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Kinetics and mechanism of the methylene blue-permanganate ion reaction in acidic medium

A. A. Osunlaja*, S. O. Idris and J. F. Iyun

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

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ABSTRACT

The kinetics of the oxidation of methylene blue by permanganate ion has been studied in aqueous acidic medium. The rate of the reaction was found to be acid dependent and first order in both oxidant and reductant. The emprical rate law conforms to the equation:

$$-\frac{d[MB^+]}{dt} = (a + b\,[H^+])[MB^+][MnO_4^-]$$

‘a’ = 4.04 x10^{-3} *dm*^{3} *mol*$^{-1}$ *s*$^{-1}$ *and ‘b’ = 0.125 dm*^{6} *mol*$^{-2}$ *s*$^{-1}$*: at* $[H^+]$ *= 1 x* 10^{-3} *mol dm*$^{-3}$*,* $\mu = 0.25$ *mol dm*$^{-3}$ *(*Na_2SO_4*),* λ_{max} *= 660 nm and T = 24 ± 1.0°C.*

The rate of reaction decreases with increase in ionic strength. Added ions and decrease in medium dielectric constant inhibited the reaction rates. The mechanism of reaction has been rationalized on the basis of both the outer-sphere and the inner-sphere pathways based on spectroscopic investigation and kinetic evidence.

Key Words: Kinetics, permanganate, oxidation, stoichiometry, mechanism.

INTRODUCTION

Potassium permanganate is widely used as an oxidizing agent in synthetic as well as in analytical chemistry and also as a disinfectant.[1,2] It has been used in the determination of content of pharmaceutical formulation,[3,4] as oxidizing agent for removal of organic molecules and heavy metals from the nuclear wastes [5] and in the estimation of ascorbic acid [6]. During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Consequently, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium [7]. In acidic medium it exists in different forms as $HMnO_4$, H_2MnO^+, $HMnO_3$, Mn_2O_7 and depending on the nature of the reductant, the oxidant has been assigned both the inner-sphere and the outer-sphere pathways in their redox reactions [8]. Methylene blue is easily reduced by various reducing agents to the colourless hydrogenated molecule, leucomethylene blue (LMB), which can be oxidized back to the original blue colour. These processes have found application in numerous inventions like data recording holographic industries, optical data storage, food and pharmaceutical industries. Such reduction is also used in checking the purity of milk [9,10]

Literature reveals that, though considerable amount of work has been done on the oxidation of organic compound by potassium permanganate, only a few studies are found on the kinetics of oxidation of industrial dyes such as methylene blue by potassium permanganate. In this paper we report on the kinetic study of methylene blue oxidation by potassium permanganate in aqueous acidic medium.

MATERIALS AND METHODS

Materials

Analar grade reagents (BDH) were used as received without further purification. Distilled water was used to prepare all solutions. Potassium permanganate solution was prepared and standardized according to literature [11]. H_2SO_4 was used as the acid medium and for investigating the effect of hydrogen ion on the rate, while sodium sulphate was used to maintain the ionic strength constant at 0.25 mol dm^{-3}.

Stoichiometric studies

Spectrophotometric titration using the mole ratio method was employed in determining the stoichiometries of the reactants. The concentration of the methylene blue was kept constant while that of permanganate was varied as follows; $[MB^+] = 1.5 \times 10^{-5}$ mol dm^{-3}; $[MnO_4^-] = (3.75 – 37.5) \times 10^{-6}$ mol dm^{-3}; $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.25$ mol dm^{-3} (Na_2SO_4), T = 24 ± 1.0°C.

The reaction mixtures were allowed to undergo complete reaction as evident from the constancy of repeated measurements of absorbance (A_∞) at 660 nm. The absorbance (A_∞) was plotted against the mole ratio of the reactants and the point of sharp inflection in the plot gave the stoichiometry of the reaction.

Kinetic Measurements

The rate of reaction was studied by monitoring the decrease in the absorbance of methylene blue at 660nm using Corning Colorimeter 253.

Kinetic measurements were carried out under pseudo-first order condition with [permanganate] in at least 10 fold excess over $[MB^+]$ at the stated conditions in Table 1. The pseudo-first order plots of log (A_t-A_∞) versus time were made. From the slopes of the plots, the pseudo-first order rate constant (k_1) were determined. The second order rate constant (k_2) were obtained from $k_2 = k_1/[MnO_4^-]^n$, where n is the order with to permanganate ion.

Effect of hydrogen ion

The effect of changes in $[H^+]$ on the reaction rate was investigated by keeping $[MB^+]$ and $[MnO_4^-]$ constant while varying $[H^+]$ between (4 - 140) x 10^{-4} mol dm^{-3} (H_2SO_4). Ionic strength, μ, was maintained at 0.25 mol dm^{-3} (Na_2SO_4) and reaction was carried out at 24 ± 1.0^0C. The 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 rate constant with $[H^+]$ was obtained by plotting k_2 against $[H^+]$.

Effect of ionic strength

The ionic strength of the reaction mixture, μ, was varied between 0.10 and 0.45 mol dm^{-3} (Na_2SO_4) while maintaining $[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, constant at 24 ± 1.0^0C. The relationship of the reaction rate with changes in the ionic strength was determined by plotting log k_1 against $\sqrt{\mu}$.

Effect of change in medium dielectric constant

The effect of medium dielectric constant, D, on the rate of reaction was investigated by using a binary solvent mixture of water and acetone. A plot of log k_1 against $\frac{1}{D}$ gave the relationship between the second order rate constant and the dielectric constant of the reaction medium.

Effect of added ions

At constant concentration of $[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.25$ mol dm^{-3} (Na_2SO_4), the effect of added ions (Mg^{2+}, Li^+ , NO_3^- or CH_3COO^-) on the rates of the reactions was investigated in the range (2.0 – 10.0) x 10^{-2} mol dm^{-3} (Table 2).

Tests for Intermediate Complex

Test for the presence of stable, detectable intermediate formed during the course of the reaction was carried out spectrophotometrically. Electronic spectra of partially reacted reaction mixtures were recorded at various time intervals depending on the speed of the reaction. A similar run was made for reactants separately in each case. This was carried out in order to determine whether shift in λ_{max} or enhancement of peak resulted as the reaction progressed.

Test for Free Radicals

About 2g of acrylamide was added to a partially oxidized reaction mixtures followed by addition of a large excess of methanol. Control experiment was carried out by adding acrylamide to solutions of MB^+ and MnO_4^- separately at the stated conditions of $[H^+]$, μ and temperature in Table 1. Gel formation indicates presence of free radicals in the reaction mixture..

Product Analysis

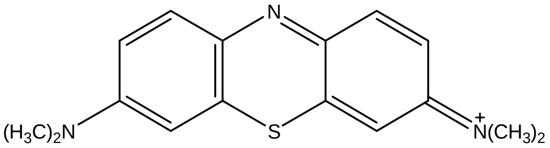
At the completion of the reaction, the reaction mixtures were analyzed for the type of products formed. Likely products tested for were leucomethylene blue (the reduced form of MB) and Mn^{2+}**.**

Mixtures of glucose/NaOH solution were added to the product in order to oxidize the colourless solution back to methylene blue. Mn^{2+} was qualitatively identified by the addition of KIO_4 solution to the product and warming gently.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies indicated that for every mole of methylene blue, two moles of MnO_4^- was reduced which is consistent with the equation below:



$+\ 2MnO_4^- \longrightarrow$ Products -----1

This is consistent with what has been reported for the oxidation of MnO_4^- with L-proline [1], L- ascorbic acid [12] and some reducing sugars [13].

Order of Reaction

Kinetic studies showed the reaction to be first order dependent on each of the reactants. Plots of log (A_t-A_∞) versus time were linear to 90% of the reaction (where A_t and A_∞ are the absorbance at time t and at the end of the reaction respectively) indicating the order with respect to MB^+ to be one. A typical plot is presented in Figure 1. Pseudo-first order rate constants, k_1, determined as the slope of above are presented in Table 1. The plot of log k_1 versus log $[MnO_4^-]$ was linear with a slope of 1 indicating first order dependence of the rate of reaction on $[MnO_4^-]$ (Figure 2). The second order rate constant, k_2, was obtained from $k_2 = \frac{k_1}{[MnO_4^-]}$ and were found to be fairly constant (Table1). The rate equation can be represented by equation 2

$$-\frac{d[MB^+]}{dt} = k_2[MB^+]\,[MnO_4^-] \qquad \ldots..2$$

at $[H^+] = 1 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.25$ mol dm^{-3} (Na_2SO_4) and $T = 24 \pm 1.0°C$ where $k_2 = 42.95 \pm 0.25$ dm^3 mol^{-1} s^{-1} . Similar first order dependence has been reported for the reduction of MnO_4^- in acidic medium by L-ascorbic acid, reducing sugars, malachite green, ester, and nicotine [12-16]. This trend has also been reported in alkaline medium [17, 1, 7].

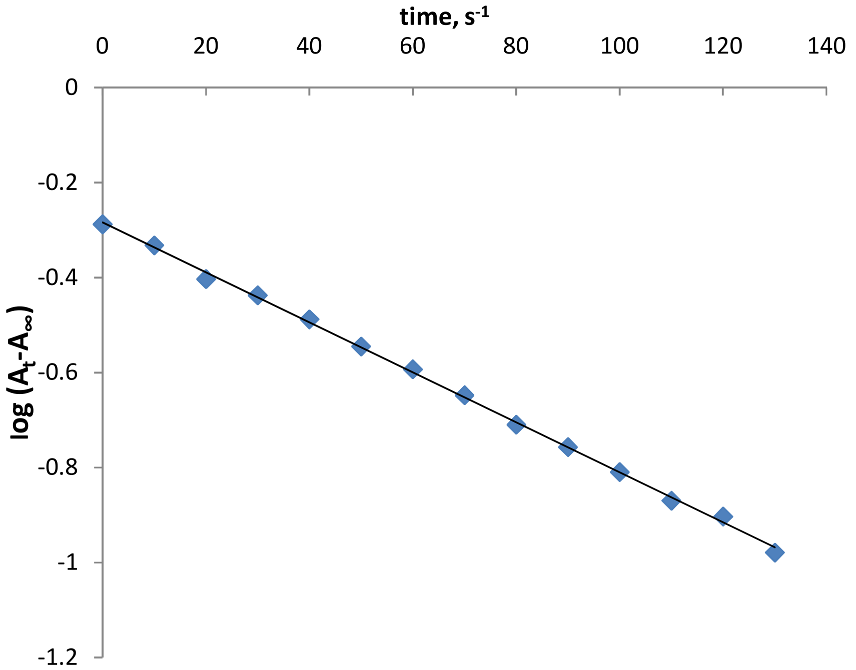


Figure 1: Typical Pseudo-first order plot for the redox reaction of MB^+ with MnO_4^-
$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}; $[MnO_4^-] = (0.84 – 4.00) \times 10^{-4}$ mol dm^{-3}
$[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.25$mol dm^{-3} (Na_2SO_4), $T = 24 \pm 1.0^oC$ and $\lambda_{max} = 660$ nm.

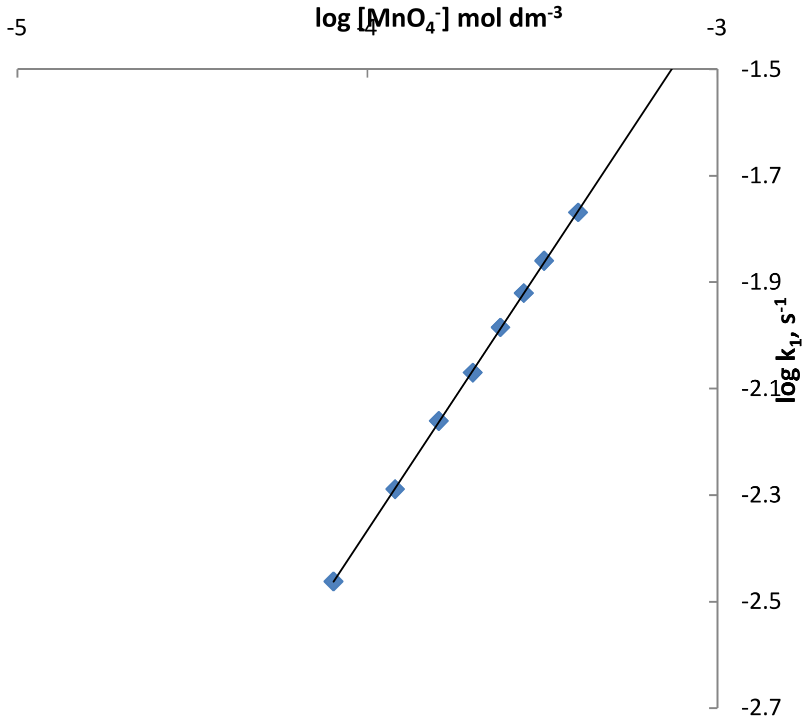


Figure 2: Plot of log k_1 versus log $[MnO_4^-]$ for the redox reaction of MB^+ with MnO_4^-
$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}; $[MnO_4^-] = (0.84 – 4.00) \times 10^{-4}$ mol dm^{-3}
$[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, $\mu = 0.25$mol dm^{-3} (Na_2SO_4), $T = 24 \pm 1.0^oC$ and $\lambda_{max} = 660$ nm.

Table 1: Pseudo-first order and second order rate constants for the reaction of MB^+ with MnO_4^-. $[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, λ_{max} = 660 nm and T = 24 ± 1.0°C

$10^4[MnO_4^-]$ (mol dm^{-3})	$10^4[H^+]$ (mol dm^{-3})	μ (mol dm^{-3})	10^3k_1 (s^{-1})	k_2 (dm^{3}mol^{-1} s^{-1})
0.84	1.0	0.25	3.45	43.13
1.20	1.0	0.25	5.14	42.83
1.60	1.0	0.25	6.91	43.19
2.00	1.0	0.25	8.52	42.60
2.40	1.0	0.25	10.36	43.16
2.80	1.0	0.25	12.01	42.90
3.20	1.0	0.25	13.82	43.18
4.00	1.0	0.25	17.04	42.61
1.20	4.0	0.25	3.56	29.66
1.20	6.0	0.25	4.26	35.50
1.20	8.0	0.25	4.72	39.33
1.20	10.0	0.25	5.18	43.16
1.20	20.0	0.25	7.14	59.50
1.20	40.0	0.25	9.90	82.50
1.20	60.0	0.25	12.21	101.75
1.20	80.0	0.25	13.82	115.75
1.20	100.0	0.25	18.19	151.58
1.20	140.0	0.25	20.00	166.66
1.20	1.0	0.10	7.68	64.00
1.20	1.0	0.15	6.54	54.50
1.20	1.0	0.20	5.39	44.90
1.20	1.0	0.25	5.16	43.00
1.20	1.0	0.30	4.15	34.60
1.20	1.0	0.35	3.68	30.70
1.20	1.0	0.40	3.22	26.80
1.20	1.0	0.45	2.76	23.00

Effect of Hydrogen ion Concentration

The effect of the $[H^+]$ on the rate of reaction is reported in Table 1. The rates were found to be first order acid dependent on $[H^+]$. The plot of k_2 versus $[H^+]$ was linear with a positive intercept. The acid dependent rate equations for the reactions can be represented by equation 3

$$-\frac{d[MB^+]}{dt} = (a + b\,[H^+])[MB^+][MnO_4^-] \qquad \text{------3}$$

where 'a' = 4.04×10^{-3} dm^3 mol^{-1} s^{-1} and 'b' = 0.125 dm^6 mol^{-2} s^{-1}

In the acid range used, $(4 \leq [H^+] \leq 140) \times 10^{-4}$ mol dm^{-3}, the rate of the reaction increases in the presence of hydrogen ions concentration (Table 1). The above equation 3 suggests that the reaction occurs via acid-dependent and acid-independent pathways. This has been explained in terms of protonation of MnO_4^- in a fast step to give $HmnO_3$ which subsequently reacts with the substrate in a slow step to give the product [18].

Effect of changes in ionic strength

The relationship of reaction rate with changes in the ionic strength was determined by plotting log k_2 against $\sqrt{\mu}$ with a negative slope of -0.0125 (Figure 3). The rate of reaction was found to decrease with increase in ionic strength of the reaction medium (Table 1). Ionic strength (μ) variation generally brings about two types of effects on chemical reaction rates, referred to as primary and secondary salt effects. The primary salt effect arises on the basis of the different types of reactive species present in the slow step. 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. A reverse trend is recorded in the case of reactions of oppositely charged species. The rates of reactions between two uncharged molecules or between an ion and a molecule are usually only slightly affected by the addition of salts. The secondary salt effect arises because of the presence of acid–base equilibria prior to the rate-limiting step. When primary and secondary salt effects are operative in the same direction, either significant acceleration or significant inhibition is observed. However, a negligible effect is recorded if primary and secondary salt effects are operative in opposite directions [19]. Results of the present study appear to be in agreement with a mechanism in which reactions between two pairs of ions of oppositely charge species are operative in the rate determining steps. A similar result has been reported [14].

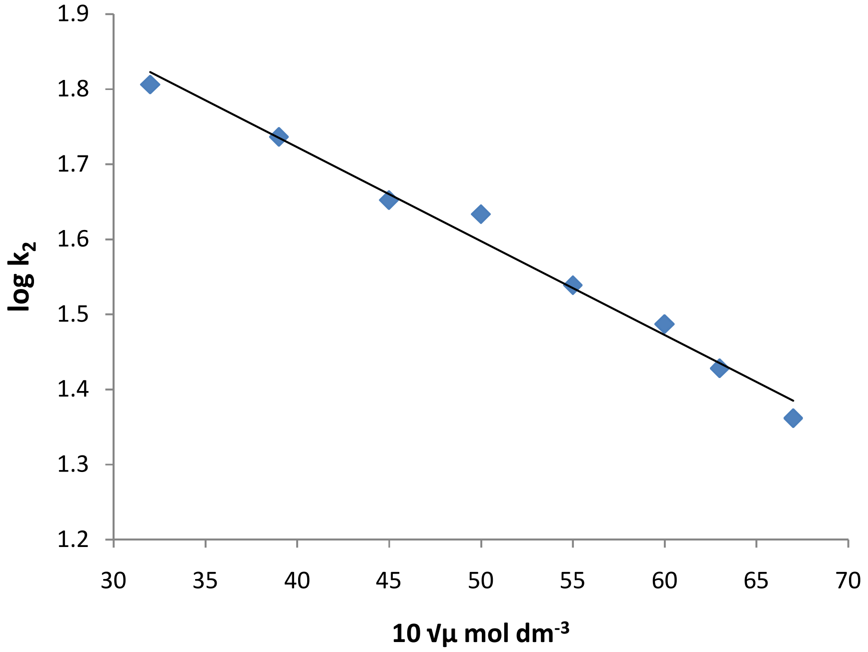


Figure 3: log k_2 versus $\sqrt{\mu}$ for the redox reaction of MB^+ and MnO_4^-
$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.10 - 0.45$ mol dm^{-3} (Na_2SO_4), T = 24 ±1.0°C and $\lambda_{max} = 660$ nm

Table 2: Rate data for the effect of cations and anions on the second order rate constant for MB^+ - MnO_4^- reaction. $[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} $\lambda_{max} = 660$ nm, μ =0.25 mol dm^{-3}, and T = 24 ± 1.0°C.

X	$10^3[X]$ mol dm^{-3}	$10^3k_1(s^{-1})$	$k_2(dm^3\ mol^{-1}\ s^{-1})$
Mg^{2+}	0	7.14	59.49
	20	6.22	51.83
	40	5.99	49.92
	60	5.76	48.00
	80	5.55	46.06
	100	5.06	42.22
Li^+	0	7.14	59.49
	20	5.99	49.92
	40	5.30	44.14
	60	5.07	42.22
	100	4.84	40.30
CH_3COO^-	0	7.14	59.49
	20	6.68	55.66
	40	5.07	42.22
	60	4.84	40.30
	80	3.92	32.63
	100	3.45	28.79
NO_3^-	0	7.14	59.49
	20	5.79	47.98
	40	5.30	44.14
	60	4.84	40.30
	80	4.38	36..46
	100	3.68	30.71

Effect of total dielectric constant

The effect of changing dielectric constant was studied by using a binary solvent mixture of water and acetone (2 to 10%). It was found that as the concentration of acetone increased, the reaction rate decreased. This is in line with observed effect on the rate of reaction on varying the ionic strength. The kinetic results of this study indicate that the rates of the reaction are faster in the solvent of high *D*.

Effect of added ions

The rate constant was found to be inhibited by the presence of both anions (NO_3^-, CH_3COO^-) and cations (Li^+, Mg^{2+}) as shown in Table 2. This is in agreement with an earlier report and is suggestive of the outer sphere pathway [20].

Table 3: Effect of changes in total dielectric constant for MB^+ - MnO_4^- reaction. $[MB^+] = 8 \times 10^{-6}$mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3} $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, λ_{max} = 660 nm, μ =0.25 mol dm^{-3}, and T = 24 ± 1.0°C

D	10^2 1/D	$10^3k_1(s^{-1})$	k_2 (dm^3 mol^{-1} s^{-1})
81.00	1.23	7.14	59.49
79.80	1.25	6.45	53.73
78.59	1.27	5.99	49.89
77.36	1.29	5.53	46.06
76.20	1.31	5.30	44.13
75.00	1.33	4.84	40.30

Michaelis-Menten Plot

The Michaelis – Menten plot gave a zero intercept (Figure 4) which suggest the probable absence of preassociation step or absence of intermediates complex formation with appreciable equilibrium constant.

Free Radical Test

Addition of acrylamide to partially oxidized reaction mixture followed by excess methanol showed gel formation. This is suggestive of the probable presence of free radical formation during the electron transfer.

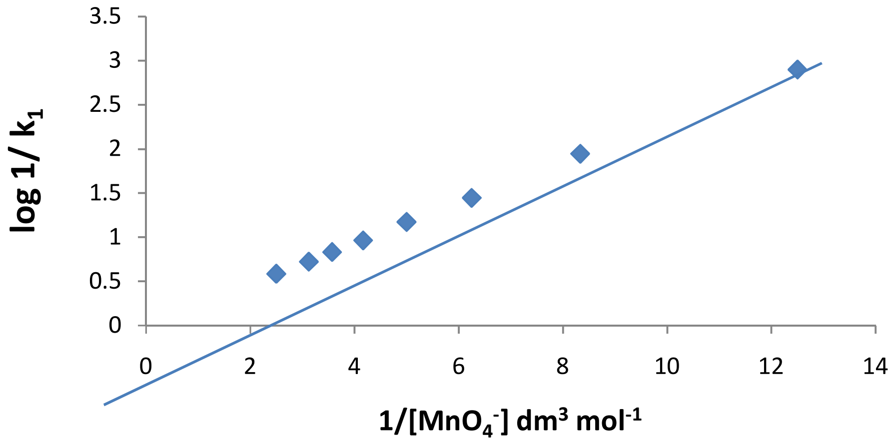


Figure 4: Michealis-Menten plot of $1/k_1$ versus $1/[MnO_4^-]$ for the redox reaction of MB^+ and MnO_4^-
$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}; $[MnO_4^-] = (0.84 – 4.00) \times 10^{-4}$ mol dm^{-3}
$[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, μ = 0.25mol dm^{-3} (Na_2SO_4), T = 24 ±1.0°C and λ_{max} = 660 nm.

Product Analysis

The blue colour of MB^+ was regenerated on the addition of NaOH/glucose mixture, showing the presence of leucomethylene blue. A characteristic purple colour occurred on addition of KIO_4 showing the presence of Mn^{2+}. This is as a result of oxidation of Mn^{2+} back to Mn^{7+} according to this equation:

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

Reaction mechanism

It has been noted that redox reactions of many oxyanions are strongly acid dependent.[21,22] Under the present experimental conditions, it is reasonable to postulate that MnO_4^- is protonated in a fast step to give $HMnO_4$ which then reacts with MB^+ in a slow step to give the products.

Also, the intercept obtained for the plot of k_2 versus $[H^+]$ indicates that the unprotonated MnO_4^- also reacts with MB^+ to form the products. Therefore, taking recourse to the experimental data, the following mechanistic steps have been posited for the reaction:

$MnO_4^- + H^+ \rightleftharpoons HMnO_4$ ……4

$MB^+ + HMnO_4 \xrightarrow{k_2}$ Products …… 5

$MB^+ + MnO_4^{-}K_1 \xrightarrow{k_3}$ Products …… 6

Rate = $k_2[MB^+][HMnO_4] + k_3[MB^+][MnO_4^-]$ …… 7

From equation 5.

$[HMnO_4] = K_1 [MnO_4^-][H^+]$ ……8

Putting equation 8 into 7,

Rate = $k_2K_1[MB^+][MnO_4^-][H^+] + k_3[MB^+][MnO_4^-]$ …… 9

Rate = $(k_3 + k_2K_1 [H+]) [MB^+][MnO_4^-]$ ……10

Equation 10 is similar to equation 3 with k_3 = 'a' = 4.04×10^{-3} $dm^3 mol^{-1} s^{-1}$ and k_2K_1 = 'b' = 0.125 $dm^6 mol^{-2} s^{-1}$

In trying to assign mechanistic pathway for this reaction, the following points are considered:

1. The inhibition of the rate of reaction by increase in ionic strength and added ions tends to suggest that the reaction occurs through the outer-sphere pathway.
2. The Michaelis-Menten plot was linear without intercept: an indication of the reaction occurring by the outer-sphere pathway
3. The presence of free radicals as indicated from gel formation may not have been a major species involved in the determining step.
4. Spectroscopic tests showed a bathochromic shift from 660 nm to 620 nm. This evidence is in favour of the inner-sphere pathway where a pre-electron transfer association exists between the reactants.

CONCLUSION

Based on the above findings, the mechanism of reaction has been rationalized on the basis of both the outer-sphere and the inner-sphere pathways. However, kinetic evidences for the outer-sphere pathway are much more than those for the inner-sphere pathway (evidence 4) which could have probably been as a result a binuclear intermediate complex involving unprotonated methylene blue and $HMnO_4$ [23].

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