

Original Research Article

KINETICS AND MECHANISM OF THE REACTION OF MALACHITE GREEN AND DITHIONITE

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ABSTRACT

The kinetics of the oxidation of malachite green, MG^+ , by dithionite ions, $S_2O_4^{2-}$ has 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, $\mu = 0.1 \text{ mol dm}^{-3}$, $\lambda = 620 \text{ nm}$ and $T = 25.5 \pm 0.5 \text{ }^\circ\text{C}$. 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.

Keywords: kinetics, mechanism, outersphere, dithionite ion, malachite green

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 as 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 from working in the dye and aquaculture industries..

In spite of these applications not much kinetic and mechanistic data have been reported in literature. 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 of its reaction, especially with oxidizing agents would give an insight into the conditions best suitable for its reactions and the mechanisms of these reactions. Mohammed et al [9 - 12] and Mushinga and Jonnalagadda [13] have earlier reported on its redox reaction with some oxyanions like $\text{Cr}_2\text{O}_7^{2-}$, NO_2^- , MnO_4^- and Ag^+ - catalysed $\text{S}_2\text{O}_8^{2-}$, 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. EXPERIMENTAL

2.1 Materials

All chemical reagents used in this work were analar grade and were used without further purification. $\text{Na}_2\text{S}_2\text{O}_4$ was used as the oxidant and NaCl, being an inert electrolyte, was used to maintain a constant ionic strength except when investigating the effect of changes in ionic strength, μ of the reaction medium. Acetone was used to vary the dielectric constant of the reaction medium. MG^+ , $\text{Na}_2\text{S}_2\text{O}_4$, MgCl_2 , NH_4Cl , NaNO_3 , Na_2SO_4 solutions were prepared with doubly 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 = $25.5 \pm 0.5^\circ\text{C}$. 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 in 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 $[\text{S}_2\text{O}_4^{2-}]$ over $[\text{MG}^+]$. The rate of reaction was monitored using Corning Colorimeter 253 by following decrease in absorbance of the MG^+ at $\lambda_{\text{max}} = 620\text{nm}$, 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 $T = 25.5 \pm 0.5^\circ\text{C}$. 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 $k_1/ [\text{S}_2\text{O}_4^{2-}]$.

Effect of changes in ionic strength of reaction medium on rates of reaction was studied by varying the ionic strength from $0.1 - 0.8 \text{ mol dm}^{-3}$ (NaCl), while maintaining $[\text{MG}^+]$ and $[\text{S}_2\text{O}_4^{2-}]$ constant at $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $2 \times 10^{-4} \text{ mol dm}^{-3}$, respectively. Reaction temperature was maintained at $25.5 \pm 0.5^\circ\text{C}$. 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 of reaction medium on reaction rates was studied by adding various quantities of acetone to adjust the dielectric constants, D , to $75.37 - 80.10$, keeping $[\text{MG}^+]$ and $[\text{S}_2\text{O}_4^{2-}]$ constant. Ionic strength of 0.1 mol dm^{-3} and temperature of $25.5 \pm 0.5^\circ\text{C}$ were maintained.

Generation and participation of free radicals in the course of the reaction was investigated by adding 5 cm^3 of $0.015 \text{ mol dm}^{-3}$ 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 $\text{S}_2\text{O}_4^{2-}$ 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 $1/ [\text{S}_2\text{O}_4^{2-}]$ 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 $\text{S}_2\text{O}_4^{2-}$ (Fig 1) , which is consistent with the equation below:

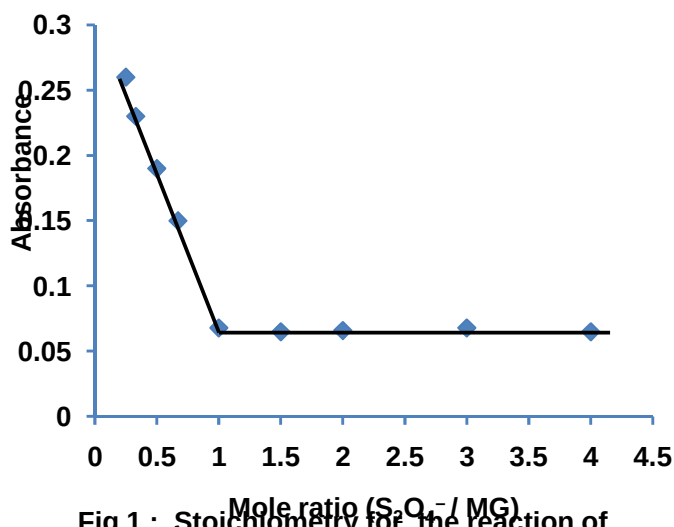
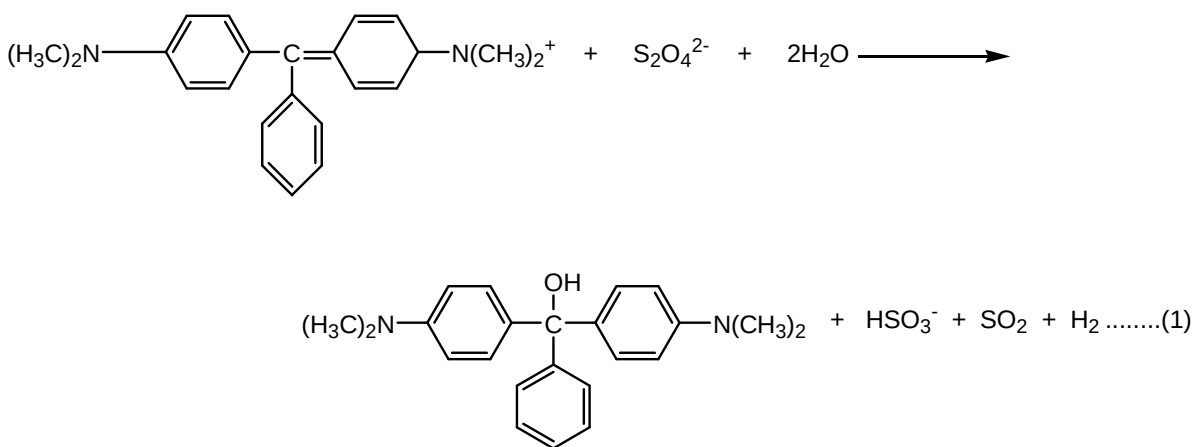


Fig 1 : Stoichiometry for the reaction of Malachite Green and $\text{S}_2\text{O}_4^{2-}$. $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_4^{2-}] = (2.5 - 40) \times$

Reactions of MG^+ with $\text{Cr}_2\text{O}_7^{2-}$, NO_2^- , MnO_4^- and Ag^+ - catalysed $\text{S}_2\text{O}_8^{2-}$ gave a stoichiometry of 1:1 [9 – 12].

3.2 Order of reaction

The pseudo – first order plots obtained from the plots of $(A_t - A_\infty)$ versus time were linear to more than 90% completion of reaction, suggesting that the reaction is first order in $[\text{MG}^+]$. The slopes of the pseudo – first order plots gave k_1 for each concentration of $\text{S}_2\text{O}_4^{2-}$. The second order rate constants, k_2 , was obtained from k_1 as $k_1/[\text{S}_2\text{O}_4^{2-}]$. Values of k_1 and k_2 for the various concentrations of $\text{S}_2\text{O}_4^{2-}$ are shown in Table 1. The derived second order rate constants, k_2 were fairly constant, further confirming that the reaction is indeed first order in $[\text{MG}^+]$. Plot of $\log k_1$ versus $\log [\text{S}_2\text{O}_4^{2-}]$ (Fig 2) was linear with a slope of unity, implying that first order in $[\text{S}_2\text{O}_4^{2-}]$. The reaction is therefore second order, overall. The rate law for the reaction can be represented by equation (2)

$$-d[\text{MG}^+]/dt = k_2[\text{MG}^+][\text{S}_2\text{O}_4^{2-}] \quad \dots\dots\dots(2)$$

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

Table 1 : Pseudo – first order and second order rate constants for the reaction of MG^+ and $\text{S}_2\text{O}_4^{2-}$ at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25.5 \pm 0.5^\circ\text{C}$ and $\lambda = 620 \text{ nm}$

$10^4[\text{S}_2\text{O}_4^{2-}]$, mol dm^{-3}	μ , mol dm^{-3}	10^3k_1 , s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
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

125	2.0	0.1	3.60	17.95
126	2.0	0.2	4.90	24.31
127	2.0	0.3	6.20	30.86
128	2.0	0.4	7.30	36.67
129	2.0	0.5	8.80	43.87
130	2.0	0.6	10.20	51.18
131	2.0	0.7	12.00	59.88
132	2.0	0.8	13.40	67.18

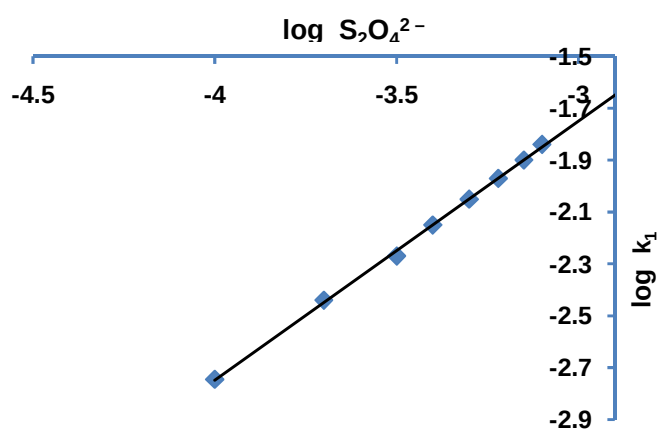


Fig 2 : Plot of $\log k_1$ versus $\log [S_2O_4^{2-}]$ for the reaction of Mg^{+} and $S_2O_4^{2-}$ $[Mg^{+}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$

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 reactions cation-cation or anion-anion in the rate determining step [14]. Plot of $\log k_2$ versus $\sqrt{\mu}$ (Figure 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 $\sqrt{\mu}$. 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).

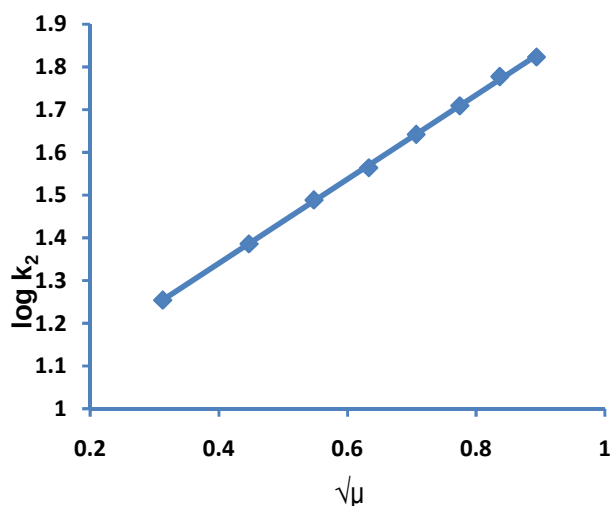


Fig 3 : A Plot of $\log k_2$ versus $\sqrt{\mu}$ for the reaction of MG^+

and $\text{S}_2\text{O}_4^{2-}$. $[\text{MG}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_4^{2-}] = 2.0 \times 10^{-4}$

Table 2 : Effect of changes of the dielectric constant of reaction medium on the rate constants for the oxidation of MG^+ by $\text{S}_2\text{O}_4^{2-}$ at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_4^{2-}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25.5 \pm 0.5^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

D

$10^3 k_1$,

k_2 ,

(s^{-1})

($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)

159	80.10	3.60	18.03
160	79.51	3.30	16.45
161	78.92	3.00	15.06
162	78.33	2.80	13.93
163	77.74	2.60	12.79
164	77.15	2.30	11.44
165	76.55	2.10	10.63
166	75.96	1.90	9.60
167	75.37	1.80	8.91

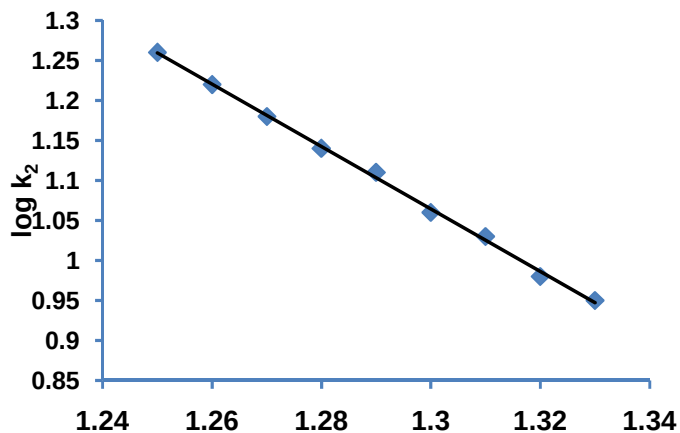


Fig 4 : Plot of $\log k_2$ versus $1/D$ for the reaction of MG and $S_2O_4^{2-}$. $[MG^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $S_2O_4^{2-} = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; $\mu =$

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^+ increased the rate had no remarkable effect on the reaction rates (Tables 3 and 4). **Anions inhibition**

and cation catalysis as observed in this reaction agrees with earlier literature [16 - 18]. This suggests that the coordination integrity of the redox partners remained intact during and prior to electron transfer.

Table 3 : Effect of added anions to the reaction medium on the rate constants for the oxidation of MG^+ by $\text{S}_2\text{O}_4^{2-}$ at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_4^{2-}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25.5 \pm 0.5 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

$10^4[\text{cation}],$	$10^3k_1,$	$k_2,$
mol dm^{-3}	(s^{-1})	$(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
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 $\text{S}_2\text{O}_4^{2-}$ at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_4^{2-}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25.5 \pm 0.5 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

	$10^4[\text{anion}],$ mol dm^{-3}	$10^2k_1,$ (s^{-1})	$k_2,$ $(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
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

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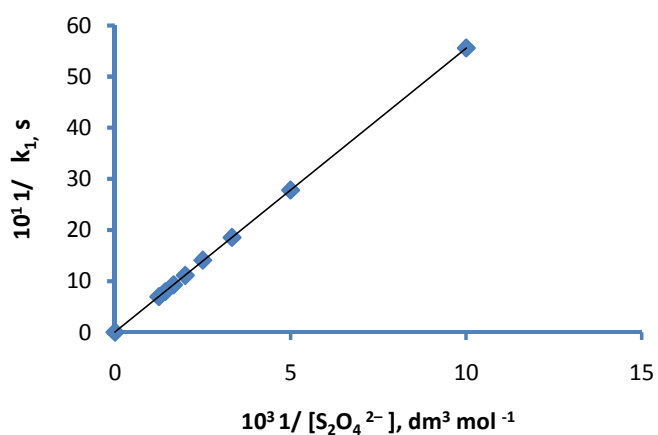


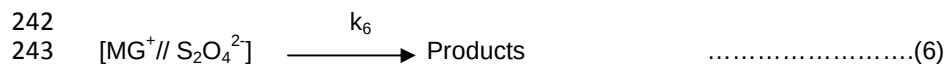
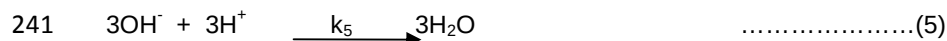
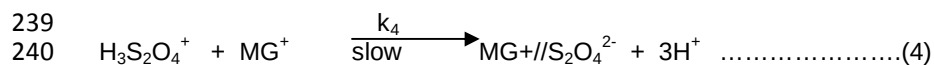
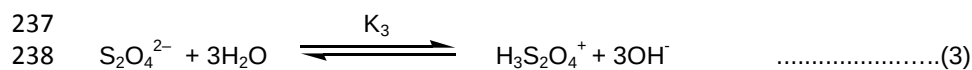
Fig 5 : Plot of $1/k_1$ versus $1/[S_2O_4^{2-}]$ for the reaction of MG and $S_2O_4^{2-}$ $[MG] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $S_2O_4^{2-} = (1.0 - 8.0) \times 10^{-4} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$, $\lambda = 620 \text{ nm}$, Temp. = $25.5 \pm 0.5^\circ\text{C}$

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236 3.5 Mechanism of reaction



244 $\text{Rate} = k_4[H_3S_2O_4^+][MG^+] \dots\dots\dots(7)$

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

246

247 $\text{Rate} = \frac{k_4 K_3 [S_2O_4^{2-}] [H_2O]^3 [MG^+]}{\dots\dots\dots} \dots\dots\dots(8)$

[OH⁻]

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

$$\text{Rate} = k_4 K_3 [S_2O_4^{2-}] [MG^+] \dots\dots\dots (9)$$

Equation (9) is similar to equation (2) where $k_2 = k_4 K_3$

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} on the reaction progress suggesting that stable reaction intermediates are not formed during the course of the reaction.

(2) The above assertion is re-enforced by the Michaelis-Menton plot of $1/k_{\text{obs}}$ 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.

4. CONCLUSION

The kinetics of the dithionite ($S_2O_4^{2-}$) oxidation of Malachite Green (MG^+) has been studied in aqueous acidic medium. The observed result at $T = 25.5 \pm 0.5$ °C showed that the reaction was first order with respect to malachite green and the dithionite ions respectively, second order overall. 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 the absence of intermediate complex formation. Based on these findings, the reaction was suspected to proceed through the outer sphere pathway.

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