

Kinetics and Mechanism of Malachite Green Oxidation by Hypochlorite Ion in Aqueous Acidic Medium

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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 wrote the protocol and the final draft of the manuscript. Author YM managed the literature searches and wrote the first draft of the manuscript. Author AT carried out the laboratory investigations. All authors read and approved the final manuscript.

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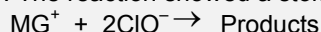
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ABSTRACT

The kinetic investigations of the redox reaction between malachite green, MG^+ , and hypochlorite ion, ClO^- , were carried out in aqueous $HClO_4$ medium at $[H^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$. The reaction showed a stoichiometry of 1:2, which conforms to the equation:



Kinetic data revealed a first order dependence on both $[MG^+]$ and $[ClO^-]$ giving a second order overall. The second order rate law for the reaction conforms to the equation:

$$-d[MG^+]/dt = k_2[MG^+][ClO^-]$$

where $k_2 = 115.55 \pm 1.21 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Reaction rate increased with increase in $[H^+]$. Changes in ionic strength and dielectric constant of

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the reaction medium did not alter the reaction rate. Addition of anions at different concentrations also did not affect reaction rate. The absence of spectroscopic evidence of intermediate complex formation suggests that the reaction proceeds through the outersphere mechanism. This suggestion is further reinforced by kinetic evidence from the Michaelis-Menten plot. A plausible mechanism based on these observations is proposed.

Keywords: Kinetics; mechanism; outer sphere; malachite green; hypochlorite ion.

1. INTRODUCTION

Malachite green, a triphenylmethane dye, for convenience, herein and hereafter referred to as MG^+ , has received some attention in recent time due to its wide application, especially in aquaculture. This has been attributed to its relatively low cost, ready availability and efficacy [1]. The dye is highly toxic to mammalian cells as it promotes hepatic tumor formation in rodents and also causes reproductive abnormality in rabbits and fish [2–5]. The compound is active against the *Oomycete saprolegnia*, which infects fish eggs in commercial aquaculture, and other fungi. Furthermore, MG^+ is also used as a parasiticide and antibacterial agent. Potential human exposure to MG^+ could result from the consumption of treated fish [6]. Kinetic data on the reaction of MG^+ with some oxyanions have been reported [7–10]. Hypochlorite ion, ClO^- is the strongest oxidizing agent of the chlorine oxyanions and is sufficiently strong enough to oxidize Mn(III) to Mn(V) during the Jacobsen epoxidation reaction and to convert Ce^{3+} to Ce^{4+} [11]. This oxidizing property makes the ions effective bleaching and stain removing agents [12]. Liquids containing sodium hypochlorite as the main active component are also used for household cleaning and disinfection. Among other applications, it can be used to remove mould stains and dental stains caused by fluorosis [13]. In our pursuit to understand the dynamics of redox properties of the redox partners (MG^+ and ClO^-), we report the kinetics and mechanism of MG^+ oxidation by ClO^- in aqueous acidic medium.

2. MATERIALS AND METHODS

2.1 Materials

All chemical reagents used in this work were of analar grade and were used without further purification. $NaClO$ (BDH, Analar) was used as the oxidant, $HClO_4$ (Sigma – Aldrich, 60%) was used to provide an acid medium and $NaClO_4$ (Sigma – Aldrich, 98%), being an inert electrolyte

was used to maintain a constant ionic strength, μ , of reaction medium (except when investigating the effect of changes in ionic strength of the reaction medium). Acetone (BDH, Analar) was used to change the dielectric constant of the reaction medium. $MgCl_2$, NH_4Cl , $NaNO_3$, Na_2SO_4 solutions were used to provide the Mg^{2+} , NH_4^+ , NO_3^- and SO_4^{2-} to investigate the effects of added ions on the reaction rates. MG^+ , the oxidant and the other solutions were prepared using double distilled water.

2.2 Methods

A stoichiometric study 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 hypochlorite to MG^+ was varied from (0.25 – 4.00) at 620nm, $[H^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ($HClO_4$), $\mu = 0.1 \text{ mol dm}^{-3}$ ($NaClO_4$) and Temperature = $25 \pm 1^\circ\text{C}$. The reactions were allowed to go to completion and the absorbance (A_∞) of each of the reactions was measured using Corning Colorimeter 253. The values obtained were plotted against the individual mole ratios of the reactants. Point of inflection on the plot gave the mole ratio of the reactants (Fig. 1).

2.2.1 Kinetic measurements

All kinetic measurements were carried out under pseudo-first order conditions with respect to $[ClO^-]$ in at least 10-fold excess over $[MG^+]$. The rate of reaction was monitored using Corning Colorimeter 253 by following the decrease in absorbance of the MG^+ at $\lambda_{\text{max}} = 620\text{nm}$, characteristic of MG^+ . The ionic strength was maintained constant at 0.1 mol dm^{-3} ($NaClO_4$), $[H^+] \text{ at } 1 \times 10^{-3} \text{ mol dm}^{-3}$ and $T = 25 \pm 1^\circ\text{C}$.

Pseudo-first order plots of $\log(A_t - A_\infty)$ against time were made (where A_t and A_∞ are the absorbances at time, t and at the end of the reaction respectively) and the slopes of the plots gave the pseudo-first order rate constants, k_{obs} . Reaction rate dependence on changes in $[H^+]$ was investigated by keeping $[MG^+]$ and $[ClO^-]$

constant, and varying $[H^+]$ from $(0.5-4.0) \times 10^{-3}$ mol dm $^{-3}$, maintaining ionic strength constant at 0.1 mol dm $^{-3}$ and the reaction temperature at $25 \pm 1^\circ\text{C}$. 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 $\log k_{\text{obs}}$ versus $\log[H^+]$.

Effect of changes in ionic strength of reaction medium on the reaction rates was studied by varying the ionic strength from 0.1 – 0.7 mol dm $^{-3}$ (NaClO $_4$), and maintaining $[MG^+]$, $[ClO^-]$ and $[H^+]$ constant at 1.0×10^{-5} mol dm $^{-3}$, 2×10^{-4} mol dm $^{-3}$, and 1.0×10^{-3} mol dm $^{-3}$ respectively. Reaction temperature was maintained at $25 \pm 1^\circ\text{C}$. 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 , in the range of 75.37 – 80.10 while keeping $[MG^+]$, $[ClO^-]$ and $[H^+]$, μ and T constant during the reaction. Test for generation and participation of free radicals

during 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 solutions of MG^+ and ClO^- at conditions of $[H^+]$, μ and temperature stated 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. Kinetic evidence as indicated by Michaelis-Menten plot of $1/k_1$ versus $1/[ClO^-]$ also could give an idea on the presence or absence of intermediate complex.

3. RESULTS AND DISCUSSION

The results of stoichiometric studies showed that one mole of MG^+ was consumed by two moles of ClO^- (Fig. 1), which is consistent with equation (1).

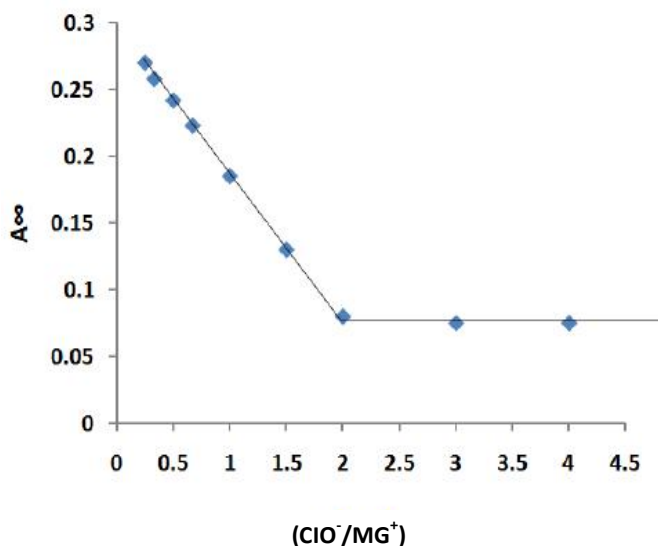
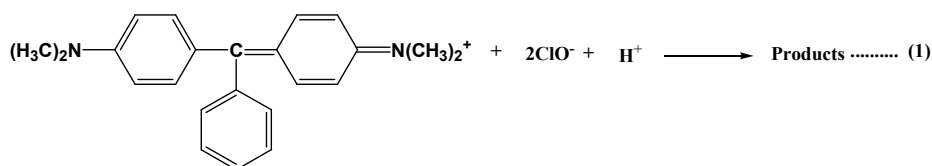


Fig. 1. Stoichiometry of the oxidation of malachite green by ClO^- at $[MG^+] = 1.0 \times 10^{-5}$ mol dm $^{-3}$, $\mu = 0.1$ mol dm $^{-3}$, $[H^+] = 1 \times 10^{-3}$, mol dm $^{-3}$ and $\lambda = 620$ nm



Earlier studies on the reactions of Mg^{2+} 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 [8–11].

3.1 Order of Reaction

The pseudo – first order plots obtained from the plots of $\log(A_t - A_\infty)$ versus time were linear to more than 90% completion of reaction, suggesting that the reaction is first order in $[\text{Mg}^{2+}]$. The slopes of the plots gave observed rate constants, k_{obs} , also referred to as k_1 , for each concentration of ClO^- . The derived second order rate constants, k_2 , were obtained as $k_1/[\text{ClO}^-]$. Values of k_1 and k_2 for the different concentrations of ClO^- are shown in Table 1. The second order rate constants were fairly constant, further confirming that the reaction is indeed first order in $[\text{Mg}^{2+}]$. Plot of $\log k_1$ versus $\log[\text{ClO}^-]$ (Fig. 2) was linear with a slope of unity and a correlation coefficient of 0.98, implying first order in $[\text{ClO}^-]$. The reaction is therefore second order overall. The rate law for the reaction can be represented by the equation

$$-d[\text{Mg}^{2+}]/dt = k_2[\text{Mg}^{2+}][\text{ClO}^-] \quad \text{..... (2)}$$

Similar order of reaction has been reported by Mushinga and Jonnalagadda [14] and Mohammed et al. [8–11].

3.2 Influence of Acidity on Reaction Rate

Influence of acid on the rate of reaction was investigated by using HClO_4 in the range $(0.5 - 4.0) \times 10^{-3} \text{ mol dm}^{-3}$ at $\mu = 0.1 \text{ mol dm}^{-3}$, and temperature = $25 \pm 1^\circ\text{C}$. Results showed that increase in $[\text{H}^+]$ led to increase in the rate constants (Table 2). Plot of $\log k_1$ versus $\log[\text{H}^+]$ gave a slope of unity with a correlation coefficient of 0.98 (Fig. 3), suggesting that the reaction is first order in $[\text{H}^+]$. When a plot of k_2 versus $[\text{H}^+]$ was made (Fig. 4), a linear plot without intercept with a correlation coefficient of 0.99 was obtained and can be represented by equation (3)

$$k_2 = a[\text{H}^+] \quad \text{..... (3)}$$

where 'a' = $22.76 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

In the range of $[\text{H}^+]$ investigated, the overall rate equation is represented by equation (4)

$$-d[\text{Mg}^{2+}]/dt = (a[\text{H}^+])[\text{Mg}^{2+}][\text{ClO}^-] \quad \text{..... (4)}$$

The acid dependence of this nature is an indication that equilibrium between the protonated and deprotonated forms of a reactant prior to the rate determining step is rapid. It also

shows that the equilibrium constant for protonated step is small and is not complete even at high acidities, only the protonated step form is reactive [15].

Table 1. Observed pseudo – first order and second order rate constants for the oxidation of Mg^{2+} by ClO^- at $[\text{Mg}^{2+}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

$10^4 [\text{ClO}^-]$ (mol dm^{-3})	$10^2 k_1$ (s^{-1})	k_2 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
1.0	1.17	116.87
2.0	2.30	115.15
3.0	3.42	114.05
4.0	4.75	118.75
5.0	5.75	114.99
6.0	6.95	115.85
7.0	8.06	115.15
8.0	9.08	113.55

Table 2. Effect of changes in $[\text{H}^+]$ on rate constants for the oxidation of Mg^{2+} by ClO^- at $[\text{Mg}^{2+}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

$10^3 [\text{H}^+]$ (mol dm^{-3})	$10^2 k_1$ (s^{-1})	k_2 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
0.5	1.15	57.58
1.0	2.28	113.91
1.5	3.45	172.73
2.0	4.61	230.30
2.5	5.87	293.45
3.0	6.91	345.45
3.5	7.95	397.27
4.0	9.08	454.20

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

(Tables 3 and 4) show that changes in ionic strength and dielectric constant of reaction medium had no significant effect on the rates of reaction. The zero Debye salt effect is consistent with reaction in which slow step involves reactants with charged and uncharged molecule [16].

3.4 Effect of Added Ions on Reaction Rates

Addition of Mg^{2+} , NH_4^+ , SO_4^{2-} and NO_3^- had no remarkable effect on the reaction rates (Tables 5 and 6). Reactions occurring by the outersphere mechanism are expected to be catalyzed by the addition of ions while added ions should have

little or no effect on reactions occurring by the innersphere mechanisms. This is because, the coordination integrity of the redox partners remain intact prior to or during the act of electron transfer process but this is not the case in the latter. However, in this investigation, the lack of

added ions catalysis is rationalized on the basis of interaction between neutral molecule (HClO) and the dye (MG^+) in the rate determining step as shown in equation 6. The reaction is, therefore, likely to proceed through the outersphere mechanistic pathway.

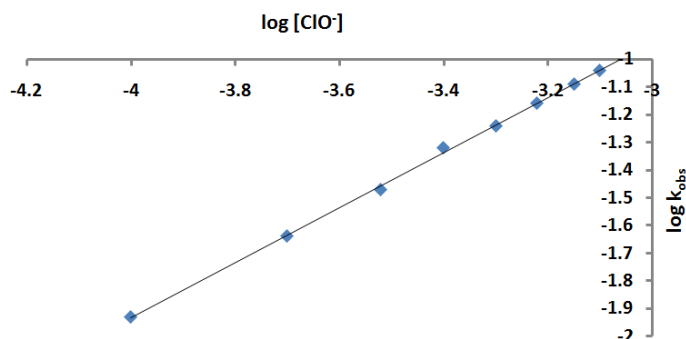


Fig. 2. Plot of $\log k_1$ versus $\log [\text{ClO}^-]$ for the reaction of MG^+ and ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = (1.0 - 8.0) \times 10^{-4} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda = 620 \text{ nm}$, Temp. = $25 \pm 1^\circ\text{C}$

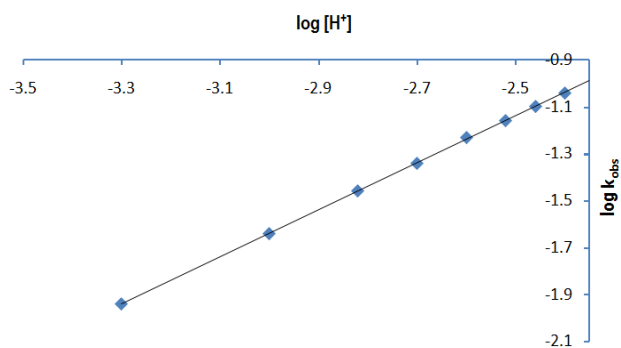


Fig. 3. Plot of $\log k_1$ against $\log [\text{H}^+]$ for the reaction of MG^+ and ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = (0.5 - 4.0) \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $\lambda = 620 \text{ nm}$ and temp. = $25 \pm 1^\circ\text{C}$

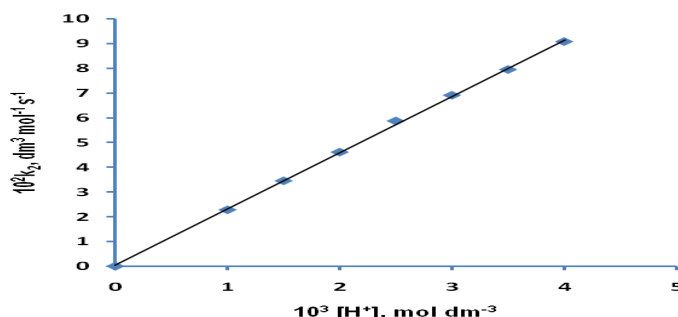


Fig. 4. Plot of k_2 against $[\text{H}^+]$ for the reaction of MG^+ and ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = (0.5 - 4.0) \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 620 \text{ nm}$ and temp. = $25 \pm 1^\circ\text{C}$

Table 3. Effect of change in ionic strength of reaction medium on the rate constants for the oxidation of MG^+ by ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

μ (mol dm^{-3})	$10^2 k_1$ (s^{-1})	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
0.10	2.30	115.15
0.20	2.26	113.06
0.30	2.35	117.28
0.40	2.51	125.62
0.50	2.44	122.06
0.60	2.22	111.11
0.65	2.34	116.95
0.70	2.38	118.93

Table 4. Effect of changes of the dielectric constant of reaction medium on the rate constants for the oxidation of MG^+ by ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

D	$10^2 k_1$ (s^{-1})	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
80.10	2.22	111.04
79.51	2.30	115.15
78.92	2.17	108.57
78.33	2.20	109.92
77.74	2.30	115.15
77.15	2.35	117.68
76.55	2.23	111.66
75.96	2.30	115.15
75.37	2.27	113.38

3.5 Test for Intermediate Complex Formation

Michaelis-Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{ClO}^-]$ gave a straight line without an intercept (Fig. 5).

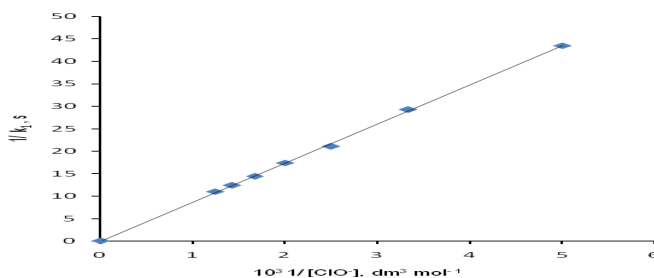


Fig. 5. Michaelis-Menten plot for the reaction between MG^+ and ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = (1.0 - 8.0) \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda = 620 \text{ nm}$, Temp. = $25 \pm 1^\circ\text{C}$

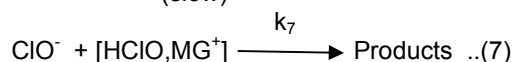
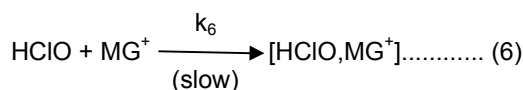
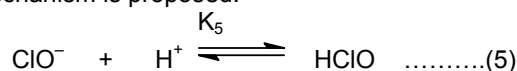
Also spectrum of partially oxidized mixture 1 minute after initiation of reaction showed no shift in λ_{max} .

3.6 Test for Participation of Free Radicals

Addition of acrylamide to the partially oxidized mixture in excess methanol did not form gel nor suspension, suggesting absence of free radicals in the course of the reaction.

3.7 Mechanism of Reaction

Based on the results obtained, the following mechanism is proposed:



If equation (6) is the rate determining step, it follows that:

$$\text{Rate} = k_6 [\text{MG}^+] [\text{HClO}] \quad \text{..... (8)}$$

$$\text{But from equation (5), } [\text{HClO}] = K_5 [\text{H}^+] [\text{ClO}^-] \quad \text{(9)}$$

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

$$\text{Rate} = k_6 K_5 [\text{MG}^+] [\text{H}^+] [\text{ClO}^-] \quad \text{.....(10)}$$

$$= (k_6 K_5 [\text{H}^+]) [\text{MG}^+] [\text{ClO}^-] \quad \text{.....(11)}$$

Equation (11) is analogous to equation (4) with 'a' = $k_2 K_1 = 22.76 \text{ dm}^6 \text{mol}^{-2} \text{s}^{-1}$

Table 5. Effect of added cations to the reaction medium on the rate constants for the oxidation of MG^+ by ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

	$10^4[\text{cation}]$ (mol dm^{-3})	10^2k_1 (s^{-1})	k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
Ion = Mg^{2+}	0.0	2.24	111.76
	1.0	2.34	116.92
	20.0	2.37	118.35
	30.0	2.34	116.75
	40.0	2.38	118.86
	50.0	2.37	118.75
	60.0	2.39	119.64
	70.0	2.42	120.81
	80.0	2.41	120.51
Ion = NH_4^+	0.0	2.30	115.15
	1.0	2.30	115.15
	20.0	2.38	118.86
	30.0	2.34	116.98
	40.0	2.36	118.03
	50.0	2.30	115.15
	60.0	2.38	118.86
	70.0	2.38	118.86
	80.0	2.39	119.58

Table 6. Effect of added anions to the reaction medium on the rate constants for the oxidation of MG^+ by ClO^- at $[\text{MG}^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{ClO}^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$ 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 = SO_4^{2-}	0.0	2.30	115.15
	1.0	2.28	114.25
	20.0	2.30	115.15
	30.0	2.32	116.20
	40.0	2.24	112.00
	50.0	2.30	115.10
	60.0	2.34	115.98
	70.0	2.30	115.15
	80.0	2.30	115.15
Ion = NO_3^-	0.0	2.29	114.30
	1.0	2.30	114.50
	20.0	2.38	113.00
	30.0	2.34	114.15
	40.0	2.36	115.30
	50.0	2.30	112.50
	60.0	2.38	116.20
	70.0	2.38	114.30
	80.0	2.39	115.15

The above mechanistic steps point to the outer sphere electron transfer process. This assertion is supported by the lack of spectrophotometric evidence for the formation of precursor complex formation prior to and during the electron transfer, when the partially oxidized mixture was scanned and lack of intercept obtained from Michaelis-Menten plot.

4. CONCLUSION

The kinetic investigations of the redox reaction between MG^+ and hypochlorite ion, ClO^- were carried out in aqueous HClO_4 medium at $T = 25 \pm 1^\circ\text{C}$. The reaction showed a stoichiometry of 1:2 (reductant: oxidant). Kinetic data revealed a first order dependence on both $[\text{MG}^+]$ and $[\text{ClO}^-]$ giving a second order overall. Reaction rate increased with increase in $[\text{H}^+]$. Changes in ionic strength and dielectric constant of the reaction medium and addition of Mg^{2+} , NH_4^+ , SO_4^{2-} and NO_3^- of different concentrations did not affect reaction rate. The absence of spectroscopic evidence of complex formation suggests that the reaction proceeds through the outersphere mechanism. This suggestion is confirmed by the evidence adduced from the Michaelis-Menten plot. A plausible mechanism based on these observations has been proposed.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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