Kinetics and Mechanism of the Periodate Oxidation of Malachite Green in Acidic Medium

S. O. Idris[1*], H. Hassan[1], J. F. Iyun[1] and Y. Mohammed[2]

[1]*Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.*
[2]*Department of Chemistry, Nasarawa State University, Keffi, Nigeria.*

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 HH managed the experimental process. All authors read and approved the final manuscript.

ABSTRACT

The kinetics of the periodate (IO_4^-) oxidation of malachite green (MG^+) have been studied in aqueous acidic medium. The observed results at $[H^+] = 1 \times 10^{-4}$ mol dm^{-3} (HCl), ionic strength of reaction medium, I = 0.5 mol dm^{-3} and T = 25.5±0.3°C are consistent with the rate law:

$$- \, d[MG^+]/dt \;=\; k_2[MG^+][IO_4^-]$$

where $k_2 = (k_7 \;+\; k_6K_5[H^+])$

The reaction was catalysed by increase in $[H^+]$ and added anions but displayed a negative BrØnsted–Debye salt effect. Spectrophotometric test showed the absence of intermediate complex formation. Based on these findings, a plausible mechanism is proposed.

_____

Corresponding author: E-mail: alhajisoidris@yahoo.com;

1. INTRODUCTION

Malachite green, herein and thereafter referred to as MG^+ 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]. In its reduced form, leuco – malachite green, it occurs as a contaminant in aquatic and terrestial ecosystem [2-3] and are therefore potential human health hazards. The versatility of malachite green as an antimicrobial agent [4-6] and therefore used as a preservative against fungal infection in fish [7], as dyes for fabric and paper [6] and as a cytochemical stain [8]) cannot be overemphasized.

In spite of these applications, there is scarcity of information on the kinetics and mechanisms of its reactions in the literature. 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. 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. However, we have earlier reported on the oxidation of malachite green by $Cr_2O_7^{2-}$, NO_2^-, MnO_4^- and Ag^+ - catalysed $S_2O_8^{2-}$ respectively [9-12].

In our desire to further explore the dynamics of redox properties of malachite green, we report the kinetics and mechanism of the periodate oxidation of malachite green in acidic medium.

2. EXPERIMENTAL

2.1 Materials

All chemicals used in this study were analar grade and used without further purification. Solutions of MG^+ (Sigma - Aldrich), $NaClO_4$ (BDH), HCl (BDH), NaCl (BDH), CH_3COONa (BDH), HCOONa (BDH) were prepared with distilled water.

2.2 Methods

2.2.1 Stoichiometric studies

Stoichiometric studies of the reaction was determined by spectrophotometric titration using the mole ratio method. Reaction mixtures containing various concentrations of periodate ion $(0.1 - 4) \times 10^{-5}$ mol dm^{-3} and constant concentrations of $MG^+ = 1 \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1 \times 10^{-4}$ mol dm^{-3} (HCl), I = 0.5 mol dm^{-3} (NaCl) were allowed to stand until reaction had gone to completion. The absorbance of the reaction mixtures was measured over the wavelength of 620 nm, the λ_{max} of malachite green using Corning Colorimeter 253. Plot of absorbance versus mole ratio was done and the point of inflection in the plot gave the number of moles of the oxidant consumed by 1 mole of the malachite green.

2.2.2 Kinetic measurements

All kinetic measurements were carried out under pseudo- first order conditions with respect to IO_4^- concentration in at least 400-fold excess over $[MG^+]$. The rate of reaction was monitored using Corning Colorimeter 253 by following decrease in absorbance of the MG^+ at wavelength, λ = 620nm, characteristic of MG^+. The ionic strength was maintained constant at 0.5 mol dm^{-3} (NaCl), $[H^+]$ at 1×10^{-4} mol dm^{-3} and T= 25.5±0.3°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_{obs}. The second order rate constants, k_2, were obtained from k_{obs} as $k_{obs}/[IO_4^-]$. Reaction rate dependence on changes in $[H^+]$ was investigated by keeping $[MG^+]$ and $[IO_4^-]$ constant, while varying $[H^+]$ from $(0.1 - 10.0) \times 10^{-4}$ mol dm^{-3}, maintaining ionic strength constant at 0.5 mol dm^{-3} and the temperature of reaction was maintained at 25.5±0.3°C. Variation of acid dependent second order rate constant with $[H^+]$ was obtained from the plot of k_2 versus $[H^+]$, while order of reaction with respect to $[H^+]$ was obtained as the slope of the plot of $\log k_{obs}$ versus $\log[H^+]$.

Effect of changes in ionic strength of reaction medium on rates of reaction was studied by varying the ionic strength, I, from 0.05 – 0.8 mol dm^{-3} (NaCl), while maintaining $[MG^+]$, $[IO_4^-]$ and $[H^+]$ constant at 1.1×10^{-5} mol dm^{-3}, 9.9×10^{-3}

mol dm^{-3}, and 1.0 x 10^{-4} mol dm^{-3}, respectively. Reaction temperature was maintained at 25.5 ± 0.3°C. Dependence of reaction rates on changes in ionic strength of reaction medium was determined by plotting log k_2 versus $\sqrt{\mu}$.

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, from 81.0 to 73.8, keeping [MG^+], [IO_4^-], [H^+], I and temperature constant. Plot of log k_2 versus 1/D was done to appreciate the effect of the variation of dielectric constant on the rate constants.

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 reaction mixture. Michaelis- Menten plot of 1/k_{obs} versus 1/[IO_4^-] also could give an idea on the presence or absence of intermediate complex.

2.2.3 Product analysis

The inorganic product of the reaction was subjected to qualitative inorganic analysis as follows:

a) Test for iodide (I^-) as a possible reduction product of periodate reduction was carried out by adding 1 cm^3 of HNO_3 and the dropwise addition of $AgNO_3$, then in excess. Appearance of a yellow precipitate would confirm the presence of iodide.

b) Test for iodine, I_2, as a possible reduction product of periodate was also investigated by the addition of starch solution to the reaction product solution. Appearance or non – appearance of blue - black colouration would confirm the presence or absence of I_2.
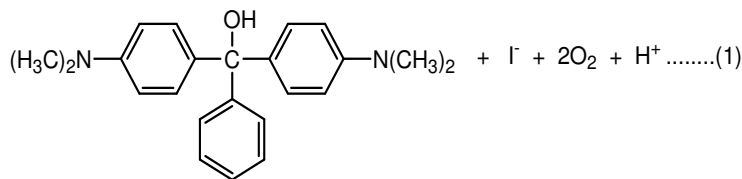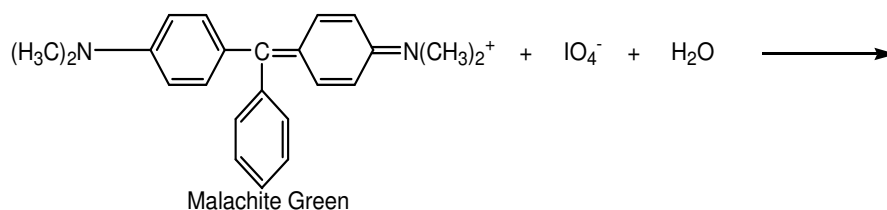
3. RESULTS AND DISCUSSION

3.1 Stoichiometry

The results of stoichiometric studies showed that one mole of MG^+ was consumed by one mole of IO_4^- (Fig. 1), which is consistent with the equation below:

Similar stoichiometry were reported for the reaction of MG^+ and $Cr_2O_7^{2-}$, NO_2^-, MnO_4^- and Ag^+ - catalysed $S_2O_8^{2-}$ [9-12].

3.2 Order of the Reaction

The pseudo – first order plots obtained from the plots of log(A_t - A_∞) versus time were linear to more than 90% completion of reaction (Fig. 2), suggesting that the reaction is first order in [MG^+]. The slopes of the pseudo – first order plots gave k_{obs} for each concentration of IO_4^-. The second order rate constants, k_2, were obtained from k_{obs} as k_{obs}/[IO_4^-]. Values of k_{obs} and k_2 for the various concentrations of IO_4^- are shown in (Table 1). The derived second order rate constants were fairly constant, further confirming that the reaction is indeed first order in [MG^+]. Plot of log k_{obs} versus log [IO_4^-] (Fig. 3) was linear with a slope of 0.7, confirming the reaction is first order with respect to [IO_4^-]. The reaction is therefore second order, overall.

$(H_3C)_2N$—⬡=C=⬡=$N(CH_3)_2^+$ + IO_4^- + H_2O ⟶

Malachite Green

$(H_3C)_2N$—⬡—C(OH)(⬡)—⬡—$N(CH_3)_2$ + I^- + $2O_2$ + H^+ ....(1)

Based on the above kinetic findings, the rate law for the reaction can be represented by the equation:

$$-\frac{d[MG^+]}{dt} = k_2[MG^+][IO_4^-] \quad \dots \quad (2)$$

Similar order of reaction has been reported by Mohammed et al. [9-12] and Mushinga and Jonnalagadda [13].

3.3 Effect of Acid on the Reaction Rate

The effect of changes [H$^+$] on the rate of reaction of malachite green and periodate ion was investigated in the acid range (1.0 – 100.0) x 10^{-5}

mol dm^{-3} (HCl). Both [MG$^+$] and [IO$_4^-$] were kept constant at 1.1 x 10^{-3} mol dm^{-3} and 9.9 x 10^{-3} mol dm^{-3}, respectively at I = 0.5 mol dm^{-3}, and temperature 25.5 ± 0.3°C. Results showed that increase in [H$^+$] led to increase in the rate constants (Table 2). Plot of k$_2$(H$^+$) versus [H$^+$] (Fig. 4) was linear with an intercept. The least square plot of log k$_{obs}$ versus log [H$^+$] as shown in (Fig. 5), gave a slope of 0.71, suggesting that the reaction is first order with respect to acid [H$^+$]. H$^+$ dependent second order rate constant can thus be represented by equation (3).
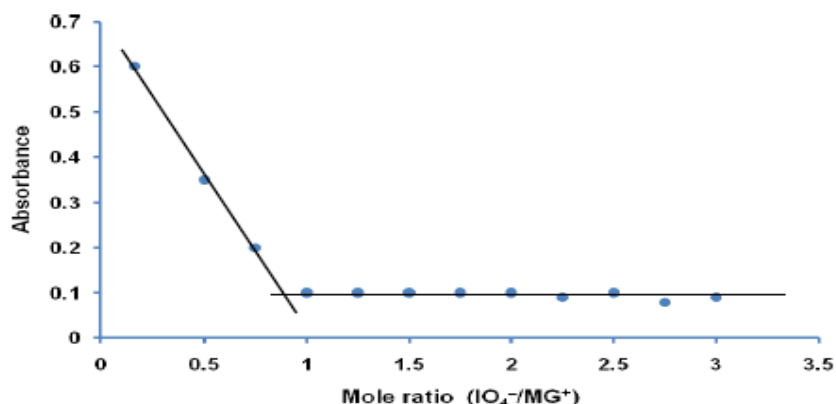
$$k_{H+} = a + b[H^+] \quad \dots \dots \dots \quad (3)$$

Fig. 1. Stoichiometry of the Oxidation of Malachite Green by IO$_4^-$ at [MG$^+$] = 1.0 x 10^{-5} mol dm^{-3}, [IO$_4^-$] = (1 - 40) x 10^{-6} mol dm^{-3}, I = 0.5 mol dm^{-3}, [H$^+$] = 1 x 10^{-4} mol dm^{-3}, λ$_{max}$ = 620 nm
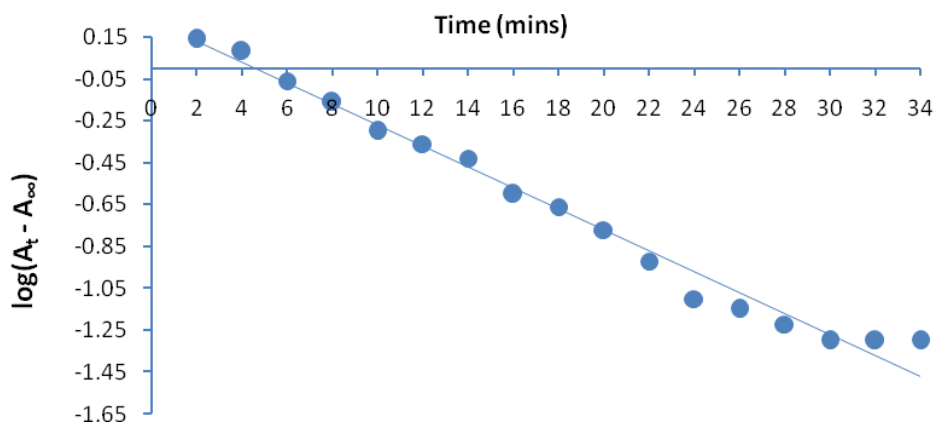

Fig. 2. Typical Pseudo- first order plot for the reaction of [MG$^+$] and [IO$_4^-$] at [MG$^+$] = 1.10 x 10^{-5} mol dm^{-3}, [IO$_4^-$] = 7.7 x 10^{-3} mol dm^{-3}, [H$^+$] = 1.0 x 10^{-4} mol dm^{-3}, I = 0.5 mol dm^{-3}, λ$_{max}$ = 620 nm and T = 25.5±0.3°C
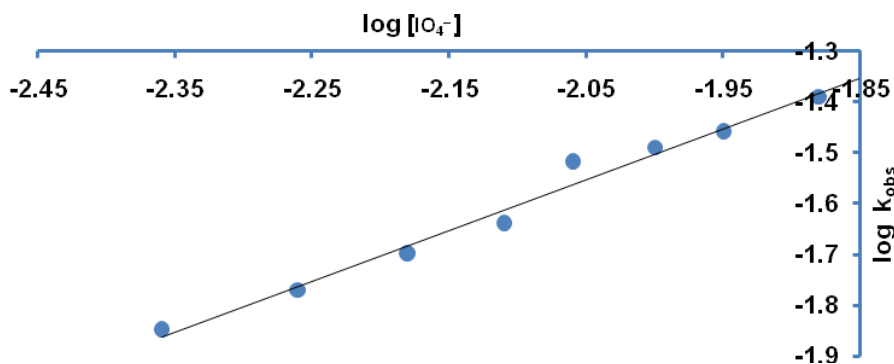
Fig. 3. Plot of log k_{obs} versus log [IO_4^-] for the reaction of MG^+ and IO_4^- at [MG^+] = 1.1 x 10^{-5} mol dm^{-3}, [IO_4^-] = (4.4 - 13.2) x 10^{-3} mol dm^{-3} , [H^+] = 1.0 x 10^{-4} mol dm^{-3} , I = 0.5 mol dm^{-3}, λ = 620 nm, Temp. = 25.5 ± 0.3°C

Table 1. Pseudo – first order and second order rate constants for the IO_4^- oxidation of MG^+ at [MG^+] = 1.1 x 10^{-5} mol dm^{-3}, [H^+] = 1 x 10^{-4} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 25.5±0.3°C and λ_{max} = 620 nm

10^3[IO_4], mol dm^{-3}	$10^2 k_{obs}$, s-1	k_2, dm^3 mol^{-1} s^{-1}
4.4	1.4	3.21
5.5	1.7	3.10
6.6	2.0	3.03
7.7	2.3	3.04
8.8	3.0	3.03
9.9	3.2	3.29
11.0	3.5	3.20
13.2	4.1	3.10

Table 2. Effect of changes in [H^+] on rate constants for the oxidation of MG^+ by IO_4^- at [MG^+] = 1.1 x 10^{-5} mol dm^{-3}, [IO_4^-] = 9.9 x 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 25.5 ± 0.3°C and λ_{max} = 620 nm

10[H^+], mol dm^{-3}	$10_2 k_{obs}$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
0.1	2.10	2.12
1.0	3.00	3.03
3.0	4.20	4.24
4.0	5.00	5.05
5.0	6.40	6.00
8.0	7.20	7.30
10.0	8.00	8.10

Acid dependence of this nature is an indication that a pre-equilibrim between protonated and deprotonated form of a reactant, IO_4^- in this case, is rapid, that the protonation equilibrium constant is small, that both the forms are reactive and the protonated form is reactive [14].

In the range of [H^+] investigated, the overall rate equation can be represented by equation (4) below.

$$- \frac{d[MG^+]}{dt} = (a + b[H^+])[MG^+][IO_4^-] \qquad (4)$$

3.4 Effect of Changes in Ionic Strength of Reaction Medium

Results of investigation of the effect of changes of ionic strength on the rates of reaction of MG^+ and periodate ions showed that the rate constants decreased with increase in ionic strength (Table 3). Plot of logk_2 versus √I was linear with a negative slope (Fig. 6), suggesting that product of the charges of reactant species that formed the activated complex is -1 [15].

Table 3. Effect of changes of ionic strength of reaction medium on the rate constants for the oxidation of MG^+ by IO_4^- at [MG^+] = 1.1 x 10^{-5} mol dm^{-3}, [IO_4^-] = 9.9 x 10^{-3} mol dm^{-3}, [H^+] = 1 x 10^{-4} mol dm^{-3}, T = 25.5±0.3°C and λ_{max}= 620 nm

I, mol dm^{-3}	$10^2 k_{obs}$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
0.05	7.4	7.50
0.10	6.4	6.50
0.20	5.3	5.40
0.30	4.6	4.65
0.40	4.0	4.04
0.50	3.0	3.03
0.80	2.1	2.12

3.5 Effect of Changes of Dielectric Constant of Reaction Medium

Results showed that for a decrease in D there was an increase of the rate constants of the reaction (Table 4). A plot of $\log k_2$ versus $1/D$ was linear with a positive slope, as shown in (Fig. 7). D is the dielectric constant of the binary solvent and is obtained as:

$$D = \frac{D_{water} \ x \ Volume_{water} \ + \ D_{acetone} \ x \ Volume_{acetone}}{Total \ Volume \ of \ solvent}$$
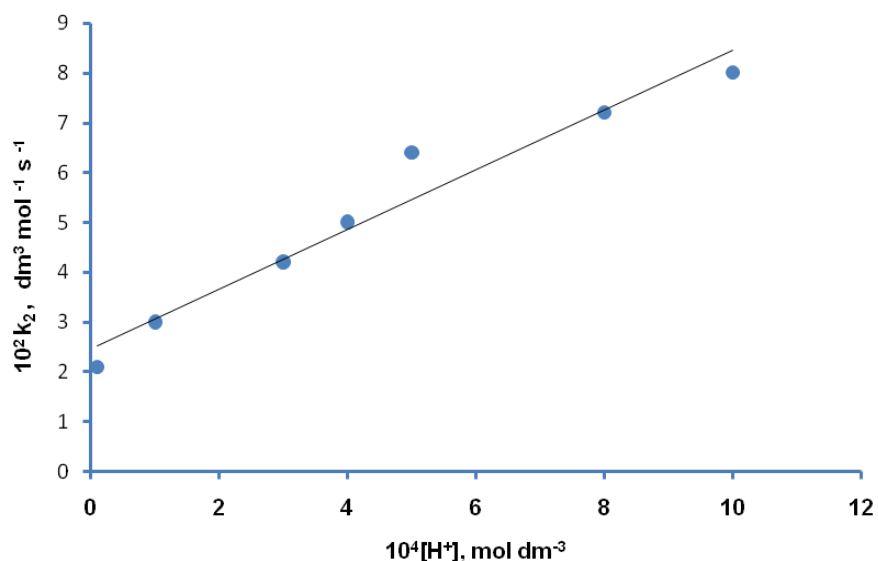

Fig. 4. Plot of k_2 against $[H^+]$ for the reaction of MG^+ and IO_4^- at $[MG^+] = 1.1 \times 10^{-5}$ mol dm $^{-3}$, $[IO_4^-] = 9.9 \times 10^{-3}$ mol dm^{-3}, $[H^+] = (1.0 - 100.0) \times 10^{-5}$ mol dm^{-3}, I= 0.5 mol dm^{-3}, $\lambda_{max} = 620$ nm and Temp. = 25.5 ± 0.3^0C

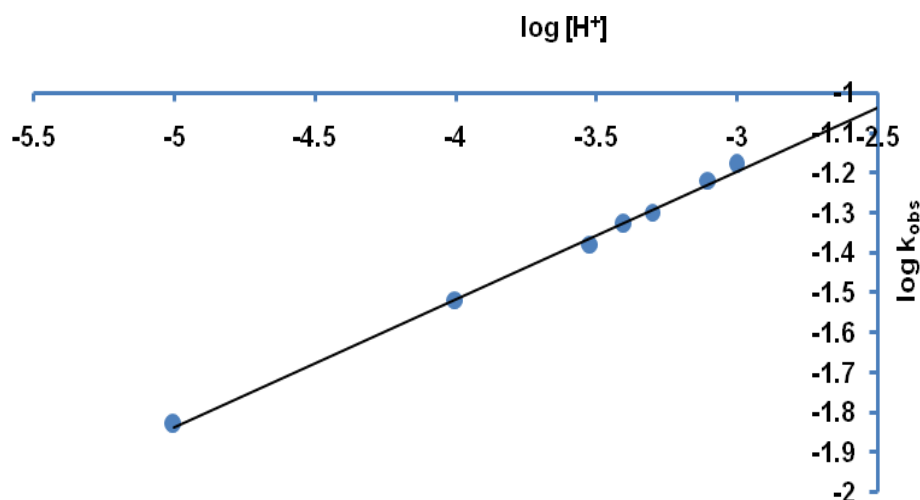**Fig. 5. Plot of log k_{obs} against $\log[H^+]$ for the reaction of MG^+ and IO_4^- at $[MG^+]=1.0 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 9.9 \times 10^{-3}$ mol dm^{-3}, $[H^+] = (1 - 100) \times 10^{-5}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, $\lambda = 620$ nm, Temp. = 25.5 ± 0.3°C**

Table 4. Effect of changes of the dielectric constant of reaction medium on the rate constants for the IO_4^- oxidation of MG^+ at $[MG^+] = 1.1 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 9.9 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1 \times 10^{-4}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 25.5 ± 0.3 °C and λ_{max} = 620 nm

D	10_2k_{obs}, s^{-1}	k_2, dm mol^{-1} s^{-1}
81.0	3.0	3.03
79.8	3.7	3.74
78.6	4.4	4.44
77.4	5.0	5.05
76.2	5.5	5.60
7.5.0	6.4	6.50
73.8	7.4	7.50

3.6 Effect of Added Anions (CH_3COO^- and $HCOO^-$) on Reaction Rates

Addition of anions CH_3COO^- and $HCOO^-$ increased the reaction rates (Table 5). This observation is typical of reactions occurring by the outersphere mechanism. This indicates that the coordination integrity of the reactants is maintained prior to and during the electron transfer process.
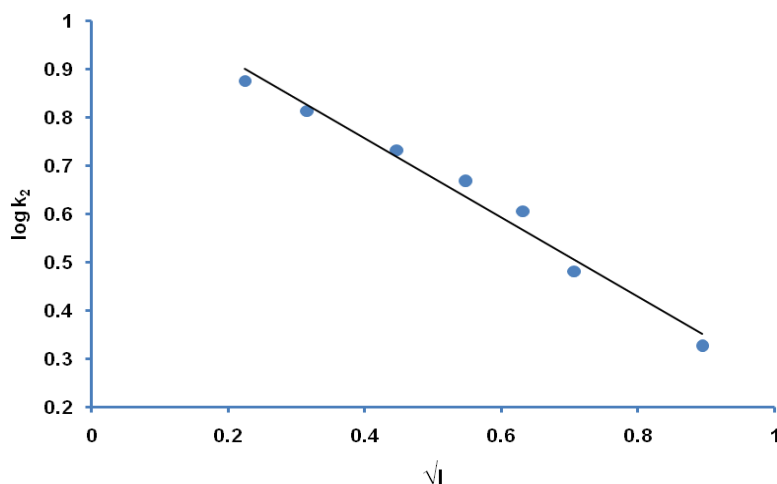

Fig. 6. A Plot of log k_2 versus √I for the reaction of MG^+ and IO_4^- at $[MG^+] = 1.1 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 9.9 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, I = (0.05 - 0.8) mol dm^{-3}, λ_{max} = 620 nm, Temp. = 25.5 ± 0.3°C

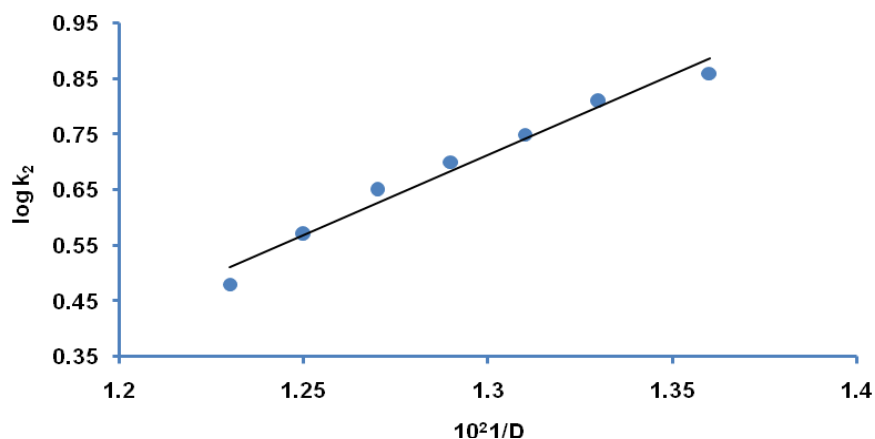**Fig. 7. Plot of log k_2 versus 1/D for the reaction of MG^+ and IO_4^- at $[MG^+] = 1.1 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 9.9 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, D = 81.0 - 73.8, λ_{max} = 620 nm and T = 25.5±0.3°C**

Table 5. Effect of added anions to the reaction medium on the rate constants for the IO_4^- oxidation of MG^+ at $[MG^+] = 1.1 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 9.9 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1 \times 10^{-4}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 25.5±0.3℃ and λ_{max}= 620 nm

10^3[anion], mol dm^{-3}	$10^2 k_{obs}$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
Ion = CH_3COO^-		
1.0	3.0	3.03
10.0	4.0	4.04
20.0	4.6	4.65
50.0	5.4	5.50
100.0	6.4	6.50
150.0	7.4	7.50
200.0	8.1	8.20
Ion = $HCOO^-$		
1.0	3.1	3.13
10.0	4.0	4.04
20.0	5.0	5.05
50.0	5.5	5.60
100.0	6.4	6.50
150.0	7.0	7.10
200.0	8.1	8.20

3.7 Test for Intermediate Complex Formation

Spectrophotometric test to determine whether spectroscopically determinable complex was formed in the course of the reaction was carried out. Reaction mixtures were made and the spectra of the product recorded immediately over a range of wavelength (400 – 700 nm). From the recorded spectra, there was no shift in λ_{max} as compared with that of the malachite green solution. This suggests that there was no intermediate complex formation. Also a Michaelis- Menten plot of $1/k_{obs}$ versus $1/[IO_4^-]$ gave a straight line with no intercept (Fig. 8).

3.8 Product Analysis

The inorganic analysis of the product of this reaction confirmed the presence of I^- by the formation of a yellow precipitate upon addition of 1 cm^3 of HNO_3 and $AgNO_3$. Also, the presence of I_2 was ruled out by the non – formation of blue – black coloration upon the addition of starch solution to the product of reaction.
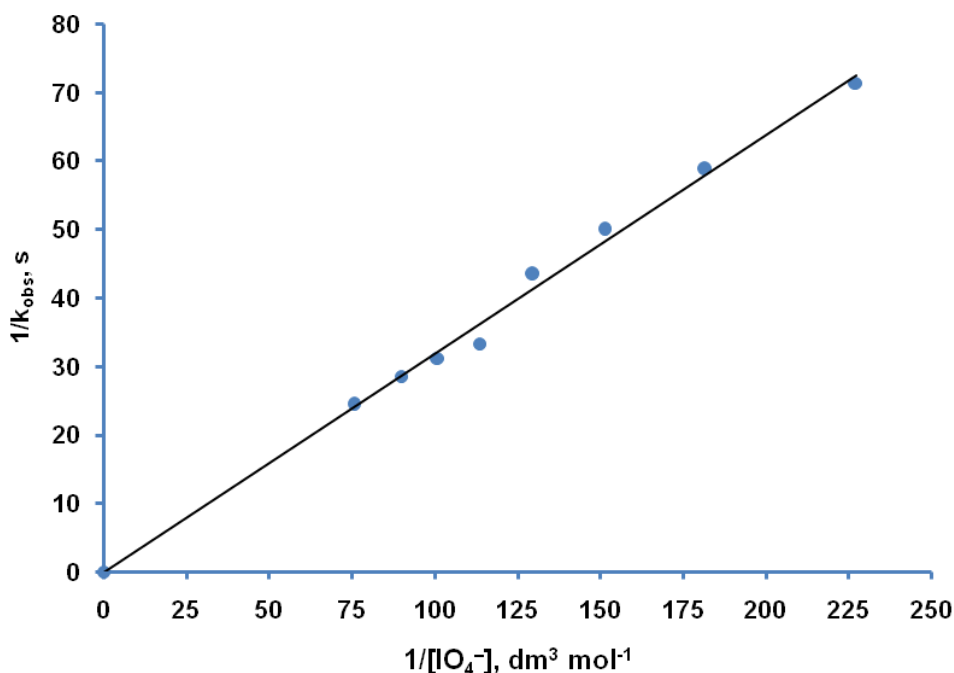

Fig. 8. Michaelis - Menten Plot for the reaction of MG^+ and IO_4^- at $[MG^+] = 1.1 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = (4.4 - 13.2) \times 10^{-3}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, $[H^+] = 1 \times 10^{-4}$, mol dm^{-3}, λ_{max} = 620 nm, Temp = 25.5±0.3℃

3.9 Mechanism of the Reaction

The positive dependence of H^+ commonly encountered in reaction of IO_4^- has been attributed to the formation of HIO_4 which reacts with the reductant in the rate determining step [16, 17]. Based on the results obtained, the mechanism of the reaction can be proposed as:

$$IO_4^- \; + \; H^+ \;\; \overset{K_5}{\underset{}{\rightleftharpoons}} \;\; HIO_4 \quad \dots\dots\dots\dots\dots\dots \quad (5)$$

$$MG^+ \; + \; HIO_4 \;\; \overset{k_6}{\longrightarrow} \;\; Products \quad \dots\dots slow\dots\dots.. \quad (6)$$

$$MG^+ \; + \; IO_4^- \;\; \overset{k_7}{\longrightarrow} \;\; Products \quad \dots\dots slow\dots\dots\dots.. \quad (7)$$

$$Rate \; = \; k_6[MG^+][HIO_4] \; + \; k_7[MG^+][IO_4^-] \qquad \dots\dots\dots\dots\dots\dots(8)$$

$$But\ from\ equation\ (5),\ [HIO_4] = K_5[H^+][IO_4^-] \qquad \dots\dots\dots\dots\dots\dots ..(9)$$

Substituting equation (9) into equation (8), we have:

$$Rate \; = \; k_6 K_5[MG^+][H^+][IO_4^-] + \; k_7[MG^+][IO_4^-] \qquad \dots\dots\dots\dots\dots\dots..(10)$$

$$= \; (k_7 \; + \; k_6 K_5[H^+])[MG^+][IO_4^-] \qquad \dots\dots\dots\dots\dots..\dots\dots\dots(11)$$

Equation (11) is consistent with equation (4) where $k_7 = $ a = 2.4 $dm^3\ mol^{-1}\ s^{-1}$ and $k_6 K_5 = b = 5.95 \times 10^3\ dm^6\ mol^{-2}\ s^{-1}$

Based on the above mechanism and the derivation of the rate law, there is a suggestion that the reaction proceeded through two acid dependent and acid independent pathways (equations 6 and 7). The acid dependent pathway was responsible for the protonation of the periodate to produce the protonated species, HIO_4. The negative salt effect observed in the reaction can be accounted for by the reaction of unlike charges in equation (7), where $Z_A Z_B = -1$.

4. CONCLUSION

The kinetics of the periodate (IO_4^-) oxidation of Malachite Green (MG^+) have been studied in aqueous acidic medium. The observed result at T = 25.5±0.3°C showed that the reaction was first order with respect to malachite green and the periodate ions respectively, second order overall. The reaction was catalysed by increase in $[H^+]$ and added anions but displayed a negative Bronsted–Debye salt effect. Spectrophotometric test showed the absence of intermediate complex formation. Based on these findings, the reaction was suspected to proceed through the outersphere pathway.

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. Burchmore S, Wilkinson M. Proposed environmental quality standards for malachite green in water (DWE 9026). United Kingdom Department of the Environment, Report no. 3167/ 2. Marlow, Buckinghamshire, United Kingdom: Water research centre; 1993.

3. Nelson CR, Hites RA. Aromatic amines in and near Buffalo River. Environ Sci Technol. 1980;14:1147.
4. Alderman DJ. *In vitro* testing of fisheries chemotherapeutics. J. Fish. Dis. 1982;5:119.
5. Alderman DJ. Malachite green: a review. J. Fish. Dis. 1985;8(3):295.
6. Culp SJ, Beland FA. Malachite green: A toxicological review. J. Am. Coll. Toxicol. 1996;15:219.
7. Schnick RA. The impetus to register new therapeutics for aquaculture. Prog Fish. Cult. 1988;50:190.
8. Lawton JR. An investigation of the fixation and staining of lipids by a combination of malachite green or other triphenylmethane dyes with glutaraldehyde. J. Microsc. 1989;154:83
9. Mohammed Y, Iyun JF, 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. 2010;20(2):105-112.
13. Mushinga T, Jonnalagadda SB. A kinetic approach for the mechanism of malachite gree – peroxydisulphate reaction in aqueous solution. Int. J. Chem. Kinet. 1991;24(1):41.
14. Gupta KS, Gupta YK. Hydrogen – ion dependence of reaction rates and mechanisms. J. Chem. Edu. 1984;61(11): 972-977.
15. Atkins PW, de Paula J. Physical Chemistry. 7th Ed., Oxford University Press. 2002;962.
16. Birk JP. Kinetics and Mechanism of the reduction of bromate ion by hexachloroiridate (III). Inorg. Chem. 1973;504-506.
17. Birk JP, Kozub SG. Mechanism of reduction of bromated ion by cyanobipyridine iron (II) complexes. Inorg. Chem. 1978;1186-1191.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=745&id=22&aid=6825