STUDIES ON MANGANESE (II) CATALYZED OXIDATION OF N-METHYLANILINE BY PERIODATE ION

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ABSTRACT

The kinetics of the periodate oxidation of N-methylaniline (NMA) in acetone-water medium has been followed by monitoring the increase in the absorbance of reaction intermediate, C_4, and the main reaction product is p-benzoquinone. Results under pseudo first order conditions, $[IO_4^-] \gg [NMA]$, are in agreement with the rate law:

$$d[C]/dt = kK_3K_4K_w[Mn^{II}] [S] [IO_4^-]_0 [H^+] /\{K_2 K_w + (K_w + K_b K_2)[H^+] + K_b [H^+]^2\}$$

where kK_3K_4 is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$, K_b is base dissociation constant of NMA i.e. Substrate [S] and $[IO_4^-]_0$ represents the concentration of periodate that has been taken in excess in most of the kinetic runs. In agreement with the rate law, the $1/k_{cat}$ versus $[H^+]$ profile passes through the minimum. Free radical scavengers do not affect the reaction rate. Thermodynamic parameters evaluated are: $Ea = 5.2$ kcal mol^{-1}, $A = 4.79 \times 10^9$ dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -16.3$ cal mol^{-1}, $\Delta G^{\#} = 9.7$ kcal mol^{-1} and $\Delta H^{\#} = 4.6$ kcal mol^{-1}.

Key words: Kinetics, Mn^{II} catalysed, Periodate, n-Methylaniline, p-Benzoquinone.

INTRODUCTION

Keeping in view our earlier studies on uncatalysed periodate oxidation[1-8] and a few reports available on the kinetic studies for the Mn^{II} catalyzed non-Malapradian periodate oxidation of aromatic amines[9-12], the kinetic-mechanistic studies have been made on Mn (II) catalysed periodate oxidation of N-methylaniline (NMA). The results of these studies in acetone-water medium are presented and discussed in this communication. The studies are important for their further expected use in developing methods for detection and treatment of the aromatic amines – the chemicals enlisted as toxic[13].

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EXPERIMENTAL

Reagents and chemicals

Sodium metaperiodate (Loba Chemie), NMA (Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[14], consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH.

Kinetic procedure

The reaction was studied in a spectrophotometric cell and initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing the NMA, Mn^{II} and buffer and maintained at the desired temperature ($\pm 0.1^0$C).

The progress of the reaction was followed by recording the absorbance on Schimadzu double beam spectrophotometer (UV Pharmaspec-1700), at 533 nm, i.e., the λ_{max} of the violet color reaction mixture. λ_{max} was not found to change with change in time under experimental conditions. Desired temperature was maintained with the help of a high precision thermostatic control.

Product analysis

Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially, the solution turned violet, thereafter reddish brown and finally the solid product settled down on standing. It was filtered and the filtrate was extracted with petroleum ether (40-60°C). The extract was evaporated at room temperature to get a solid yellow residue that was found to be TLC single (using plate thickness of 0.5 mm, silica gel 'G' as adsorbant, chloroform+ acetone+ benzene in the ratio 4 : 6 : 4 mL used as eluent and 30 minutes as the time for development). The remaining part of filtrate may be having other products of this reaction, which could not be separated and identified. The yellow crystalline compound was recrystallised in ethanol and characterized as p-benzoquinone on the basis of positive test for quinone[15], M.P. 116°C (literature value 115-117°C[16]), UV spectrum in ethanol giving absorption maxima at 240, 280 and 440 nm, suggested the presence of quinonoid structure in the compound (literature values 244, 280 and 436 nm [17]). The IR spectrum of this compound (in KBr) showed the presence of bands at 1645 cm^{-1} (s) (indicating the presence of C=O on benzoquinone pattern[18]), 3280 cm^{-1}(s) (may be due to overtones of C=O stretch as the frequency is about twice that of C=O stretch).

Further, the bands at 1470 cm^{-1} (s) may be due to due to C=C ring stretch, 1365 cm^{-1} (m) and 1100 cm^{-1} (m) may be due to in plane C-H bending. The bands at 830 cm^{-1} (m) (due to out of plane C-H bending in case of two adjacent H atoms) and 680 cm^{-1} (m) (due to out of plane C=C bending mode) were also obtained.

Stoichiometry

Stoichiometry of the reaction was determined by allowing a known excess of $NaIO_4$ to react with substrate. After completion of the reaction, the precipitated product was filtered out and in the filtrate, unconsumed $NaIO_4$ was determined iodimetrically. The results indicated the stoichiometry to be 1 mol NMA : 2 moles periodate for the initial part of the reaction as in eq. (1).

$$C_6H_5NHCH_3 + 2\ IO_4^- + 2\ H^+ + H_2O \xrightarrow{\ Mn^{II}\ } C_6H_4O_2 + 2\ HIO_3 + NH_3 + CH_3OH \qquad ...(1)$$
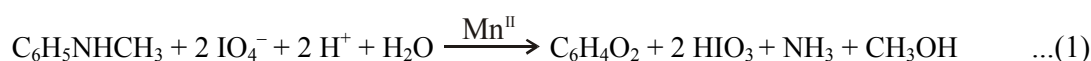
RESULTS AND DISCUSSION

Preliminary observations

On mixing the reactants, the solution becomes violet, which later changes into reddish brown. On keeping for long time, it finally gives the product. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. The rapid scan of the violet solution showed the λ_{max} of the intermediate, C_4, to be 533 nm. The UV-visible spectra of IO_4^-, NMA and Mn^{II} indicated that these do not show absorption in visible region. Hence, for following the kinetics, the absorbance changes were recorded at 533 nm at which only the intermediate C_4 absorbs.

Rate law

The kinetics was studied under pseudo-first order conditions by keeping periodate concentration in excess. Guggenheim's method was used for evaluation of pseudo-first order rate constants, k_{obs}. Under these conditions, the kinetics was defined by the rate law (2).

$$d[C]/dt = k_{cat}\ [S]\ [IO_4^-]_0\ [Mn^{II}] \qquad ...(2)$$

where $k_{obs} = k_{cat}\ [IO_4^-]_0\ [Mn^{II}]$ and k_{cat} is the rate constant for Mn^{II} catalysed pathway. $[IO_4^-]_0$ represents the initial concentration of periodate that has been taken in excess. In the absence of Mn^{II}, no significant reaction occurred. The values of k_{cat} obtained for different $[Mn^{II}]$, $[IO_4^-]_0$ and [S] are seen to be in good agreement and consistent with the rate law (2) (Table 1, Fig. 1).

Table 1: **Values of k_{obs} and k_{cat} at 35 ± 0.1^oC**

[NaIO$_4$] (mol dm^{-3})	[NMA] (mol dm^{-3})	[Mn (II)] $\times 10^7$ (mol dm^{-3})	Acetone [% (v/v)]	pH	$k_{obs} \times 10^4$ (s^{-1})	$k_{cat} \times 10^{-7}$ (dm^6 mol^{-2} s^{-1})
0.0002	0.002	1.456	5.0	6.0	3.99	0.140
0.0002	0.003	1.456	5.0	6.0	5.60	0.130
0.0002	0.004	1.456	5.0	6.0	7.06	0.120
0.0002	0.005	1.456	5.0	6.0	8.32	0.110
0.0002	0.006	1.456	5.0	6.0	9.47	0.110
0.003	0.0003	6.0	10.0	6.0	24.6	0.136
0.004	0.0003	6.0	10.0	6.0	31.5	0.131
0.005	0.0003	6.0	10.0	6.0	37.6	0.130
0.003	0.0003	1.456	10.0	6.0	5.37	0.123
0.003	0.0003	2.912	10.0	6.0	10.05	0.115
0.003	0.0003	4.368	10.0	6.0	16.00	0.122
0.003	0.0003	5.824	10.0	6.0	21.30	0.122
0.003	0.0003	7.280	10.0	6.0	26.60	0.122
0.003	0.0003	1.456	10.0	4.0	3.11	0.071
0.003	0.0003	1.456	10.0	4.5	4.22	0.097
0.003	0.0003	1.456	10.0	5.0	4.57	0.104
0.003	0.0003	1.456	10.0	5.5	4.68	0.107
0.003	0.0003	1.456	10.0	6.0	5.37	0.123
0.003	0.0003	1.456	10.0	6.5	9.15	0.210
0.003	0.0003	1.456	10.0	7.0	6.29	0.144
0.003	0.0003	1.456	10.0	7.5	4.40	0.100
0.003	0.0003	1.456	10.0	8.0	3.93	0.090
0.003	0.0003	1.456	2.5	6.0	7.68	0.180
0.003	0.0003	1.456	5.0	6.0	6.83	0.160
0.003	0.0003	1.456	7.5	6.0	5.99	0.140
0.003	0.0003	1.456	10.0	6.0	5.37	0.123
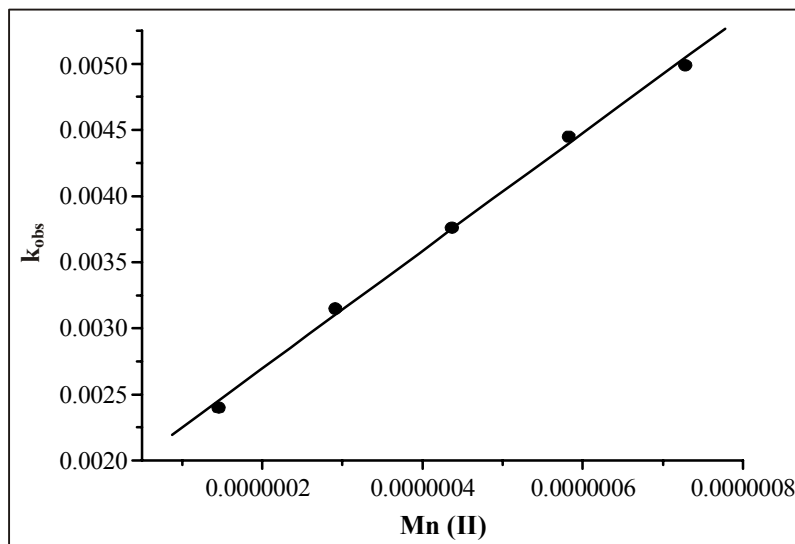
Fig. 1: Effect of [Mn(II)] on reaction rate at [NMA] = 3.0 × 10⁻⁴ mol dm⁻³,
[NaIO₄] = 3.0 × 10⁻³ mol dm⁻³, pH = 6.0, Acetone = 10.0 % (v/v), Temp. = 35 ± 0.1°C

Effect of pH, ionic strength, acetone, free radical scavengers and temperature

The effect of pH was examined in the range 4.0-8.0. $1/k_{cat} - [H^+]$ profile indicates a minimum at pH = 6.5 (Table 1, Fig. 2), which could be due to change in the nature of species and their relative reactivity, when the pH is changed. An increase in ionic strength caused almost no effect on the rate. An increase in the acetone (2.5-10.0%) led to about 39% decrease in the rate. Free radical scavengers, viz., acrylamide and allyl alcohol had no effect on the reaction rate. By determining the rate constants at four different temperatures (35.0 to 50.0°C), the values of different thermodynamic parameters were found and these are given in Table 2.
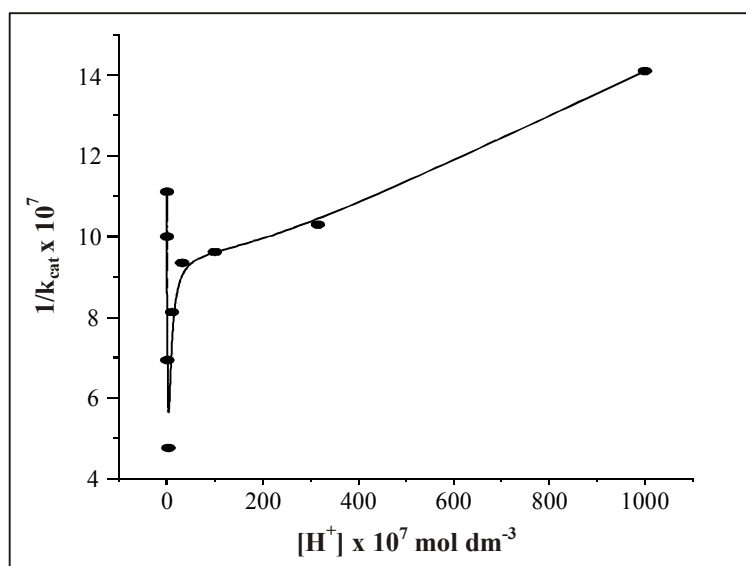
Preliminary examinations reveal that faster colour changes in the reaction mixture relative to the separation of product on standing for long time indicates the formation of the colored intermediate on a time scale of minutes and that of the final product on a time scale of hours. The overall reaction appears to involve several steps and possibly several transient intermediates, in addition to comparatively stable one C_4, during the oxidation of NMA into p-benzoquinone. Further, the kinetic order of one in periodate against the requirement of two periodate molecules for each NMA molecule in the stoichiometry (Eq. 1) requires the involvement of only one periodate in the rate determining step and second IO_4^- ion to be consumed in a fast step leading to the formation of the intermediate, C_4. Since the concentration of C_4 increases continuously with time and reaches a limiting value, its

concentration can not be in steady state. Finally, $1/k_{cat} - [H^+]$ profile indicates the presence of at least three differently reactive reactant species in the pH region chosen for study. Finally, the observation that free radical scavengers have no effect on reaction rate rules out the involvement of free radicals in the oxidation mechanism.

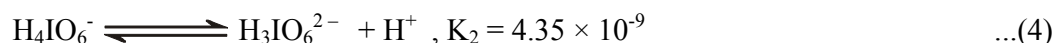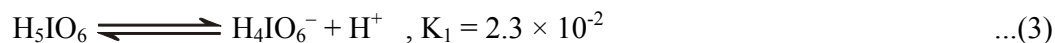**Table 2: Activation parameters**

$[NMA] = 3.0 \times 10^{-4}$ mol dm^{-3}, $[NaIO_4] = 3.0 \times 10^{-3}$ mol dm^{-3},
$[Mn^{II}] = 1.456 \times 10^{-7}$ mol dm^{-3}, Acetone = 10.0 % (v/v), pH = 4.5

Temp. (^{o}C)	$10^4 k_{obs}$ (s^{-1})	$10^{-7} k_{cat}$ (dm^6 mol^{-2} s^{-1})	Ea (kcal mol^{-1})	A (dm^3 mol^{-1} s^{-1})	$\Delta S^{\#}$ (cal mol^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})
35	4.22	0.097					
40	4.84	0.111	5.2	4.8×10^9	- 16.3	9.7	4.6
45	5.53	0.127					
50	6.29	0.144					

Fig. 2: Effect of [H$^+$] on the rate at Acetone = 10% (v/v), [NMA] =3.0 × 10^{-4} mol dm^{-3}, [NaIO$_4$] = 3.0× 10^{-3} mol dm^{-3}, [Mn^{II}] = 1.456 × 10^{-7} mol dm^{-3} and Temp.= 35 ± 0.1^{o}C

Construction of a mechanism requires discussion on the speciation of NMA and periodate. In aqueous solutions, periodate exists in the three forms governed by the equilibria (3 – 4).
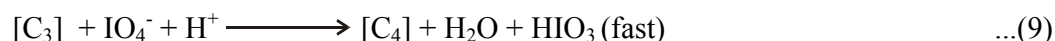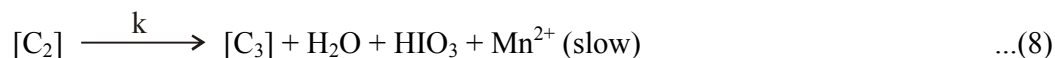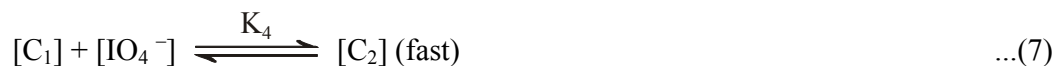
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad , K_1 = 2.3 \times 10^{-2} \qquad \text{...(3)}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad , K_2 = 4.35 \times 10^{-9} \qquad \text{...(4)}$$

The value of K_1 indicates that in the pH range 4.0 − 8.0, species H_5IO_6 shall be practically non-existent and hence, only species $H_4IO_6^-$ and $H_3IO_6^{2-}$ need be considered for explaining observed pH - dependence. In aqueous solution, NMA[19], undergoes the following acid − base equilibrium with $K_b = 7.1 \times 10^{-10}$.

$$C_6H_5NHCH_3 + H_2O \rightleftharpoons C_6H_5N^+H_2CH_3 + OH^- \qquad \text{...(5)}$$
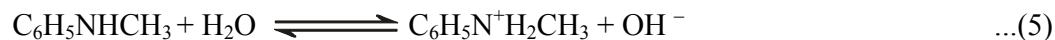
Since in the studied pH-range, both $C_6H_5NHCH_3$ and $C_6H_5N^+H_2CH_3$ exist, these species have been taken into account. The pH effect may be explained by assuming the unprotonated amine and periodate monoanion to be reactive. This requires the reaction rate to decrease when the concentration of either of these or both decreases on changing the pH.

Based on the observed kinetic rate law (Eq. 2) and pH- dependence, the following mechanism, which assumes, $C_6H_5NHCH_3$ and $H_4IO_6^-$ to be the reactive species, is proposed.

$$C_6H_5NHCH_3 + Mn^{2+} \xrightleftharpoons{K_3} [C_1] \qquad \text{...(6)}$$

$$[C_1] + [IO_4^-] \xrightleftharpoons{K_4} [C_2] \text{ (fast)} \qquad \text{...(7)}$$

$$[C_2] \xrightarrow{k} [C_3] + H_2O + HIO_3 + Mn^{2+} \text{ (slow)} \qquad \text{...(8)}$$

$$[C_3] + IO_4^- + H^+ \longrightarrow [C_4] + H_2O + HIO_3 \text{ (fast)} \qquad \text{...(9)}$$

In steps (6 − 9), $[C_1]$, $[C_2]$, $[C_3]$ and $[C_4]$, are intermediates, out of which $[C_4]$ appears to undergo very slow reorganization/ hydrolysis to yield the reaction product, C_5.

$$[C_4] \longrightarrow [C_5] \text{ (Product)} \qquad \text{...(10)}$$

In the mechanism for simplicity, $H_4IO_6^-$ has been written as IO_4^-. Since the elementary reactions in liquid phase are a rarity, the formation of intermediates $[C_1]$ and $[C_2]$ in a rapid step having low values of equilibrium constants, K_3 and K_4, is assumed in the proposed gross mechanism. In the detailed mechanism **(Scheme 1)**, the catalytic role of Mn^{2+} appears to be due to the formation of a ternary complex, $[(NMA) Mn (H_4IO_6)]^+$, in which Mn acts as a conduit for electron transfer.

Scheme 1
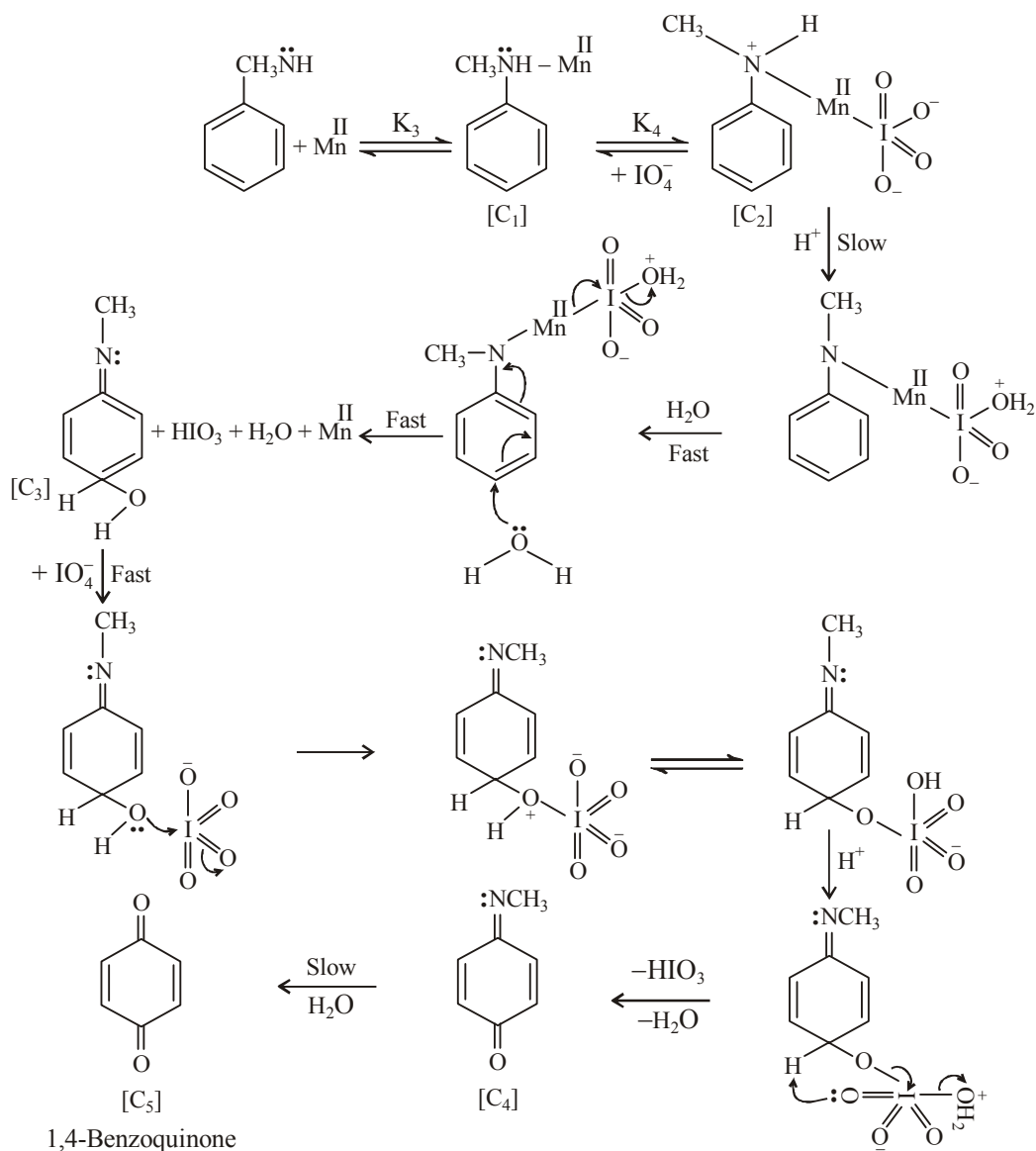
The proposed mechanism (6 – 9) leads to the rate law (11).

$$d[C_4]/dt = kK_3K_4 \ [Mn^{II}][IO_4^-] \ [C_6H_5NHCH_3] \qquad\qquad ...(11)$$

On substituting the values of concentrations of the reactive species $[C_6H_5NHCH_3]$ and $[IO_4^-]$ in terms of equilibria (3-4) and (5), respectively, in eq. (2), the complete rate law including $[H^+]$ - dependence becomes:

$$d[C]/dt = kK_3K_4[Mn^{II}]\{([S]\,[OH^-]/(\,[OH^-] + K_b)\}\{([IO_4^-]_0\,[H^+]\,/(K_2 + [H^+])\} \quad ...(12)$$

On replacing the term, $[OH^-][H^+]$, by K_w in numerator, and $[OH^-]$ by $K_w/[H^+]$ in denominator, and on rearranging, the Eq. (12) becomes Eq. (13).

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[S][IO_4^-]_0\,[H^+]\,/\{K_2\,K_w + (K_w + K_b\,K_2)[H^+] + K_b[H^+]^2\} \quad ...(13)$$

On comparing eqs.(2) and (13), we get

$$k_{cat} = k\,K_3K_4\,K_w[H^+]/\{K_2\,K_w + (\,K_w + K_b\,K_2\,)\,[H^+] + K_b\,[H^+]^2\} \quad\quad ...(14)$$

Eq. (14) on rearranging becomes eq. (15).

$$1/k_{cat} = (K_2\,/\,kK_3K_4\,[H^+]) + \{(K_w + K_b\,K_2)\,/\,kK_3K_4\,K_w\} + K_b[H^+]\,/\,kK_3K_4\,K_w \quad ...(15)$$

The nature of the rate law (15) shows that a plot of $1/k_{cat}$ versus $[H^+]$ shall pass through a minimum[20]. On differentiating $1/k_{cat}$ with respect to $[H^+]$ in eq. (15), we get the values of $d^2[1/k_{cat}]\,/\,d[H^+]^2$. The value of second derivative is found to be positive showing the plot of $1/k_{cat}$ versus $[H^+]$ to pass through a minimum. Thus, on setting $d[1/k_{cat}]\,/\,d[H^+]$ equal to zero for obtaining hydrogen ion concentration at which the $1/k_{cat}$ vs $[H^+]$ profile will pass through minimum, we obtain,

$$[H^+]_{min} = (K_2\,K_w\,/\,K_b)^{1/2} \quad\quad ...(16)$$

On substituting the values of K_2, K_w and K_b, we get

$$[H^+]_{min} = 2.48 \times 10^{-7}\text{ mol dm}^{-3}$$

It is noteworthy that the calculated value of $[H^+]_{min}$ is in satisfactory agreement with the experimental value of $[H^+]_{min}$ of 3.16×10^{-7} mol dm^{-3} obtained from $1/k_{cat}$ versus $[H^+]$ plot (Fig. 2) and this provides strong support to the proposed mechanism.

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