

Kinetics and Mechanism of the Oxidation of Indigo Carmine by Permanganate Ion in Aqueous Acidic Medium

S. O. Falodun^{1, *}, S. O. Idris², E. O. Ojo¹, J. F. Iyun²

¹Department of Science Infrastructure, National Agency for Science and Engineering Infrastructure (NASeni), Idu-Industrial Area, Abuja, Nigeria

²Department of Chemistry, Faculty of Science, Ahmadu Bello University, Zaria, Nigeria

Abstract

The kinetics of the oxidation of indigo carmine (disodium 3, 3'-dioxobi-indolin-2, 2'-ylidene-5, 5' disulphonate) with permanganate ion have been studied in aqueous sulphuric acid at $26 \pm 1^\circ\text{C}$, $I = 0.25 \text{ mol dm}^{-3}$ (Na_2SO_4) by monitoring the absorbance of indigo carmine (IC) at 610 nm. The reaction is first order in $[\text{IC}]$ and $[\text{MnO}_4^-]$ and a stoichiometric mole ratio of IC: MnO_4^- is 1:1. The rate of reaction is independent on changes in ionic strength and added cations did not affect the reaction rate which further supports the effect of changes in ionic strength. The experiment rate law obtained is: $\text{Rate} = (K + K''[\text{H}^+]) [\text{IC}][\text{MnO}_4^-]$. A plausible mechanism has been proposed on the basis of our experimental results.

Keywords

Kinetic, Mechanism, Indigo Carmine, Permanganate, Acidic Medium

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1. Introduction

Permanganate ions are widely used as oxidizing agent in synthetic and analytical chemistry [1] and also as a disinfectant [2]. It has been used in the determination of content of pharmaceutical formulation [3], as oxidizing agent for removal of organic molecules and heavy metals from the nuclear wastes [4]. In acidic medium, it exists in different forms as HMnO_4 , H_2MnO^+ , HMnO_3 , and Mn_2O_7 and depending on the nature of the reductant, the oxidant has been assigned both the inner-sphere and the outer-sphere pathways in their redox reactions [5].

Indigo carmine with a molecular formula of $\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$ is a dye and a derivative of indigo tin, which comes from tropical leguminous plants, *Indigofera species*. Due to its sharp absorption peak, it has been used as indicator substance in a number of kinetic analytical methods [6]. It is used as microscopic stain and as diagnostic dye [7]. It is also useful

in food industry, as food additive [8], in pharmaceuticals and cosmetics Industry [9]. The indigo carmine is considered as a highly toxic indigoid class of dye. Contact with it can cause skin and eye irritations. It can also cause permanent injury to cornea and conjunctiva [10].

For effective use and application of both oxidant and reductant in industries and laboratories, the kinetics and mechanisms of their reactions is therefore reported in this paper.

2. Materials and Methods

2.1. Materials

Stock solution of indigo carmine $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ (BDH, AR) and 0.1 mol dm^{-3} of permanganate ion were prepared by dissolving 0.66 g and 2.42 g of MnO_4^- in distilled water in

* Corresponding author

E-mail address: serifatolamide@gmail.com (S. O. Falodun), emmacyosy13@gmail.com (E. O. Ojo)

100 dm³ volumetric flasks respectively. The electronic spectrum of solution was run and the $\lambda_{\text{max}} = 610$ nm of indigo carmine and the resulting solution of permanganate were standardized.

Sodium sulphate (BDH, AR) was used to maintain the ionic strength of the medium constant and 0.1 mol dm⁻³ solution of sulphuric acid (BDH) was also prepared (96.50%, specific gravity 1.83) to investigate the effect of hydrogen ion on the rate of the reaction. All other reagents used were of analar grade.

2.2. Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [16]. The concentration of indigo carmine (IC) was kept constant at 2.8×10^{-5} mol dm⁻³, $[\text{H}^+] = 1 \times 10^{-5}$ mol dm⁻³, and $I = 0.25$ mol dm⁻³, $\lambda_{\text{max}} = 610$ nm while that of permanganate ion was varied in the range $(0.7 - 7.0 \times 10^{-5})$ mol dm⁻³. The reactions were allowed to go to completion and the stoichiometries were determined from the plots of absorbances versus mole ratio of the reactants. Points of inflexion on the curves of the absorbances versus mole ratio correspond to the stoichiometries of the reactions (Fig 1).

2.3. Kinetic Measurements

The kinetic of the reaction was monitored using a Jenway 6405 UV/VIS spectrophotometer at $26 \pm 1^\circ\text{C}$, $I = 0.25$ mol dm⁻³ (Na_2SO_4) and $[\text{H}^+] = 1 \times 10^{-5}$ mol dm⁻³ (H_2SO_4). The rates of the reaction were monitored by following the rate of the decrease in absorbance of the dye (in each case) at $\lambda_{\text{max}} = 610$ nm. All kinetics measurement was carried out under pseudo-first order conditions with the respective oxidants in at least 10-fold excess over the dye concentration. The hydrogen ion concentration, ionic strength and the temperature of each of the reaction systems were kept constant. Pseudo-first order rate constants for the reactions were obtained from the plots of the logarithm of absorbance difference against time i.e. $\log(A_t - A_\infty)$ versus time where A_t is the absorbance at the time t while A_∞ is the absorbance at infinity. The pseudo-first order rate constant (k_1) was determined. The second order rate constant (k_2) was obtained from k_1 as $k_2 = k_1 / [\text{MnO}_4^-]$. A typical pseudo first order plot is presented in Fig. 2.

2.4. Observable Effects

2.4.1. Effect of Ionic Strength of the Reaction Medium on the Reaction Rate

The effect of ionic strength of the rate of the reaction was investigated in the range of 0.1-0.4 mol dm⁻³ (Na_2SO_4) while the concentration of other reactants was kept constant at $26 \pm 1^\circ\text{C}$. The result is presented in Table 1.

2.4.2. Effect of Added Cations and Anions on the Reaction Rate

The effect of added cations and anions were investigated for $X = 10 \times 10^{-3} - 80.0 \times 10^{-3}$ mol dm⁻³ ($X = \text{K}^+$ and Mg^{2+}) and the concentration of other reactants was kept constant at $26 \pm 1^\circ\text{C}$ and ionic strength of 0.25 mol dm⁻³ (Na_2SO_4). The result is presented in Table 2.

2.4.3. Effect of Changes of Acid Concentration on the Reaction Rate

The effect of $[\text{H}^+]$ on the rate of the reaction was studied using sulphuric acid in the range $(0.25 - 1.75) \times 10^{-5}$ mol dm⁻³ while the concentration of MnO_4^- and IC were constant at $I = 0.25$ mol dm⁻³ (Na_2SO_4) and $T = 25 \pm 1^\circ\text{C}$. The results are presented in Table 1.

2.5. Test for Intermediate Complex Formation

Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture one minute after the start of the reaction with that of the final product within a wavelength of 500-700 nm. Michaelis-Menten's plot of $1/k_1$ versus $1/[\text{MnO}_4^-]$ was also made (Fig. 3).

2.6. Test for Free Radicals

Acrylamide was added to test for the presence of any free radical under working conditions in the presence of excess methanol. There was no polymerization after the addition of excess methanol confirming that no free radical was detected.

2.7. Product Analysis

At the completion of the reaction, the reaction mixtures were analyzed for the type of products formed. Mn^{2+} was qualitatively identified.

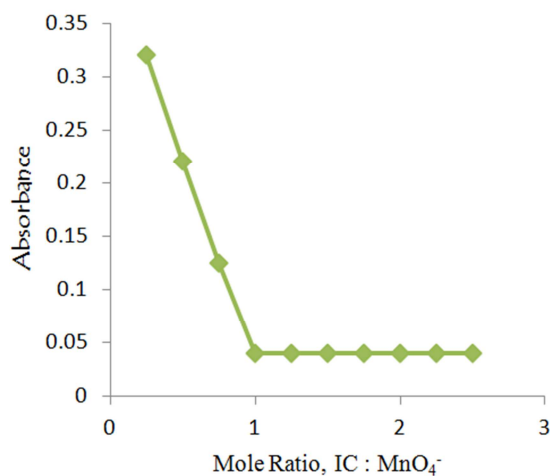


Figure 1. Plot of absorbance versus mole ratio for the redox reaction of indigo carmine with MnO_4^- at $[\text{IC}] = 2.80 \times 10^{-5}$ mol dm⁻³, $[\text{MnO}_4^-] = (0.7 - 7.0) \times 10^{-5}$ mol dm⁻³, $[\text{H}^+] = 1.0 \times 10^{-5}$ mol dm⁻³, $I = 0.25$ mol dm⁻³, $\lambda_{\text{max}} = 610$ nm and $T = 26 \pm 1^\circ\text{C}$.

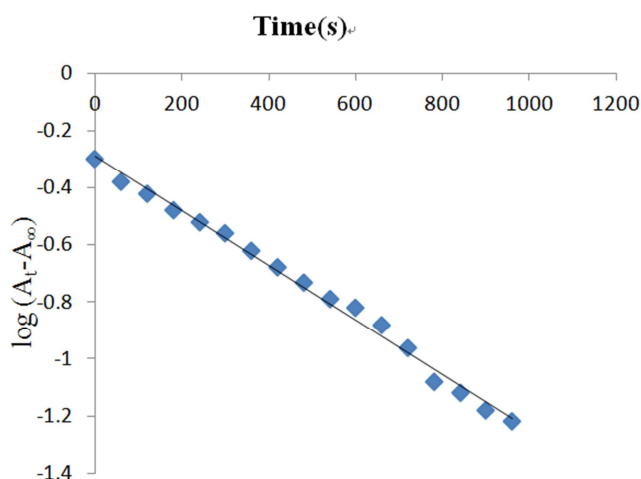


Figure 2. Typical pseudo first order plot for the redox reaction of indigo carmine with MnO_4^- at $[\text{IC}] = 2.8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 4.20 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.25 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 610 \text{ nm}$ and $T = 26 \pm 1^\circ\text{C}$.

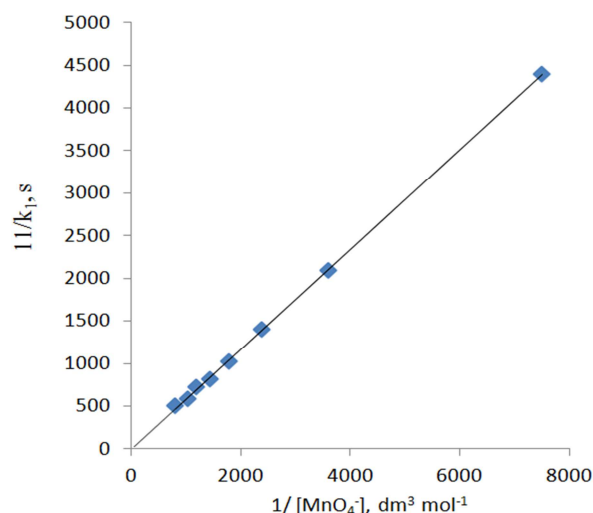


Figure 3. Michealis - Menten for the redox reaction between indigo carmine and MnO_4^- at $[\text{IC}] = 2.80 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2.80 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.25 \text{ mol dm}^{-3}$ and $T = 26 \pm 1^\circ\text{C}$.

Table 1. Pseudo-first order and second order rate constants for the reaction of indigo carmine and MnO_4^- at $[\text{IC}] = 2.8 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 610 \text{ nm}$ and $T = 26 \pm 1^\circ\text{C}$

$10^4[\text{MnO}_4^-]$, mol dm^{-3}	$10^5[\text{H}^+]$, mol dm^{-3}	$10^1 I$, mol dm^{-3}	$10^3 k_1$, s^{-1}	$10^4 k_2$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
1.40	1.0	2.5	0.22	0.16
2.80	1.0	2.5	0.49	0.18
4.20	1.0	2.5	0.71	0.17
5.60	1.0	2.5	0.98	0.18
7.00	1.0	2.5	1.23	0.18
8.40	1.0	2.5	1.38	0.16
9.80	1.0	2.5	1.73	0.18
11.20	1.0	2.5	2.02	0.18
4.20	0.25	2.5	0.19	0.05
4.20	0.50	2.5	0.55	0.13
4.20	0.75	2.5	0.75	0.15
4.20	1.00	2.5	0.77	0.18
4.20	1.25	2.5	1.09	0.25
4.20	1.50	2.5	1.10	0.26
4.20	1.75	2.5	1.41	0.28
4.20	1.0	1.0	0.71	0.17
4.20	1.0	1.5	0.73	0.17
4.20	1.0	2.0	0.75	0.18
4.20	1.0	2.5	0.71	0.16
4.20	1.0	3.0	0.82	0.19
4.20	1.0	3.5	0.71	0.16
4.20	1.0	4.0	0.73	0.17

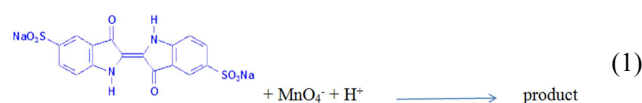
Table 2. Rate data for the effect of added anions (CH_3COO^- and HCOO^-) on the rate of reaction of indigo carmine with MnO_4^- at $[\text{IC}] = 2.80 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 4.20 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.25 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 610 \text{ nm}$ and $T = 26 \pm 1^\circ\text{C}$.

Ion	$10^3 [\text{ion}]$, mol dm^{-3}	$10^3 k_1$, s^{-1}	$10^4 k_2$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
K^+	10.0	0.80	0.19
	30.0	0.60	0.15
	40.0	0.70	0.17
Mg^{2+}	10.0	0.71	0.17
	20.0	0.65	0.15
	30.0	0.75	0.18
	50.0	0.73	0.17

3. Results and Discussion

3.1. Stoichiometry and Product Analysis

The stoichiometric studies showed that one moles of indigo carmine was consumed by one mole of MnO_4^- . The overall stoichiometric equation is;



Similar stoichiometry has been reported for the reduction of permanganate [11]. Mn^{2+} , one of the products was confirmed qualitatively.

3.2. Order of Reaction

Kinetic studies showed the reaction to be first order dependent on each of the reactants. Plots of $\log(A_t - A_\infty)$ versus time were linear to 90% of the reaction (where A_t and A_∞ are the absorbance at time t and at the end of the reaction respectively) indicating the order with respect to IC to be one. A typical plot is presented in Figure 2. Pseudo first order rate constants, k_1 , determined as the slope of above are presented in Table 1. The plot of $\log k_1$ versus $\log [\text{MnO}_4^-]$ was linear with a slope of 1 indicating first order dependence of the rate of reaction on $[\text{MnO}_4^-]$ figure 4. The second order rate constant, k_2 , was obtained from $k_2 = K_1/[\text{MnO}_4^-]$ and were found to be fairly constant (Table 1).

The rate equation can be represented by equation (2)

$$\text{Rate} = (K + K''[\text{H}^+])[\text{IC}][\text{MnO}_4^-] \quad (2)$$

Similar order has been reported for the reduction of MnO_4^- [12] [13].

3.3. Effect of Changes in Acid Concentration on the Reaction Rate

The results of the acid dependence show that the rate constant increases with increase in $[H^+]$. Plot of $\log k_H^+$ versus $\log [H^+]$ gave a slope of 0.8, indicating that the reaction is first order with respect to $[H^+]$. Plot of k_2 versus $[H^+]$ gave a straight line with an intercept. A graph of this nature indicates that the reaction occurs via acid dependent and acid independent pathways [14].

3.4. Effect of Changes in Ionic Strength and Added Ions on the Reaction Rate

Changes in the ionic strength of the reaction medium had no effect on the oxidation of IC by MnO_4^- . The observed zero Brownsted-Debye salt effect suggests that charged and neutral specie is reacting at the rate determining step. The result is presented on Table1. This is a common feature of most reactions of indigo carmine [15] [16].

3.5. Effect of Added Ions

There was no effect of added cations on the rate of the reaction. This further supports the result obtained from the effect of changes in ionic strength as one of the reactants in the rate determining step is neutral specie [17] [18].

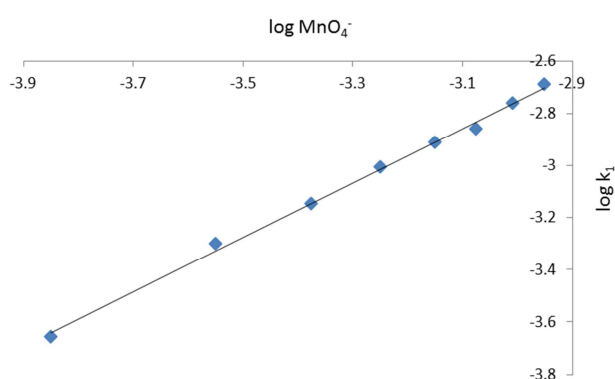


Figure 4. Plot of $\log k_1$ versus $\log [MnO_4^-]$ for the redox reaction of indigo carmine with MnO_4^- at $[IC] = 2.80 \times 10^{-5} \text{ mol dm}^{-3}$, $[MnO_4^{2-}] = 4.20 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.25 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 610 \text{ nm}$ and $T = 26 \pm 1^\circ \text{C}$.

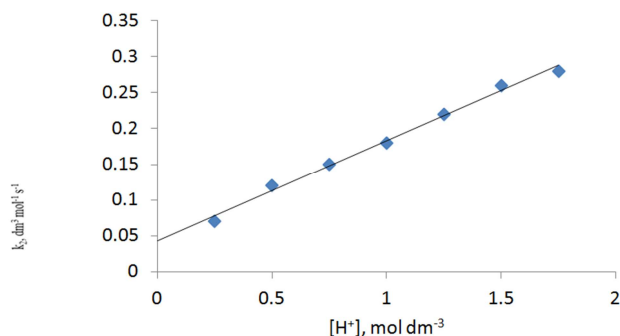


Figure 5. Plot of k_2 versus $[H^+]$ for the redox reaction between indigo carmine and MnO_4^- at $[IC] = 2.80 \times 10^{-5} \text{ mol dm}^{-3}$, $[MnO_4^-] = 4.20 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = (0.25 - 1.75) \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.25 \text{ mol dm}^{-3}$ and $T = 26 \pm 1^\circ \text{C}$.

3.6. Test for Intermediate Complex Formation

Spectroscopic Studies indicate no shift from the absorption maxima of 610nm characteristic of $[MnO_4^-]$. This indicated absence of the formation of an intermediate complex suggesting the absence of inner-sphere mechanism in the reaction. Plots of $1/k_1$ versus $1/[MnO_4^-]$ were linear with zero intercept (Fig. 3).

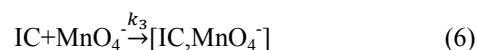
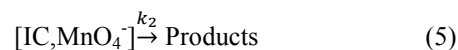
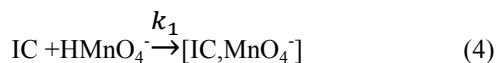
3.6.1. Polymerisation Test

Acrylonitrile was added to the partially oxidized reacting mixture. No gel formation was observed even on addition of large excess of methanol. This suggests absence of free radical in the reaction mixture.

Based on the above results, it is evident that the reaction is operating through the outer-sphere mechanism.

3.6.2. Reaction Mechanism

It has been noted that redox reactions of many oxy-anions are strongly acid dependent. Under the present experimental conditions, it is reasonable to postulate that MnO_4^- is protonated in a fast step to give $HMnO_4$ which then reacts with IC in a slow step to give the products.



$$\text{Rate} = k_1[IC][HMnO_4] + k_3[IC][MnO_4^-] \quad (8)$$

from equation (3).

$$[HMnO_4] = K_{eq} [MnO_4^-][H^+] \quad (9)$$

Substitution of (9) into (8)

$$\text{Rate} = k_1 K_{eq} [IC][MnO_4^-][H^+] + k_3 [IC][MnO_4^-] \quad (10)$$

$$\text{Rate} = (k_3 + k_1 K_{eq} [H^+]) [IC][MnO_4^-] \quad (11)$$

where $k_3 = K$ and $k_1 K_{eq} = K''$

$$\text{Rate} = (K + K'' [H^+]) [IC][MnO_4^-] \quad (12)$$

4. Conclusion

The redox reactions of indigo carmine were studied with permanganate ion, the reaction IC- reductants and MnO_4^- -

oxidants were carried out in H₂SO₄ acid. On the basis of the results of this investigation, the absence of kinetic and spectrophotometric evidence for intermediate complex formation, these views are further supported by the fact that Michaelis Mentens plot was linear with no appreciable intercept. The reactions of reductant with the oxidant follow the outer – sphere mechanism.

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