Full Length Research Paper

Kinetic approach to the mechanism of the redox reaction of malachite green and permanganate ion in aqueous acidic medium

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The redox kinetic and mechanistic studies of the reactions of malachite green (MG^+) and MnO_4^- were carried out in aqueous acidic medium, at a temperature of 32.5 ± 0.5°C; ionic strength, μ = 0.50 mol dm^{-3} (Na_2SO_4), $[H^+]$ = 5.00 x 10^{-3} mol dm^{-3} (H_2SO_4). In the stoichiometry, one mole of malachite green was consumed by one mole of MnO_4^-. The reaction is first order in both $[MG^+]$ and the $[MnO_4^-]$. The rates of redox reaction showed dependence on acid concentrations (in the acid range used). Rate equation for the reaction has been proposed as: $-d[MG^+]/dt = (a + b[H^+])[MG^+][MnO_4^-]$. At $[H^+]$ = 5.00 x 10^{-3} mol dm^{-3}, the second order rate constant for the malachite green – MnO_4^- reaction was found to be (11.96 ± 0.13) x 10^{-3} dm^3 mol^{-1} s^{-1}. The rates of reaction displayed negative salt effect. Log k_1 versus 1/D gave positive slope for the reaction. Added anions and cations catalysed the malachite green – MnO_4^- reaction. Results of the Michaelis- Menten analysis gave no evidence of intermediate complex formation. Based on the results obtained experimentally, the outer sphere mechanism is proposed for the malachite green – MnO_4^- reaction.

Key words: kinetics, mechanism, catalysis, salt effect.

INTRODUCTION

Malachite green (4 – [(4 - dimethylaminophenyl) – phenylmethyl] – N,N – dimethylaniline) is a basic dye for wool, silk or for suitable mordanted cotton. It is also widely used to dye materials such as jute, leather, ceramics and paper (Culp and Beland, 1996), in addition to being used as a cytochemical staining agent (Lawton, 1989). It is antimicrobial (Culp and Beland, 1996; Alderman, 1982; Alderman, 1985). It has, in fact, been widely used as the most efficacious antifungal agent in the fish farming industry (Alderman, 1982; Alderman, 1985). Its worldwide use in aquaculture will probably continue due to its relatively low cost, ready availability and efficacy; therefore, potential human exposure to malachite green could result from the consumption of treated fish (Alderman and Clifton – Hadley, 1993) and from working in the dye and aquaculture industries. The dye can also be used as a detection method for latent blood in criminalistics and for spot detection of cerium and sulphurous acid (Finar, 1973).

Mn (VII) is a potent oxidizing and hydroxylating agent. This fact has been reported by several authors over many years (Halpern, 1961; Stewart and Mocek, 1963; Lee and Stewart, 1964; Saran et al., 1979). Its wide use as an oxidizing agent in synthetic as well as in analytical chemistry was reported (Hiremath et al., 1996), so also its intense colouration which confers on it an advantage to serve as a self – indicator (Insauti et al., 1995). The oxidizing ability of Mn (VI) is a function of the pH of the medium (Hiremath et al., 1996; Iyun et al., 1992a). In acidic medium, the expected oxidizing species are mainly Mn (VII), Mn (IV) and Mn (III) (Rao et al., 1979; Rajanna et al., 1996). In acid medium, the oxidizing Mn (VII) species are $HMnO_4$, H_2MnO_{4+}, Mn_2O_7 and MnO_3^+ (Rao et al., 1979; Iyun et al., 1992a; Rajanna et al., 1996). The explanation for the positive $[H^+]$ dependence on the rate of MnO_4^- oxidation has been rationalized in terms of the

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protonation of MnO_4^- in a fast step to give $HMnO_4$, which subsequently reacts with the reductant in a slow step to give the products (Hassan, 1991; Sen et al., 1995).

Reduction – oxidation reaction of malachite green and peroxydisulphate ion had a stoichiometry of 1:1 (Malachite green: peroxydisulphate), first order dependence on the reductant (malachite green) and fractional order (one half) dependence on the oxidant (peroxydisulphate ion) and rates of reaction were enhanced under both high or low pH relative to neutral conditions (Mushinga and Jonnalagadda, 1991).

This work is carried out to obtain relevant kinetic data which would give an idea on the conditions best suitable for the reactions of malachite green and the mechanisms for such reactions. The knowledge would be very beneficial to workers in the aquaculture and dye industries, as well as to those involved in its handling when used for staining purposes.

EXPERIMENTAL

Materials

All chemicals and reagents used in the work were analar grade and were used without further purification. H_2SO_4 was used to furnish H^+ to the reaction, $KMnO_4$ was used as the oxidant and Na_2SO_4 was used to maintain a constant ionic strength for each run. Acetone was used to vary the dielectric constant of the reaction medium (Panari et al., 1997). Malachite green, the oxidant and the other solutions were prepared with distilled water.

Methods

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method (Yusuf et al., 2004). The concentration of malachite green was kept constant while that of permanganate was varied between the mole ratio 1: 0.25 – 1: 4 ([Malachite green]/ [MnO_4^-]) keeping [H^+] and ionic strength, μ, constant at 5.0×10^{-3} mol dm^{-3} and 0.50 mol dm^{-3} respectively. The reaction was allowed to go to completion and the absorbance of the solutions monitored at 620 nm, characteristic of malachite green (Keusch, 2007), using Seward digital biomedical colorimeter. The stoichiometry of this reaction was determined from the plot of absorbance versus the mole ratio.

All kinetic measurements were carried out under pseudo – first order conditions with respective MnO_4^- concentrations at least 50 – fold in excess of the malachite green concentration at temperature of $32.5 \pm 0.50°C$, ionic strength of 0.50 mol dm^{-3} (Na_2SO_4) and [H^+] = 5.0×10^{-3} (H_2SO_4).

The pseudo – first order plots of log ($A_t - A_\infty$) against time were made and the slope of the plots gave the pseudo – first order rate constants, k_1 (Keusch, 2007). The second order rate constants, k_2, were determined from k_1 as $k_1/ [MnO_4^-]$.

The effect of changes in [H^+] on the reaction rate was investigated by keeping [MG^+] and [MnO_4^-] constant while varying [H^+] between 5.0×10^{-4} and 10.0×10^{-3} mol dm^{-3}. Ionic strength, μ, was maintained at 0.50 mol dm^{-3} (Na_2SO_4) and reaction was carried out at $32.5 \pm 0.50°C$. Order of reaction with respect to [H^+] was obtained as the slope of the plot of log k_1 against log [H^+]. Variation of acid dependent second order rate constant with [H^+] was obtained by plotting k_{H+} against [H^+].

The ionic strength of the reaction mixture was varied between

0.10 and 0.80 mol dm^{-3} and maintaining [MG^+], [MnO_4^-] and [H^+] constant. Reaction temperature was maintained at $32.5 \pm 0.50°C$. Relationship of reaction rate with changes in the ionic strength was determined by plotting log k_2 against $\sqrt{\mu}$.

Effect of changes in dielectric constant of the reaction medium on the reaction rate was investigated adding $0.10 – 0.80$ cm^3 (accounting for 2 – 16%) acetone to the reaction mixture, keeping [MG^+], [MnO_4^-] and [H^+] constant. The ionic strength of 0.50 mol dm^{-3} and temperature of $32.5 \pm 0.50°C$ were maintained. A plot of log k_2 against 1/D gives the relationship between the second order rate constant and the total dielectric constant of the reaction medium, D.

The effect of added ions on the reaction rate was observed by the addition of 1.0×10^{-3} to 1.0×10^{-1} mol dm^{-3} of ions (Mg^+ and NO_3^-) keeping [MG^+], [MnO_4^-] and [H^+] constant. The ionic strength of 0.50 mol dm^{-3} and temperature of $32.5 \pm 0.50°C$ were maintained.

To each of the partially oxidized reaction mixture containing various concentrations of oxidant, reductant and hydrogen ions, 5 cm^3 of acrylamide solution was added, followed by a large excess of methanol. Any polymerization evidenced by gel formation would provide a suspicion for the presence of free radicals in the reaction mixture.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies showed that one mole of Malachite green was consumed by one mole of MnO_4^-, which is consistent with the equation below:

$$(1)$$
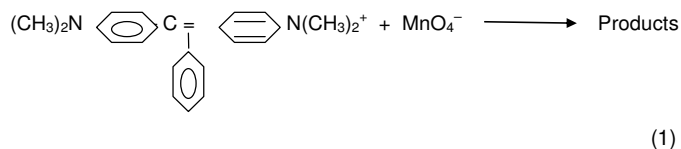
Order of reaction

Plots of log log ($A_t - A$) versus time obtained under pseudo-first order conditions were linear for about 100% of the reactions. (A_t and A_∞ are the absorbances of the complex at time 't' and at the end of the reaction respectively), suggesting that the reaction is first order with respect to [MG^+]. Pseudo-first order rate constants, k_1, for the plots were obtained from the slope of the plots of log ($A_t - A_\infty$) versus time (Figure 1). Order of reaction was obtained from the slope of the plots of log k_1 versus log [MnO_4^-] (Figure 2), which was 1.03 ± 0.02, suggesting that the reaction is first order in [MnO_4^-]. This means that the reaction is second order overall and the second order rate constant determined from $k_1/ [MnO_4^-]$ are reported in Table 1. The rate law can therefore be represented by equation (2):

$$\frac{-d[MG]}{dt.} = k_2 [MG^+][MnO_4^-.]$$

$$(2)$$

Time (min)

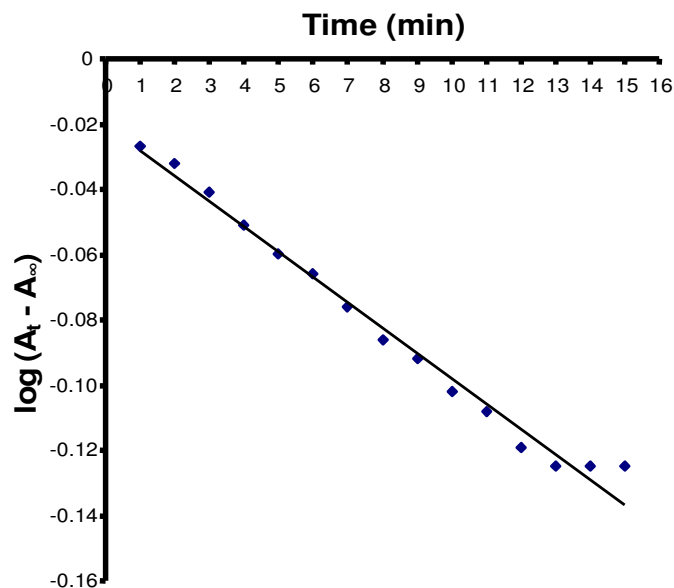**Figure 1.** Typical pseudo - first order plot for the redox reaction of malachite green with MnO_4^-. $[MG^+] = 1.30 \times 10^{-4}$ mol dm^{-3}, $[MnO_4^-]$ = 11.70×10^{-3} mol dm^{-3}, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3}, $\lambda = 620$ nm and T = 32.5 ± 0.50 °C.
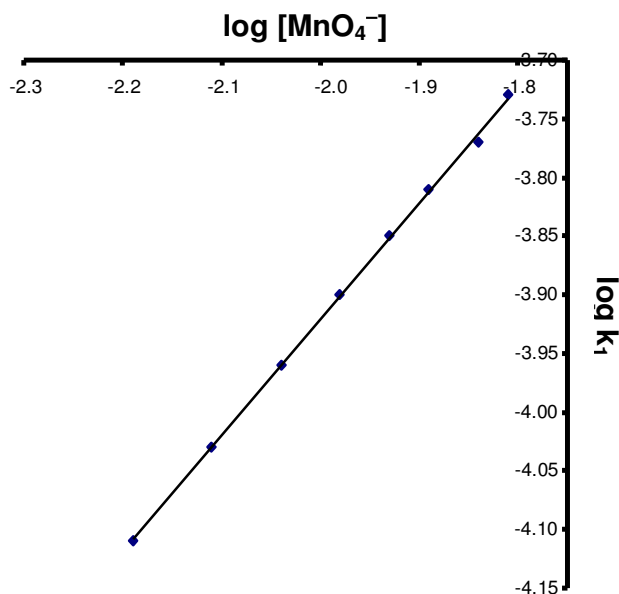
log $[MnO_4^-]$

Figure 2. Plot of log k_1 versus log $[MnO_4^-]$ for the redox reaction of malachite green with MnO_4^-. $MG^+] = 1.30 \times 10^{-4}$ mol dm^{-3}, $[MnO_4^-] = (6.50 - 16.9) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3}, $\lambda = 620$ nm and T = 32.5 ± 0.5 °C.

The second order rate constants, k_2, calculated from $k_1/[S_2O_8^{2-}]$ were fairly constant and the average was found to be $(11.96 \pm .13) \times 10^{-3}$ dm^3 mol^{-1}s^{-1}.

Table 1. Pseudo – first order and second order rate constants for the reaction of malachite green and MnO_4^- $[MG^+] = 1.30 \times 10^{-4}$ mol dm^{-3}, $\lambda = 620$ nm and Temp. 32.5 ± 0.50 °C.

10^2 [MnO$_4^-$], dm^3 mol^{-1}	10^4 [H$^+$], dm^3 mol^{-1}	μ dm^3 mol^{-1}	$10^4 k_1$,s	$10^3 k_2$, dm^3 mol^{-1} s
6.50	50.00	0.50	0.78	12.00
7.80	50.00	0.50	0.93	11.92
9.10	50.00	0.50	1.10	12.09
10.40	50.00	0.50	1.25	12.02
11.70	50.00	0.50	1.40	11.97
14.30	50.00	0.50	1.70	11.89
15.60	50.00	0.50	1.85	11.86
11.70	5.00	0.50	0.14	4.54
11.70	20.00	0.50	0.54	7.23
11.70	30.00	0.50	0.84	8.21
11.70	50.00	0.50	1.40	11.97
11.70	60.00	0.50	1.68	13.01
11.70	80.00	0.50	2.25	16.04
11.70	100.00	0.50	2.81	19.31
11.70	50.00	0.10	3.17	27.09
11.70	50.00	0.30	1.95	16.67
11.70	50.00	0.40	1.70	14.53
11.70	50.00	0.50	1.41	12.05
11.70	50.00	0.60	1.27	10.85
11.70	50.00	0.70	1.08	9.23
11.70	50.00	0.80	0.63	5.38

Effect of changes in acid concentration

In the acid range used, $1.00 \times 10^{-4} \leq [H^+] \geq 1.00 \times 10^{-2}$ mol dm^{-3} (below 1.00×10^{-4} mol dm^{-3} the reaction becomes very slow and above 10.00×10^{-3} mol dm^{-3} the malachite green becomes unstable), the rate of reaction increased with increase in $[H^+]$ (Table 1). Plot of k_{H+} versus $[H^+]$ is linear with an intercept (Figure 3). The H^+ dependent second order rate constant can thus be presented by equation (3):

$$k_{H+} = a + b[H^+] \tag{3}$$

'a' = 2.25 dm^3 mol^{-1} s^{-1} and 'b' = 1.98 dm^6 mol^{-2} s^{-1}. In the range of $[H^+]$ used, the overall rate equation is represented by equation (4) below:

$$\frac{-d[MG]}{dt} = -d[MG^+]/dt = (a + b[H^+])[MG^+][MnO_4^-] \tag{4}$$

Effect of changes in ionic strength and total dielectric constant of the reaction medium
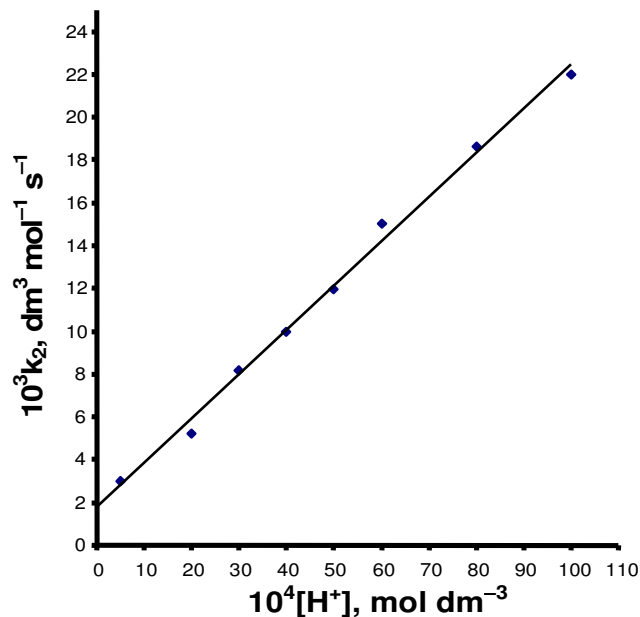
The rate of reaction was found to decrease with increase

Figure 3. Plot of k_{H+} versus $[H^+]$ for the redox reaction between malachite green and MnO_4^-. $[MG^+] = 1.30 \times 10^{-4}$ mol dm^{-3}, $[MnO_4^-] = 11.70 \times 10^{-3}$ mol dm^{-3}, $[H^+] = (5.0 - 100.0) \times 10^{-4}$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3}, $\lambda = 620$ nm and $T = 32.5 \pm 0.5°C$.

Table 2. Effect of changes in total dielectric constant of the reaction medium on the reaction of malachite green and MnO_4^- $[MG^+] = 1.30 \times 10^{-4}$ mole dm^{-3}; $[MnO_4^-] = 11.70 \times 10^{-3}$ mole dm^{-3}; $[H^+] = 5.00 \times 10^{-3}$ mole dm^{-3}; $\mu = 0.50$ mole dm^{-3} ; $\lambda = 620$ nm; Temp. $32.5 \pm 0.50°C$

D	$10^4 k_1$, s	$10^3 k_2$, dm^3 mol^{-1} s
81.00	1.40	11.97
79.80	1.45	12.39
78.60	1.61	13.76
77.40	1.77	15.13
76.20	2.08	17.78
75.00	2.28	19.49
73.80	2.56	21.88
72.60	2.87	24.53
71.40	3.53	30.17

Table 3. Rate data for the effect of added ions (Mg^{2+} and NO_3^-) on the rate of reaction of malachite green and MnO_4^- $[MG^+] = 1.30 \times 10^{-4} \times 10^{-3}$ mol dm^{-3}; $[MnO_4^-] = 11.70 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 5.00 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3}; $\lambda = 620$ nm; Temp. $= 32.5 \pm 0.50°C$.

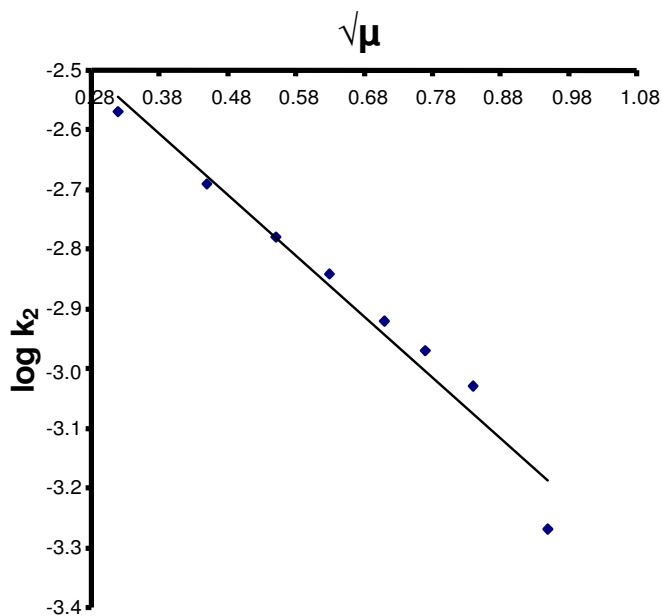| Ion	10^3 [ion], dm^3 mol^{-1}	$10^4, k_1$ s	$10^3 k_2$, dm^3 mol^{-1}s
Mg^{2+}	1.00	1.40	11.97
	20.00	1.35	11.54
	30.00	1.32	11.28
	40.00	1.28	10.94
	60.00	1.23	10.51
	80.00	1.20	10.25
	100.00	1.13	9.66
NO_3^-	1.00	1.47	9.39
	20.00	1.67	13.68
	30.00	1.77	14.35
	40.00	1.95	14.80
	60.00	2.12	16.00
	80.00	2.40	17.33
	100.00	2.67	18.27

Figure 4. Plot of log k_2 versus $\sqrt{\mu}$ for the redox reaction of malachite green and MnO_4^- $[MG^+] = 1.30 \times 10^{-4}$ mol dm^{-3}, $[MnO_4^-] = 11.70 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1 - 0.8$ mol dm^{-3}, $\lambda = 620$ nm and $T = 32.5 \pm 0.5°C$

in ionic strength. The results are presented in Table 2. The reaction showed a negative Bronsted – Debye salt

effect (Figure 4) and the rates of reaction increased with increase in the percentage of acetone (increase in 1/D) (Table 3). These two observations suggest that the reactant ions in the rate determining step are oppositely charged.

Effect of added ions

Added Mg^{2+} and NO_3^- in the range $1 \times 10^{-3} \leq$ [Ion] $\geq 1 \times 10^{-1}$ mol dm^{-3} catalysed the reaction (Table 4). This is possibly due to coulombic bridging in which the closeness

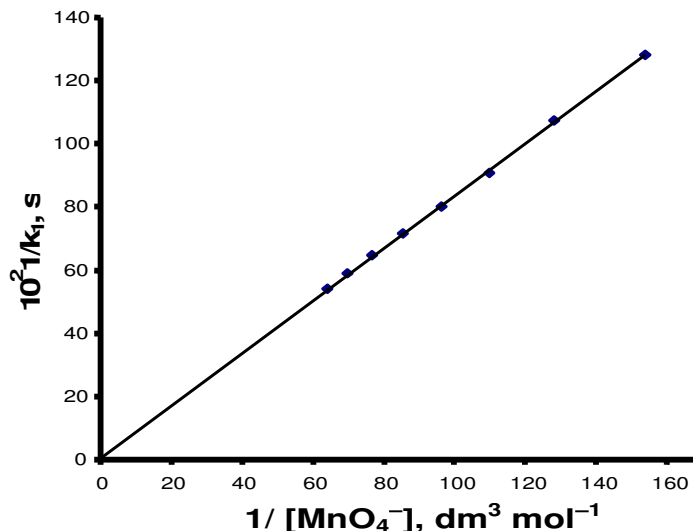**Figure 5.** Michaelis Menten plot for the redox reaction between malachite green and MnO_4^-. $[MG^+] = 1.30 \times 10^{-4}$ mol dm^{-3}, $[MnO_4^-]$ = $(6.50 - 16.90) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3}, $\lambda = 620$ nm; T = $32.5 \pm 0.50\,°C$

of approach of the reactant ions in the activated complex is such as to allow added ions to come in between them, thereby affecting the rates of reaction. This is seen when the reaction is proceeding through the outer sphere pathway in which the reactant ions maintain their coordination integrity in the activated complex prior to and during electron transfer (Sharpe, 1981).
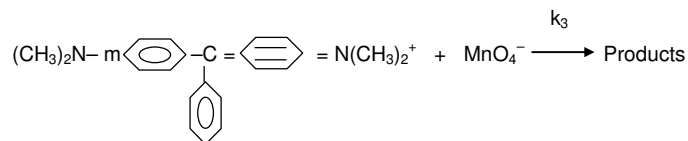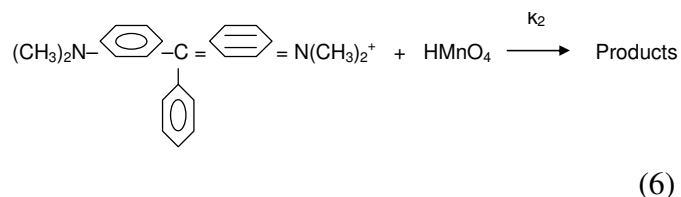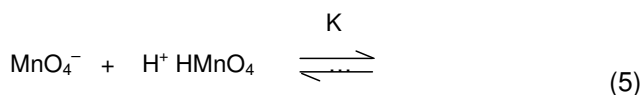
Test for intermediate complex

Michaelis – Menten plot of $1/k_1$ versus $1/[MnO_4^-]$ gave a straight line passing through the origin that is, zero intercept (Figure 5), suggesting the absence of intermediate complex.

Test for free radicals

Addition of acrylamide (0.001 – 0.015 M) solution to partially oxidized reaction mixture with addition of excess methanol gave no gel indicative of the absence of free radicals in the reaction mixture.

The acid dependence in this system showed both the acid dependent and acid independent pathways, suggesting that the protonated and unprotonated species of the oxidant are oxidising.

Possible mechanism consistent with above result is presented below:

$$MnO_4^- + H^+ \; HMnO_4 \;\; \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \tag{5}$$

$$(CH_3)_2N-\langle\bigcirc\rangle-C=\langle\bigcirc\rangle=N(CH_3)_2^+ \; + \; HMnO_4 \; \xrightarrow{k_2} \; \text{Products} \tag{6}$$

$$(CH_3)_2N- m\langle\bigcirc\rangle-C=\langle\bigcirc\rangle=N(CH_3)_2^+ \; + \; MnO_4^- \; \xrightarrow{k_3} \; \text{Products}$$

$$\text{Rate} = k_2[MG^+][HMnO_4] + k_3[MG^+][MnO_4^-] \tag{8}$$

From equation (5),

$$[HMnO_4] = K[MnO_4^-][H^+] \tag{9}$$

Substituting equation (9) into equation (8) gives equation (10)

$$\text{Rate} = k_2K[MG^+][MnO_4^-][H^+] + k_3[MG^+][MnO_4] \tag{10}$$

$$= (k_3 + k_2K[H^+])[MG^+][MnO_4^-] \tag{11}$$

Equation (11) is similar to equation (4) which is the observed rate law, where k_3 = 'a' = 1.98 dm^3 mol^{-1} s^{-1} and k_2K = 'b' = 2.25 dm^6 mol^{-2} s^{-1}.

The negative Bronsted – Debye salt effect observed in the reaction of malachite green with MnO_4^- indicates the

interaction of reactants of opposite charges in the rate determining step (Wilkins, 1974). This assertion agrees with equation (7) in the proposed mechanism.

The Michaelis – Menten plot gave no intercept (Figure 5), suggesting the absence of intermediate complex formation. .

The catalysis of added ions on the reaction rate is suggestive of the reaction proceeding through the outer – sphere mechanism (Adegite et al., 1977; Pennington and Haim, 1967 and Przytas and Sutin, 1973).

Conclusion

The redox reaction of malachite green and permanganate ions in aqueous acidic medium showed a stoichiometry of 1:1, order of reaction of first order with respect to Malachite green and permanganate ions respectively – second order overall. The rate of reaction increased with increase in hydrogen ion concentration, decreased with increase in ionic strength of reaction medium, increased with decrease in total dielectric constant of reaction medium and affected by added ions. An intermediate complex was not detected.

Based on the above results, it is evident that the reaction is probably operating through the outer – sphere mechanism.

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