Kinetics and Mechanism of the Reaction of Malachite Green and Dithionite Ion

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Authors' contributions

This work was carried out in collaboration among all the authors. Authors SOI and JFI (now deceased) designed the study. Author SOI managed the literature searches and corrected the final manuscript. Author YM wrote the protocol and the first draft of the manuscript. Author AT did the laboratory study. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The kinetics of the oxidation of malachite green, MG^+, by dithionite ions, $S_2O_4^{2-}$ have been studied spectrophotometrically in an aqueous acid free medium. The investigation was carried out under pseudo- first order conditions of an excess of dithionite concentration. Reaction conditions were ionic strength of reaction medium, μ = 0.1 mol dm^{-3}, λ_{max} = 620nm and T = 25.5±0.5°C. The stoichiometry of the reaction, determined by spectrophotometric titration, was 1:1. Reaction rates increased with increase in μ and dielectric constant (D) of reaction medium. Added ions catalysis of the reaction and the result of the Michaelis - Menten analysis suggest that the reaction proceeded through the outersphere pathway. A plausible mechanism is proposed.

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1. INTRODUCTION

Malachite green, herein and hereafter represented by MG^+ for convenience, also called aniline green, basic green 4, diamond green B or Victoria green dye, with IUPAC name 4 – [(4 - dimethylaminophenyl) – phenylmethyl] – N,N – dimethylaniline is a triphenylmethane dye and a derivative of bis (*p* – aminophenyl) phenylmethane [1]. It is highly toxic to mammalian cells, as it promotes hepatic tumour formation in rodents and also causes reproductive abnormalities in rabbits and fish [2-5]. The structural similarity of this dye to other carcinogenic triphenylmethane dyes also raises suspicion of its carcinogenicity. In fact, it has been reported to be mutagenic [6-7].

The compound has a wide range of application, in aquaculture as antifungal agent, biological stains and in dyeing industry which may probably continue due to its relatively low cost, ready availability and efficacy [8]. Therefore, potential human exposure to malachite green could result from the consumption of treated fish [1] and improper handling of the dye by workers in dye and aquaculture industries.

In spite of these applications literature on kinetic and mechanistic data of the dye is scanty. Data generated in kinetic and mechanistic studies, especially in collaboration with data from toxicological studies and experts in fish diseases could be of importance in improving its uses, as well as its handling when used as an antimicrobial agent, as biological stain and in the dyeing industry. Relevant data on the kinetics and mechanisms of these reactions, especially with oxidizing agents would give an insight into the conditions best suitable to optimize the uses of the compound. Mohammed et al. [9 - 12] and Mushinga and Jonnalagadda [13] have earlier reported on its redox reaction with some oxyanions like $Cr_2O_7^{2-}$, NO_2^-, MnO_4^- and Ag^+ - catalysed $S_2O_8^{2-}$, respectively.

In our continuing effort to understand the redox dynamics of malachite green, we present the redox kinetics and mechanism of the reaction of malachite green and dithionite ion.`

2. EXPERIMENTALS

2.1 Materials

All chemical reagents used in this work were analar grade and were used without further purification. $Na_2S_2O_4$ was used as the oxidant and NaCl, being an inert electrolyte, was used to maintain a constant ionic strength, μ of the reaction medium. Acetone was used to vary the dielectric constant of the reaction medium. MG^+, $Na_2S_2O_4$, $MgCl_2$, NH_4Cl, $NaNO_3$, Na_2SO_4 solutions were prepared with distilled water.

2.2 Method

2.2.1 Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of MG^+ was kept constant and the mole ratio of dithionite to MG^+ was varied from (0.25 – 4.00) at $\mu = 0.1$ (NaCl) and Temperature = 25.5 $\pm$ 0.5°C. The absorbances of these mixtures were taken at 620nm using Corning Colorimeter 253 after the reactions had gone to completion. This is indicated by constant absorbance values. The observed value for each mole ratio at completion of reaction was plotted against the individual mole ratios. Point of inflection on the plot gave the mole ratio of the reactants (Fig. 1).

2.2.2 Kinetic measurements

All kinetic measurements were carried out under pseudo- first order conditions with respect to $[S_2O_4^{2-}]$ over $[MG^+]$. The rate of reaction was monitored using Corning Colorimeter 253 by following decrease in absorbance of the MG^+ at λ_{max} = 620nm, characteristic of MG^+. The products of the reaction had no appreciable absorbance at this wavelength. The ionic strength was maintained constant at 0.1 mol dm^{-3} (NaCl), mol dm^{-3} and T = 25.5 $\pm$ 0.5 °C. Pseudo – first order plots of log $(A_t - A_\infty)$ against time were made and the slopes of the plots gave the pseudo-first order rate constants, k_1. The second order rate constants, k_2, were obtained from k_1 as $k_1/[[S_2O_4^{2-}]$.

Effect of changes in ionic strength of reaction medium on rates of raction was studied by varying the ionic strength from 0.1 – 0.8 mol dm^{-3} (NaCl), while maintaining $[MG^+]$ and $[S_2O_4^{2-}]$ constant at 1.0 x 10^{-5} mol dm^{-3} and 2 x 10^{-4} mol dm^{-3}, respectively. Reaction temperature was maintained at 25.5±0.5°C. Dependence of reaction rates on changes in ionic strength of reaction medium was determined by plotting log k_2 against $\sqrt{\mu}$.

Effect of changes of dielectric constant, D of reaction medium on reaction rates was studied by adding various quantities of acetone to adjust D in the range of 75.37 – 80.10, keeping $[MG^+]$ and $[S_2O_4^{2-}]$ constant. Ionic strength of 0.1 mol dm^{-3} and temperature of 25.5±0.5°C were maintained.

Generation and participation of free radicals in the course of the reaction was investigated by adding 5 cm^3 of 0.015 mol dm^{-3} acrylamide to a partially oxidised reaction mixture followed by the addition of a large excess of methanol. A control experiment was carried out by adding acrylamide to separate solution of MG^+ and $S_2O_4^{2-}$ at the stated conditions of μ and temperature in Table 1. Gel formation is indicative of participation of free radicals in the reaction.

Test for the formation of stable and detectable intermediate complex was carried out spectrophotometrically by comparing the λ_{max} of the MG^+ and that of the partially reacted mixture. Michaelis- Menten plot of $1/k_1$ versus $1/[S_2O_4^{2-}]$ also could give an idea on the presence or not of intermediate complex.

3. RESULTS AND DISCUSSION

3.1 Stoichiometry

The results of stoichiometric studies showed that one mole of MG^+ was consumed by one mole of $S_2O_4^{2-}$ (Fig. 1), which is consistent with the equation below:
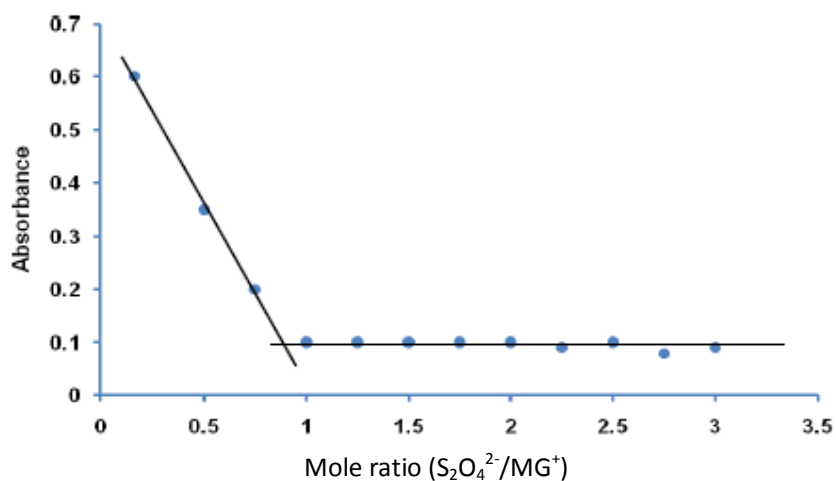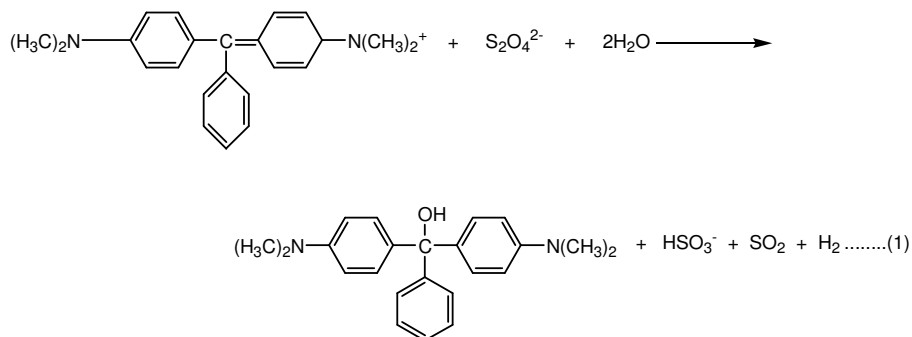
$$(H_3C)_2N-\text{C}_6H_4-C(-C_6H_5)=C_6H_4-N(CH_3)_2^+ \; + \; S_2O_4^{2-} \; + \; 2H_2O \longrightarrow$$

$$(H_3C)_2N-\text{C}_6H_4-C(OH)(C_6H_5)-C_6H_4-N(CH_3)_2 \; + \; HSO_3^- \; + \; SO_2 \; + \; H_2 \; ....(1)$$

Fig. 1. Stoichiometry for the reaction of Malachite Green and $S_2O_4^{2-}$ at $[MG^+]$ = 1.0 x 10^{-5} mol dm^{-3}, μ = 0.1 mol dm^{-3}, $[S_2O_4^{2-}]$ = (2.5 - 40) x 10^{-6} mol dm^{-3}, λ_{max} = 620 nm, T = 25.5 ± 0.5°C

Reactions of MG^+ with $Cr_2O_7^{2-}$, NO_2^-, MnO_4^- and Ag^+ - catalysed $S_2O_8^{2-}$ gave a stoichiometry of 1:1 [9 – 12].

3.2 Order of Reaction

The pseudo – first order plots obtained from the plots of (A_t - A_∞) versus time were linear to more than 90% completion of reaction, suggesting that the reaction is first order in $[MG^+]$. The slopes of the pseudo – first order plots gave k_1 for each concentration of $S_2O_4^{2-}$. The second order rate constants, k_2, was obtained from k_1 as $k_1/[S_2O_4^{2-}]$. Values of k_1 and k_2 for the various concentrations of $S_2O_4^{2-}$ are shown in Table 1.

Table 1. Pseudo – first order and second order rate constants for the reaction of MG^+ and $S_2O_4^{2-}$ at $[MG^+]$ = 1.0 x 10^{-5} mol dm^{-3}, μ = 0.1 mol dm^{-3}, T = 25.5 ± 0.5 ℃ and λ = 620 nm

$10^4[S_2O_4^{2-}]$, mol dm^{-3}	μ, mol dm^{-3}	$10^3 k_1$, s^{-1}	k_2, dm3 mol^{-1} s^{-1}
1.0	0.1	1.80	17.95
2.0	0.1	3.60	17.95
3.0	0.1	5.40	18.15
4.0	0.1	7.10	17.75
5.0	0.1	9.00	17.96
6.0	0.1	10.80	18.04
7.0	0.1	12.60	17.95
8.0	0.1	14.40	17.95
2.0	0.1	3.60	17.95
2.0	0.2	4.90	24.31
2.0	0.3	6.20	30.86
2.0	0.4	7.30	36.67
2.0	0.5	8.80	43.87
2.0	0.6	10.20	51.18
2.0	0.7	12.00	59.88
2.0	0.8	13.40	67.18

The derived second order rate constants, k_2 were fairly constant, further confirming that the reaction is indeed first order in $[MG^+]$. Plot of log k_1 versus log $[S_2O_4^{2-}]$ (Fig. 2) was linear with a slope of unity, implying that first order in $[S_2O_4^{2-}]$. The reaction is therefore second order, overall. The rate law for the reaction can be represented by equation (2)

$$- d[MG^+]/dt = k_2[MG^+][S_2O_4^{2-}] \qquad (2)$$

Similar order of reaction has been reported by earlier researchers [9 – 13].

3.3 Effect of Changes in Ionic Strength and Dielectric Constant of Reaction Medium on Rate of Reaction

Increase in ionic strength of reaction medium increased the reaction rate. This is consistent with interaction between cation - cation or anion-anion in the rate determining step [14]. Plot of log k_2 versus $\sqrt{\mu}$ (Fig. 3) gives a straight line with a slope of unity, implying that the product of the charges of these ions in the rate determining steps is also unity. For reactions of ions in aqueous media, the rate of reaction is directly dependent on the square root of the ionic strength of the media. If ionic strength is varied, the various values of k_2 obtained could be plotted as $\log k_2$ against $\sqrt{I}$. The magnitude of the slopes of the plots gives an idea of the product of the charges on the species' reacting in the rate determining step [15]. This positive salt effect is supported by the observed increase in reaction rate with increase in dielectric constant of reaction medium (Table 2). A plot of log k_2 versus D is presented as Fig. 4.
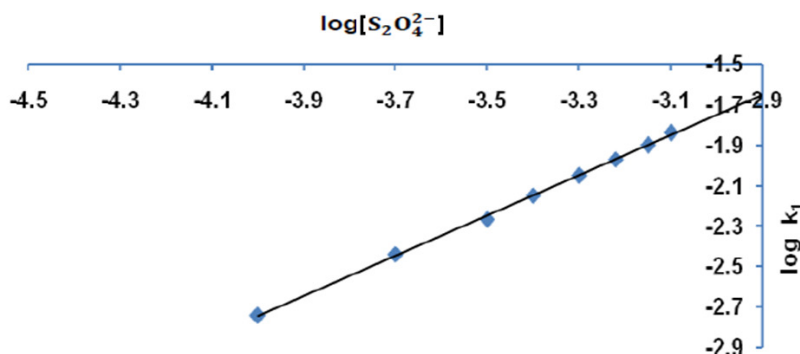

Fig. 2. Plot of log k_1 versus log$[S_2O_4^{2-}]$ for the reaction of MG^+ and $S_2O_4^{2-}$ at $[MG^+]$= 1.0 x 10^{-5} mol dm^{-3}, $S_2O_4^{2-}$ = (1.0 - 8.0) x 10^{-4} mol dm^{-3}, μ = 0.1 mol dm^{-3}, $λ_{max}$ = 620 nm and Temp. = 25.5 ± 0.5⁰C
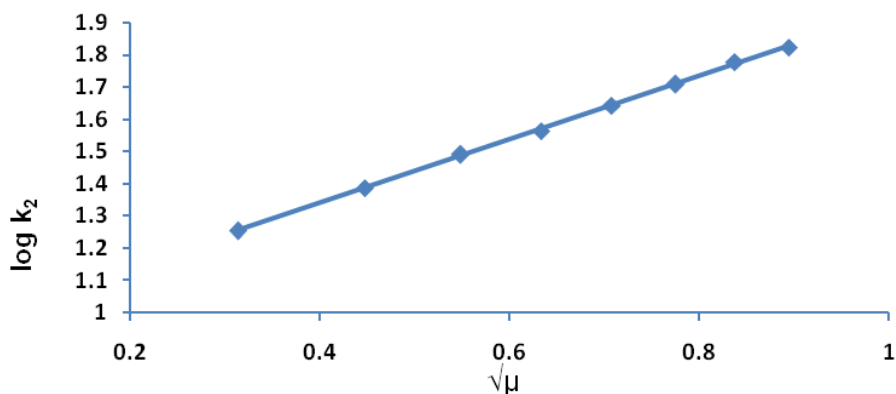
Fig. 3. A Plot of log k_2 versus $\sqrt{\mu}$ for the reaction of MG^+ and $S_2O_4^{2-}$ at $[MG^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $\mu = (0.1 - 0.8)$ mol dm^{-3}, $\lambda_{max} = 620$ nm and Temp. = 25.5 ± 0.5^{0}C

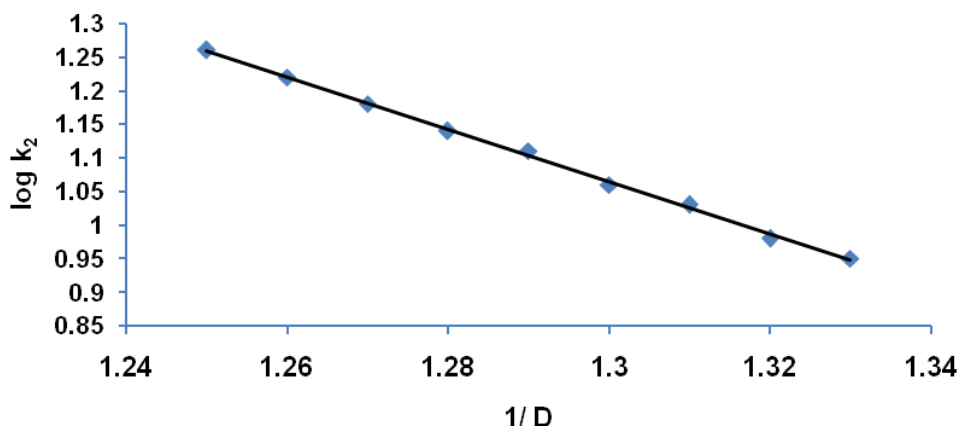**Fig. 4. Plot of log k_2 versus 1/D for the reaction of MG^+ and $S_2O_4^{2-}$ at $[MG^+]=1.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3}, D = 75.37 - 80.1, $\lambda_{max} = 620$ nm and T = 25.5 ± 0.5^{0}C**

Table 2. Effect of changes of the dielectric constant of reaction medium on the rate constants for the oxidation of MG^+ by $S_2O_4^{2-}$ at $[MG^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 2 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3}, T = 25.5 ± 0.5°C and $\lambda_{max} = 620$ nm

D	$10^3 k_1$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
80.10	3.60	18.03
79.51	3.30	16.45
78.92	3.00	15.06
78.33	2.80	13.93
77.74	2.60	12.79
77.15	2.30	11.44
76.55	2.10	10.63
75.96	1.90	9.60
75.37	1.80	8.91

3.4 Effect of Added Ions on Reaction Rates

Added SO_4^{2-} and NO_3^- led to decrease in reaction rate while increase in the concentrations of Mg^{2+} and NH_4^+ led to increase in reaction rate (Tables 3 and 4). Anions inhibition and cation catalysis as observed in this reaction agree with earlier literature [16-18].

Table 3. Effect of added anions to the reaction medium on the rate constants for the oxidation of MG^+ by $S_2O_4^{2-}$ at $[MG^+]$ = 1.0 x 10^{-5} mol dm^{-3}, $[S_2O_4^{2-}]$ = 2 x 10^{-4} mol dm^{-3}, μ = 0.1 mol dm^{-3}, T = 25.5 ± 0.5 °C and $λ_{max}$ = 620 nm

10^4[anion], mol/dm^3	$10^3 k_1$, s^{-1}	k_2, dm mol s^{-1}
Ion = SO_4^{2-}		
0.0	3.60	17.99
1.0	3.57	17.85
20.0	3.10	15.69
30.0	3.00	14.78
40.0	2.70	13.42
50.0	2.30	12.46
60.0	2.39	11.52
70.0	2.00	10.18
80.0	1.80	9.20
Ion = NO_3^-		
0.0	3.60	17.81
1.0	3.60	17.73
20.0	3.10	15.69
30.0	3.10	15.35
40.0	2.90	14.43
50.0	2.70	13.67
60.0	2.50	12.57
70.0	2.40	11.88
80.0	2.20	10.85

Table 4. Effect of added cations to the reaction medium on the rate constants for the reaction of MG^+ and $S_2O_4^{2-}$ at $[MG^+]$ = 1.0 x 10^{-5} mol dm^{-3}, $[S_2O_4^{2-}]$ = 2 x 10^{-4} mol dm^{-3}, μ = 0.1 mol dm^{-3}, T = 25.5 ± 0.5 °C and $λ_{max}$ = 620 nm

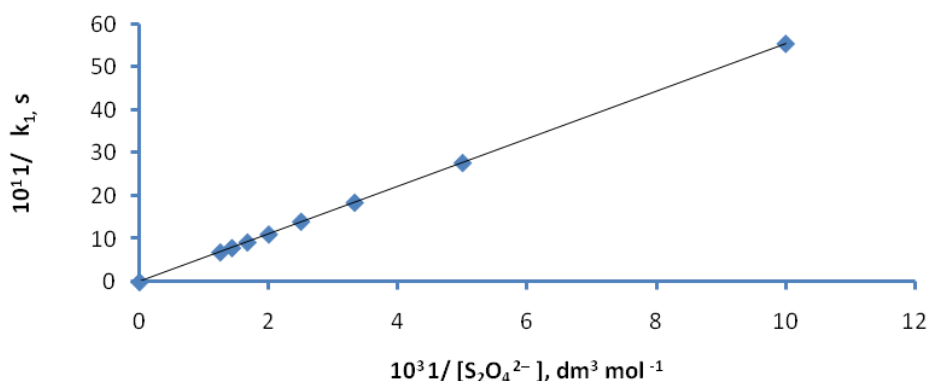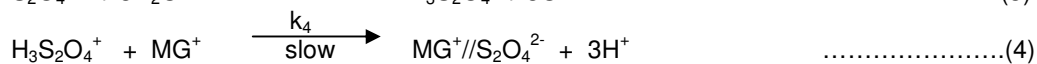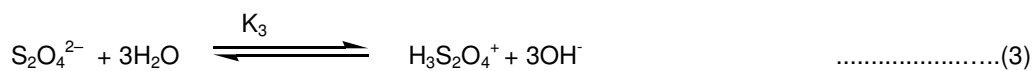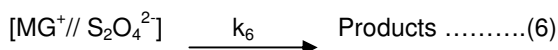| 10^4[cation], mol/dm^3	$10^2 k_1$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
Ion = Mg^{2+}		
0.0	3.60	17.80
1.0	3.60	18.21
20.0	5.40	26.99
30.0	6.50	32.48
40.0	7.40	36.85
50.0	8.20	41.00
60.0	9.10	45.51
70.0	10.20	51.18
80.0	11.10	55.27
Ion = NH_4^+		
0.0	3.60	17.89
1.0	3.70	18.32
20.0	4.80	24.00
30.0	5.50	27.42
40.0	6.20	30.79
50.0	6.90	34.36
60.0	7.40	37.21
70.0	8.10	40.30
80.0	8.70	43.57

Fig. 5. Michelis- Menten plot of $1/k_1$ versus $1/[S_2O_4^{2-}]$ for the reaction of MG^+ and $S_2O_4^{2-}$ at $[MG]$ = 1.0 x 10^{-5} mol dm^{-3}, $S_2O_4^{2-}$ = (1.0 - 8.0) x 10^{-4} mol dm^{-3}, μ = 0.1 mol dm^{-3}, $λ_{max}$ = 620nm andTemp. = 25.5 ± 0.5 °C

3.5 Mechanism of Reaction

$$S_2O_4^{2-} + 3H_2O \overset{K_3}{\rightleftharpoons} H_3S_2O_4^+ + 3OH^- \quad ....(3)$$

$$H_3S_2O_4^+ + MG^+ \underset{slow}{\overset{k_4}{\longrightarrow}} MG^+//S_2O_4^{2-} + 3H^+ \quad ....(4)$$

$$3OH^- + 3H^+ \xrightarrow{k_5} 3H_2O \quad \ldots\ldots\ldots\ldots(5)$$

$$[MG^+ // S_2O_4^{2-}] \xrightarrow{k_6} \text{Products} \quad \ldots\ldots(6)$$

$$\text{Rate} = k_4[H_3S_2O_4^+][MG^+] \quad \ldots\ldots\ldots\ldots(7)$$

Substitution of $[H_3S_2O_4^+]$ in equation (7) gives

$$\text{Rate} = \frac{k_4K_3[S_2O_4^{2-}][H_2O]^3[MG^+]}{[OH^-]} \quad \ldots\ldots(8)$$

In kinetics, $[H_2O] \approx 1$ and if $[OH^-]$ is negligible, equation (8) reduces to

$$\text{Rate} = k_4K_3[S_2O_4^{2-}][MG^+] \quad \ldots\ldots\ldots\ldots(9)$$

Equation (9) is similar to equation (2) where $k_2 = k_4K_3$

Based on the kinetic and non-kinetic parameters obtained in this investigation, the outersphere mechanism is proposed for this reaction on the ground that:

(1) Spectrophotometric evidence did not indicate any shift in λ_{max} as the reaction progressed suggesting that stable reaction intermediates are not formed during the course of the reaction or if formed, had a small formation constant;
(2) The above assertion is further re-enforced by the Michaelis-Menten plot (Fig. 5) of $1/k_{obs}$ versus $1/[S_2O_4^{2-}]$ which was linear without intercept. Lack of such kinetic evidence removes the chance of innersphere mechanism [15].
(3) Ions catalysis and ions inhibition as observed in this reaction have been observed by earlier studies [15-17] in favour of outersphere mechanism. Such observation is an indication that coordination integrity of the redox partners remained intact during and prior to electron transfer process.

6. CONCLUSION

The kinetics of the dithionite $(S_2O_4^{2-})$ oxidation of Malachite Green (MG^+) has been studied in aqueous medium. The observed result at T = $25.5\pm0.5°C$ showed that the reaction was first order with respect to [malachite green] and [dithionite ion] with an overall second order. Reaction rates increased with increase in the ionic strength and decreased with decrease in

the dielectric constant of the reaction medium. Added ions catalysis was observed. Spectrophotometric test showed absence of intermediate complex formation. Based on these findings, the reaction is suspected to proceed through the outersphere mechanistic pathway.

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COMPETING INTERESTS

Authors have declared that there is no competing interests exist.

REFERENCES

1. Alderman DJ, Clifton – Hadley RS. Malachite green: A pharmacokinetic study in rainbow trout. J. Fish. Dis. 1993;16:307
2. Fernandes C, Lalitha VS and Rao KVK. Enhancing effect of malachite green on the development of hepatic pre – neoplastic lesions induced by N – nitrosodiethylamine in rats. Carcinogenesis. 1991;12:839.
3. Rao KVK. Comparative cytotoxic effects of the non – permitted food colouring agents metanil yellow, orange II, rhodamina B and malachite green on hamster dermal and C3H/10 T1/2 fibroblasts. Bombay Hosp. J. 1990;32:61.
4. Rao KVK. The cytotoxic properties of malachite green are associated with the increased demethylase, aryl hydrocarbon hydroxylase and lipid peorxidation in primary cultures of Syrian hamster embryo cells. Cancer Lett. 1992;67:93.
5. Rao KVK. Inhibition of DNA synthesis in primary rat hepatocyte cultures by malachite green: A new liver tumor promoter. Toxicol Lett. 1995;81:107.
6. Clemmensen S, Jensen JC, Jensen NJ, Meyer O, Olsen P and Wurtzen G. Toxicological studies on malachite green: A triphenylmethane dye. Arch. Toxicol. 1984;56:43.
7. Fessard V, Godard T, Huet S, Mourot A, and Poul JM. Mutagenecity of malachite

green and leucomalachite green in *in- vitro* tests. J. Appl. Toxicol. 1999;19:421.

8. Schnick RA. The impetus to register new therapeutics for aquaculture. Prog Fish. Cult. 1988;50:190.

9. Mohammed Y, Iyun JF and Idris SO. Redox kinetics of triphenylmethane dye: Dichromate oxidation of malachite green in aqueous acidic medium. International Journal Of Chemical Sciences. 2008;1(2):277-287

10. Mohammed Y, Iyun JF, Idris SO. Kinetic Approach to the mechanism of the redox reaction of malachite green and permanganate ion in aqueous acidic medium. African Journal of Pure and Applied Chemistry. 2009;3(12):269-274.

11. Mohammed Y, Iyun JF, Idris SO. Studies into the kinetics and mechanism of the redox reaction of malachite green and nitrite ions in aqueous acidic medium. Journal of Chemical Society of Nigeria. 2010;35(1):116-127.

12. Mohammed Y, Iyun JF, Idris SO. Silver - Catalysed peroxydisulphate oxidation of malachite green in aqueous acidic medium: kinetic and mechanistic approach. International Journal of Chemistry. 2010b;20(2):105-112.

13. Mushinga T, Jonnalagadda SB. A kinetic approach for the mechanism of malachite green – peroxydisulphate reaction in aqueous solution. Int. J. Chem. Kinet. 1991;24:1,41.

14. Atkins PW and de Paula J. Physical Chemistry. 7th Ed., Oxford University Press. 2002;962.

15. BrØnsted JM. Actitvities of ions in solution. Z. Phys. Chem. 1922;102:106.

16. Idris SO, Raji KO, Ukoha PO. Nigeria Journal of Science Research. 2005;5(1):86-90.

17. Pryzstas TJ, Sutin N. Kinetic studies of anion- assisted outer-sphere electron transfer reactions. Journal of American Chemical Society. 1973;95:5545.

18. Adegite A, Iyun JF, Ojo JF. Kinetics and Mechanisms of Electron transfer Reactions between Uranium (III) and some Ruthenium (III) ammine complexes. J C S Dalton. 1977;115-120.

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