.89
	100.0	1.97	3.03
NO_3^-	0.0	1.39	2.14
	40.0	1.54	2.36
	60.0	1.75	2.69
	80.0	1.94	2.98
	100.0	2.01	3.09

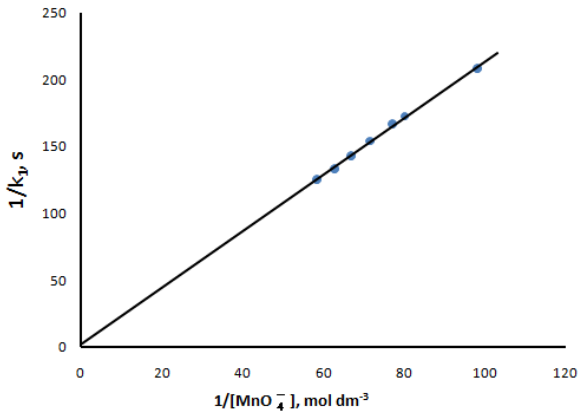


Figure 2: Michaelis-Menten sketch of $1/k_1$ against $1/[MnO_4^-]$ for the redox reaction between Methyl Orange and MnO_4^- at [MO] = 4.8 × 10^{-5} mol dm^{-3}, $[MnO_4^-]$ = (4.7 – 8.0) × 10^{-3} mol dm^{-3}, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, I = 0.50 mol dm^{-3} , λ = 465 nm and T= 24 ± 1 °C

The results illustrated in (Table 2) shows that added ions increased the rate of the reactions, which is an evidence of outersphere mechanism (Mayer & Taube, 1987). Michaelis-Menten sketch of $1/k_1$ against $1/[MnO_4^-]$ is similar to the report in Adetoro *et al.* (2023) which yielded a straight line with zero intercept (Fig. 2). This indicates lack of intermediate complex, thereby supporting outersphere mechanism. Polymerisation test to determine the participation of free radicals in the reaction was negative as no gel was formed on the addition of acrylonitrile to partially reacted reaction mixture in excess methanol. Based on the results obtained, the evidence suggests that this reaction is probably operating by the outersphere mechanism. From the results, the plausible mechanism is given in equations 3 – 5.

$$2MO + HMnO_4 + H^+ \xrightarrow{k_1} Mn^{2+} + 2MOH^- + 2O_2 \quad (3)$$

$$MO + MnO_4^- \xrightarrow{k_2} Mn^{2+} + MO^- + O_2^{2-} + O_2 \text{ slow} \quad (4)$$

$$\text{Rate} = k_2[MO][MnO_4^-] \quad (5)$$

Equation 5 is similar to Equation 2 where $k_2 = k_2$

CONCLUSION

Spectrophotometric investigation of redox reaction between MO and tetraoxomanganate(VII) studied in the presence of acid showed a 2:1 stoichiometric, first order with respect to [MO] and $[MnO_4^-]$. The rate of reaction showed lack of hydrogen ion concentration dependence. The result of ionic strength showed no effect on the rate of the reaction. Added ions accelerated the reaction and addition of acrylonitrile in partially reacted mixture lead to no gel formation. Sketch of $1/k_1$ against $1/[MnO_4^-]$ gave a straight line that passes through origin. Conclusively the result can be proposed for the operation of probably outersphere mechanism.

Conflict of interest: The authors declare that there are no conflicts of interest.

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