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KINETICS AND MECHANISM OF THE ELECTRON TRANSFER REACTION OF MALACHITE GREEN WITH SULPHITE ION IN ACIDIC MEDIUM

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Abstract: Electron transfer reaction between malachite green and sulphite ion have been investigated in aqueous hydrochloric acid medium under pseudo-first order conditions at 27 ± 1°C, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, I = 0.1 mol dm^{-3} (NaCl) and λ_{max} = 620 nm. The reaction was first order in $[MG^+]$ and $[SO_3^{2-}]$. Effect of changes in hydrogen ion concentration on reaction rate is negligible and the reaction displayed a positive Bronsted-Debye salt effect. There was no evidence of intermediate complex formation and free radicals were absent. The observations suggest an outer-sphere mechanism for the reaction. The reaction obeys the rate law: $-d[MG^+]/dt = k_2 [MG^+][SO_3^{2-}]$. A plausible mechanism has been proposed for the reaction.

Keywords: Kinetics, malachite green, mechanism, outer-sphere, sulphite

Introduction

Malachite green (MG^+) is a basic dye extensively used as biocide in the aquaculture industry world-wide. It is highly effective against important protozoal and fungal infections. Basically, it works as an ectoparasiticide: it has also been used to control skin flukes and gill flukes (Srivastava *et al.*, 2004). It is also used as a food colouring agent, food additive, medical disinfectant and anthelminthic as well as a dye in silk, wool, jute, leather, cotton, paper and acrylic industries (Mohammed *et al.*, 2009).

Sulphite is used as a preservative to prevent spoilage and oxidation at several stages of wine production. It is also used in dried fruits and potato products (Edokpayi *et al.*, 2010). It was observed to reduce metal ions and other oxidants by a variety of mechanisms with varying stoichiometries. The stoichiometry and products of reactions involving sulphite allows a distinction to be made between one-equivalent or two-equivalent oxidizing agents (Babatunde and Iyun, 2009). Report shows that free SO_3^{2-} is always oxidized to SO_4^{2-} without $S_2O_6^{2-}$ or with very negligible amount of it.

Despite the rich articles in literature about the kinetic studies of MG^+, the redox chemistry of this dye with SO_3^{2-} has not been reported. In the present study, an attempt is made to investigate the kinetics of redox reaction of malachite green with sulphite ion in acidic medium. The effect of changes in the concentration of acid, ionic strength and added ions were studied.

Materials and Methods

All chemical reagents used were of analytical grade. Malachite green was obtained from M&B Laboratory Chemicals in the laboratory grade and used without further purification. Distilled water was used to prepare all solutions. A stock solution of Na_2SO_3 and MG^+ were prepared by dissolving the required amount in distilled water. A NaCl solution was added to reaction mixture in order to maintain a constant ionic strength of the solution.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of MG^+ was kept constant while that of SO_3^{2-} was varied in the reaction mixtures. Excess MG^+ was determined by measuring the absorbance of the solutions at 620 nm (λ_{max} of MG^+) until a constant value was obtained. The stoichiometry was evaluated from the plot of absorbance against mole ratio (Tanimu *et al.*, 2012).

Kinetics studies

The kinetic studies were carried out under pseudo-first order conditions with the $[SO_3^{2-}]$ in excess over the $[MG^+]$ at λ_{max}= 620 nm. The pseudo-first order rate plots of log (A_t-A_∞) versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t) and from the slopes of the plots, the pseudo-first order rate constants (k_1) were determined (Idris *et al.*, 2014). The second order rate constants (k_2) were obtained from equation 1.

$$k_2 = k_1/[SO_3^{2-}] \qquad (1)$$

Acid dependence studies

The effect of changes in $[H^+]$ on the reaction rate was studied by varying the $[H^+]$ between $(0.6 – 8.0) \times 10^{-3}$ mol dm^{-3} while keeping the concentration of all other reactants constant. Variation of acid dependent rate constant with $[H^+]$ was obtained by plotting k_2 against $[H^+]$ (Ibrahim and Hamza, 2016).

Effect of varying ionic strength

The effect of ionic strength on the rate of reaction was studied in the range (0.05 – 0.5) mol dm^{-3} while the concentration of other reactants were kept constant and the temperature maintained at 27 ± 1°C.

Influence of added ions

The effect of added ions was investigated for $[X] = (10 – 80) \times 10^{-4}$ mol dm^{-3} for NH_4^+ and NO_3^- at constant $[MG^+]$, $[SO_3^{2-}]$, $[H^+]$ and ionic strength (Tanimu *et al.*, 2012).

Test for intermediate complex

The spectrum of the reaction mixture was obtained over a wavelength range of (480–700) nm shortly after the initiation of the reaction. This was carried out in order to determine whether there is significant shift in λ_{max} or enhancement of peak as reaction progressed. Michaelis-Menten plot of $1/k_1$ versus $1/[SO_3^{2-}]$ was also made (Mohammed *et al.*, 2010).

Test for free radicals

To a partially oxidized reaction mixture containing various concentrations of oxidant, about 5 cm^3 of acrylamide was added followed by large excess of methanol to initiate free radical polymerization. A control experiment was carried out by adding acrylamide to each of the reactants separately (Adetoro *et al.*, 2010).

Results and Discussion

Stoichiometry

The result of the stoichiometric investigation indicates that one mole of MG^+ consumed one mole of sulphite ion (Fig. 1), and is represented in Equation (2).

$$MG^+ + SO_3^{2-} \rightarrow \text{products} \qquad (2)$$

Similar stoichiometry was reported for the oxidation of sulphite ion by indigo carmine (Edokpayi *et al.*, 2010), decolorization of methylene blue with sodium sulphite in aqueous media (Olajire and Olajide, 2014) and the reduction of toluidine blue with sulphite ion (Jonnalagada and Gollapalli, 2000).

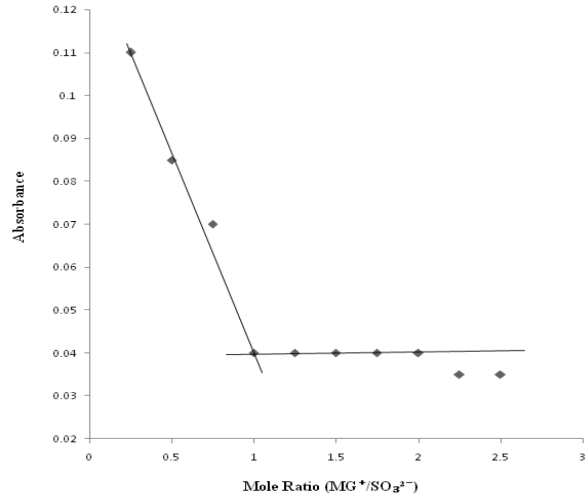

Fig. 1: Plot of absorbance versus mole ratio for the redox reaction of malachite green with sulphite ion at $[MG^+]$ = 1.0 × 10^{-4} mol dm^{-3}, $[H^+]$ = 5.0 × 10^{-3} mol dm^{-3}, I = 0.10 mol dm^{-3} and T = 27 ± 1°C

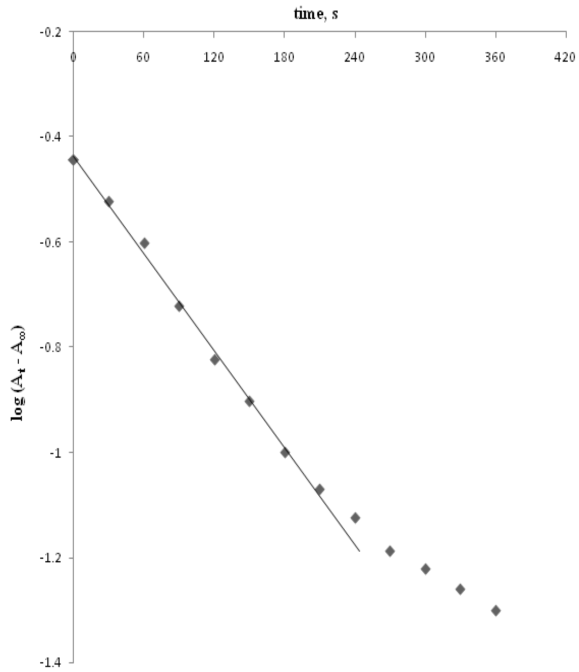

Fig. 2: Typical pseudo-first order plot for the redox reaction of malachite green with sulphite ion at $[MG^+]$ = 1.0 × 10^{-4} mol dm^{-3}, $[SO_3^{2-}]$ = 5.6 × 10^{-3} mol dm^{-3}, $[H^+]$ = 5.0 × 10^{-3} mol dm^{-3}, I = 0.10 mol dm^{-3} and T= 27 ± 1°C

Kinetics

The pseudo-first order plots of log (A_t - A_∞) versus time were linear to about 80% extent of the reaction. The linearity of these plots indicates that these reactions are first order with respect to $[MG^+]$. Typical pseudo-first order plot is shown (Fig. 2). The slopes of the pseudo-first order plots which represent the pseudo-first order rate constants, k_1 are reported (Table 1). Least square plot of log k_1 versus log $[SO_3^{2-}]$ at constant $[H^+]$ was linear, with a slope of 0.99 (Fig. 3) suggesting a first order with respect to $[SO_3^{2-}]$. The values of second order rate constants k_2 were also fairly constant (Table 1).

The rate equation for the reaction can therefore be written as;

$$\frac{-d[MG^+]}{dt} = k_2[MG^+][SO_3^{2-}] \qquad (3)$$

where k_2 = (24.56 ± 0.37) × 10^{-2} dm^3 mol^{-1} s^{-1}

Table 1: Pseudo-first order and second order rate constants for the redox reaction of malachite green with sulphite ion in aqueous HCl medium at $[MG^+]$ = 1.0 × 10^{-4} mol dm^{-3}, T= 27 ± 1°C and λ_{max} = 620 nm

$10^3[SO_3^{2-}]$, mol dm^{-3}	$10^3[H^+]$, mol dm^{-3}	I, mol dm^{-3}	10^4 k_1, s^{-1}	10^1 k_2, dm^3 mol^{-1} s^{-1}
3.00	5.00	0.10	7.30	2.43
3.60	5.00	0.10	8.83	2.45
4.00	5.00	0.10	9.98	2.49
4.40	5.00	0.10	10.75	2.44
4.80	5.00	0.10	11.90	2.48
5.20	5.00	0.10	13.05	2.51
5.60	5.00	0.10	13.43	2.40
6.00	5.00	0.10	14.58	2.43
5.60	0.60	0.10	14.67	2.62
5.60	0.80	0.10	14.67	2.62
5.60	1.00	0.10	14.67	2.62
5.60	2.00	0.10	14.17	2.53
5.60	4.00	0.10	13.83	2.47
5.60	5.00	0.10	13.83	2.47
5.60	6.00	0.10	13.50	2.41
5.60	8.00	0.10	13.83	2.47
5.60	5.00	0.05	11.17	1.99
5.60	5.00	0.10	13.83	2.47
5.60	5.00	0.15	15.33	2.74
5.60	5.00	0.20	18.50	3.30
5.60	5.00	0.30	23.83	4.26
5.60	5.00	0.40	27.33	4.88
5.60	5.00	0.50	31.50	5.63

Table 2: Pseudo-first order and second order rate constants for the effect of added ions on the rate of redox reaction of malachite green with sulphite ion at [MG$^+$] = 1.0 × 10^{-4} mol dm^{-3}, [SO_3^{2-}] = 5.6 × 10^{-3} mol dm^{-3}, I = 0.10 mol dm^{-3} and T= 27 ± 1°C

X	10^4 [X], mol dm^{-3}	10^3 k$_1$, s^{-1}	10^1 k$_2$, dm^3 mol^{-1} s^{-1}
NH_4^+	0	1.35	2.40
	20	1.38	2.47
	30	1.42	2.54
	40	1.42	2.54
	50	1.47	2.54
	60	1.50	2.67
	70	1.50	2.67
	80	1.55	2.74
NO_3^-	0	1.38	2.47
	10	1.85	3.29
	20	2.00	3.58
	30	2.12	3.77
	40	2.15	3.84
	50	2.23	3.98
	60	2.30	4.11
	80	2.42	4.32

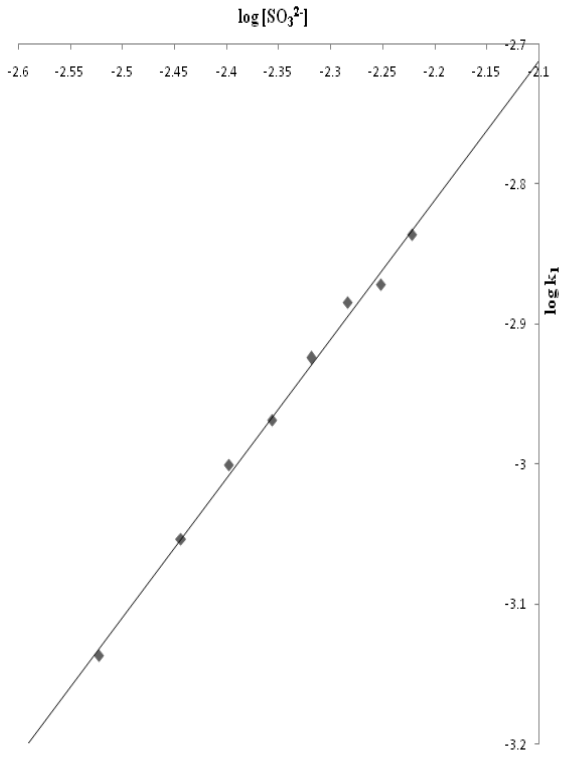

Fig. 3: Pseudo-first order plot of log k$_1$ versus log [SO_3^{2-}] for the redox reaction of malachite green with sulphite ion at [MG$^+$] = 1.0 × 10^{-4} mol dm^{-3}, [H$^+$] = 5.0 × 10^{-3} mol dm^{-3}, I = 0.10 mol dm^{-3}, λ_{max} = 620 nm and T= 27 ± 1°C

Effect of [H$^+$]

The effect of changes in hydrogen ion concentration on reaction rate is negligible, suggesting that the reaction occurred through an acid-independent pathway. The non-dependence of this reaction on [H$^+$] is in accord with the fact that neither the oxidant nor the reductant undergo significant protonation or deprotonation under the given reaction conditions. Similar result was reported by Edokpay *et al.* (2010).

Effect of ionic strength

The rate of reaction increases with increasing ionic strength. Plot of log k$_2$ against √I gave a positive slope (Fig. 4). This implies that activated complex was formed from reactants of similar charges in the rate determining step and the product of the charges is +1. Reactions between two pairs of ions of like charge are usually accelerated by increasing ionic strength because of the favorable interactions of the activated complex with the denser ionic environment (Idris *et al.*, 2010). This suggests a positive salt effect.

Effect of added ions

Increase in concentration of added anion (NO_3^-) was found to increase the rate of reaction (Fig. 5). This observation is typical of reactions occurring by the outer-sphere mechanism with the characteristic feature of the coordination integrity of the reactants maintained prior to and during the electron transfer process (Ibrahim and Hamza, 2016)

The effect of added cation (NH_4^+) was small and quite negligeable.

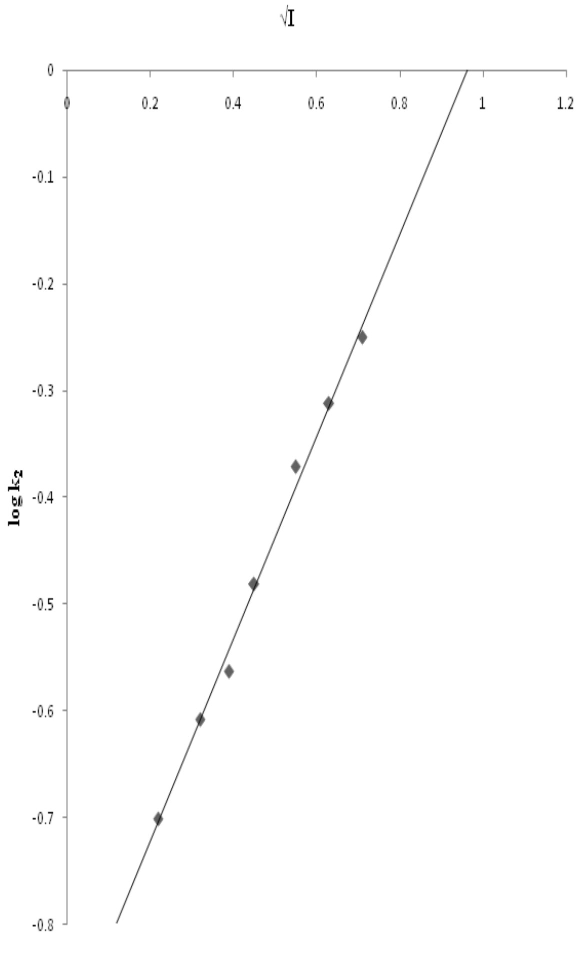

Fig. 4: Plot of log k$_2$ versus $\sqrt{I}$ for redox reaction of malachite green with sulphite ion at [MG$^+$] = 1.0 × 10^{-4} mol dm^{-3}, [SO_3^{2-}] = 5.6 × 10^{-3} mol dm^{-3}, [H$^+$] = 5.0 × 10^{-3} mol dm^{-3} and T= 27 ± 1°C

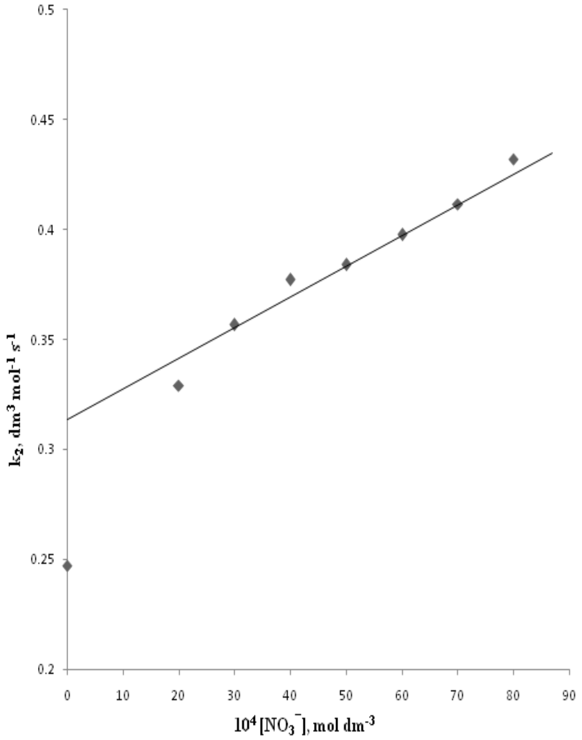

Fig. 5: Plot of k_2 versus $[NO_3^-]$ for the redox reaction of malachite green with sulphite ion at $[MG^+]$ = 1.0 × 10^{-4} mol dm^{-3}, $[SO_3^{2-}]$ = 5.6 × 10^{-3} mol dm^{-3}, I = 0.10 mol dm^{-3} and T= 27 ± 1°C

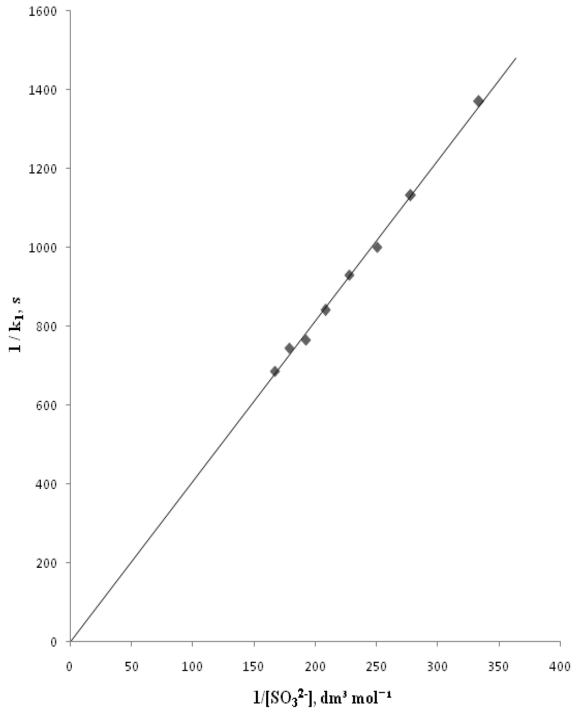

Fig. 6: Michaelis-Menten plot of $1/k_1$ versus $1/[SO_3^{2-}]$ for the redox reaction of malachite green with sulphite ion at $[MG^+]$ = 1.0 × 10^{-4} mol dm^{-3}, $[H^+]$ = 5.0 × 10^{-3} mol dm^{-3}, I = 0.10 mol dm^{-3} and T= 27 ± 1°C

Test for intermediate complex formation

There was no shift in λ_{max} of reaction mixture spectrum when compared with that of MG^+. Lack of spectrophotometric evidence for the formation of intermediate complex suggests an outer-sphere mechanism. Also the linearity of Michaelis-Menten plot further suggests the absence of an intermediate complex (Fig. 6).

Polymerization studies

A gelatinous precipitate was formed after the addition of acrylamide to the partially reacted solution. This indicates the presence of free radicals in the reaction.

Reaction mechanism

On the basis of the above results, the scheme in equation (4) - (13) is thus proposed for the reaction which occurred via the outer-sphere mechanism.

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(fast)} \quad (4)$$

$$MG^+ + OH^- \xrightarrow{k_3} MGO^- + H^+ \quad (5)$$

$$SO_3^{2-} + H^+ \overset{K_4}{\rightleftharpoons} HSO_3^- \quad \text{(fast)} \quad (6)$$

$$MGO^- + HSO_3^- + H_2O \xrightarrow{k_5} \text{Products} + SO_4^{2-} \quad \text{(slow)} \quad (7)$$

Equation 7 is the rate determining step. Therefore:

$$\text{Rate} = k_5 [MGO^-] [HSO_3^{2-}] [H_2O] \qquad (8)$$

Applying steady state hypothesis to intermediate specie $[MGO^-]$, we have

$$\frac{-d[MGO^-]}{dt} = k_3 [MG^+] [OH^-] \qquad (9)$$

And $[HSO_3^-] = K_4 [SO_3^{2-}] [H^+]$ from equation 6 (10)

Substituting equations 9 and 10 in 8, we have;

$$\text{Rate} = k_3K_4 k_5 [MG^+] [SO_3^{2-}] [H_2O] [H^+] [OH^-] \qquad (11)$$

$$= k_3K_4 k_5 K_w [MG^+] [SO_3^{2-}] \qquad (12)$$

$$= k^{III} [MG^+] [SO_3^{2-}] \qquad (13)$$

where $k^{III} = k_3K_4 k_5 K_w$

And $K_w = [H^+] [OH^-] = 10^{-14}$ and $[H_2O] = 1$

Equation 13 is analogous to equation 3

where $k^{III} = k_2$= (24.56 ± 0.37) × 10^{-2} dm^3 $mol^{-1}s^{-1}$

Conclusion

The electron transfer reaction between malachite green and sulphite ion in acidic medium revealed a stoichiometry of 1:1. The reaction is second order overall. The reaction is acid independent. It also displayed a positive Bronsted-Debye salt effect. Both kinetic and spectroscopic investigations showed no evidence of intermediate complex formation. Based on the foregoing, the outer-sphere mechanism is proposed as the plausible mechanistic pathway for this reaction.

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