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KINETICS AND MECHANISM OF Mn^{II} CATALYZED PERIODATE OXIDATION OF o-ANISIDINE

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ABSTRACT

The kinetics of the periodate oxidation of *o*-anisidine (ANIS) 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 methoxy-1, 4-benzoquinone. Results under pseudo first order conditions, $[IO_4^-] << [ANIS]$, are in agreement with the rate law:

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

Where kK_3K_4 is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$ and K_b is base dissociation constant of ANIS. 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. The values of thermodynamic parameters are: $\Delta E = 9.95$ kJ mol^{-1}, $A = 1.18 \times 10^8$ dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -99.18$ J mol^{-1} K^{-1}, $\Delta G^{\#} = 38.62$ kJ mol^{-1} and $\Delta H^{\#} = 7.33$ kJ mol^{-1}.

Key words: Kinetics, Mn^{II} catalysed, Periodate oxidation, o-Anisidine, Methoxy-1, 4-benzoquinone.

INTRODUCTION

Reports are available on the kinetic-mechanistic studies for the uncatalysed non-Malapradian periodate oxidation of aromatic amines[1-9]. Some of the recent reports include the Mn^{II} catalyzed periodate oxidation of 2, 4-xylidine[10], 2,6-xylidine[11], N-methylaniline[12], p-toluidine[13] and 4-chloro, 2-methyl aniline[14]. With CAS no. 90-04-0, o-anisidine[15] has been enlisted as carcinogen in the toxic release inventory of US EPA, 2001 and placed in group 2B of international agency for research on cancer, which includes the chemicals that are possibly carcinogenic to humans. The kinetic-mechanistic studies have been made on Mn^{II} catalyzed periodate oxidation of o-anisidine (ANIS) in acetone-water medium and the results of these studies are being presented and discussed in this paper. The studies are important for their further expected use in developing methods for detection and treatment of o-anisidine.

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EXPERIMENTAL

Reagents and chemicals

Sodium metaperiodate (Loba Chemie), o-anisidine (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[16] 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 ANIS, Mn^{II} and buffer and maintained at the desired temperature (± 0.1^0C).

The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV-2550), at 490 nm, i.e., the λ_{max} of the reaction intermediate absorbs. 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 light yellow colour, thereafter wine red colour and then brown followed by precipitation in about 24 hrs. The reaction mixture was extracted with petroleum ether, the extract was evaporated at room temperature to get a yellow colored compound which was subjected to TLC analysis (using plate thickness of 0.5 mm, silica gel 'G' as adsorbant, chloroform + acetone + benzene in the ratio 40:60:40 mL used as eluent and 40 min. as the time for development). The yellow component was recrystallised in chloroform, obtained as yellow needles and characterized as methoxy-1, 4-benzoquinone. The melting point of separated compound was found to be 144^oC (Lit. 145^oC for methoxy-1, 4-benzoquinone[17]). This compound responded positive for a quinone[18]. The absorption maxima for this compound in $CHCl_3$ solvent were 250 and 352 nm (Lit. values: 254 and 357 nm for methoxy-1, 4-benzoquinone[19]). The IR spectrum of compound (in KBr) showed a strong band at 2971 cm^{-1} (s) (due to ring C–H stretch), 1635 cm^{-1} (s) (indicating the presence of C=O on 1, 4-benzoquinone pattern with the possibility that the position of this band got lowered due to + I effect of methoxy group[20]), 3222 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 1393 cm^{-1} (s), 1492 cm^{-1} (s) may be due to C=C ring stretch. The bands at 1245 cm^{-1} (m) to 1041 cm^{-1} (m) may be due to asymmetric and symmetric C-O-C stretch and at 612 cm^{-1} (m) (s) and 518 cm^{-1} (m) (due to out of plane C=C bending mode[21]). The observed values are in good agreement with reported for methoxy-1, 4-benzoquinone.

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 ANIS: 2 moles $NaIO_4$ for the reaction as in Eq. (1).

$$CH_3OC_6H_4NH_2 + 2IO_4^- + 2H^+ \xrightarrow{Mn^{II}} CH_3OC_6H_3O_2 + 2HIO_3 + NH_3 \quad ...(1)$$

RESULTS AND DISCUSSION

Preliminary observations

On mixing the reactants, the solution turned light yellow colour, thereafter wine red colour and then brown colour. 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 brown solution showed the λ_{max} of the intermediate, C_4, to be 490 nm (Fig. 1).

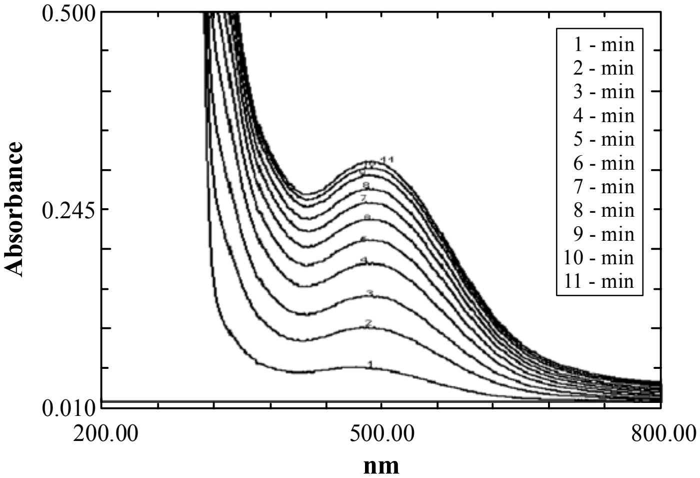


Fig. 1: Rapid UV-VIS scan of reaction solution at different time at pH = 6.5, $[NaIO_4] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[ANIS] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[Mn (II)] = 7.28 \times 10^{-6}$ mol dm^{-3}, Acetone = 5.0 % (v/v), Temp = 35.0 ± 0.1^0C

IO_4^-, ANIS and Mn^{II} show no absorption in visible region as indicated by their UV-VIS spectra. Hence, for following the kinetics the absorbance changes were recorded at 490 nm at which only the intermediate C_4 absorbs.

Rate law

The kinetics was studied under pseudo order conditions by keeping ANIS 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).

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

where $k_{obs} = k_{cat}\,[IO_4^-]_0\,[Mn^{II}]$ and k_{cat} is the rate constant for Mn^{II} catalysed pathway. $[IO_4^-]_0$ and $[ANIS]_0$ represent respectively, the initial concentrations of periodate and ANIS out of which later one is 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 $[ANIS]_0$ are seen to be in good agreement and consistent with the rate law (2) (Table 1).

Table 1: Effect of different factors on the reaction rate at 35.0 ± 0.1°C

$[NaIO_4] \times 10^5$ (mol dm^{-3})	$[ANIS] \times 10^4$ (mol dm^{-3})	$[Mn^{II}] \times 10^7$ (mol dm^{-3})	Acetone (%v/v)	$[NaCl] \times 10^3$ (mol dm^{-3})	pH	$k_{obs} \times 10^2$ (s^{-1})	$k_{cat} \times 10^{-8}$ (dm^6 mol^{-2} s^{-1})
7.0	6.0	7.28	5.0	-	6.5	10.82	2.4
7.0	7.0	7.28	5.0	-	6.5	12.34	2.4
7.0	8.0	7.28	5.0	-	6.5	14.13	2.4
7.0	9.0	7.28	5.0	-	6.5	15.95	2.4
7.0	10.0	7.28	5.0	-	6.5	17.56	2.4
7.0	11.0	7.28	5.0	-	6.5	18.91	2.4
3.0	7.0	7.28	5.0	-	6.5	11.67	2.3
4.0	7.0	7.28	5.0	-	6.5	11.89	2.3
5.0	7.0	7.28	5.0	-	6.5	12.10	2.4
6.0	7.0	7.28	5.0	-	6.5	12.21	2.4
7.0	7.0	7.28	5.0	-	6.5	12.34	2.4
8.0	7.0	7.28	5.0	-	6.5	12.40	2.4
7.0	7.0	1.82	5.0	-	6.5	3.22	2.5
7.0	7.0	3.64	5.0	-	6.5	6.22	2.4
7.0	7.0	5.46	5.0	-	6.5	9.21	2.4
7.0	7.0	7.28	5.0	-	6.5	12.36	2.4

Cont…

$[NaIO_4] \times 10^5$ (mol dm^{-3})	$[ANIS] \times 10^4$ (mol dm^{-3})	$[Mn^{II}] \times 10^7$ (mol dm^{-3})	Acetone (%v/v)	$[NaCl] \times 10^3$ (mol dm^{-3})	pH	$k_{obs} \times 10^2$ (s^{-1})	$k_{cat} \times 10^{-8}$ (dm^6 mol^{-2} s^{-1})
30.0	30.0	7.28	5.0	-	4.5	6.05	0.28
30.0	30.0	7.28	5.0	-	5.0	8.98	0.41
30.0	30.0	7.28	5.0	-	5.5	10.60	0.49
30.0	30.0	7.28	5.0	-	6.0	11.33	0.52
30.0	30.0	7.28	5.0	-	6.5	11.67	0.53
30.0	30.0	7.28	5.0	-	7.0	11.10	0.51
30.0	30.0	7.28	5.0	-	7.5	10.33	0.47
30.0	30.0	7.28	5.0	-	8.0	8.13	0.37
7.0	7.0	7.28	5.0	2.0	6.5	10.36	2.0
7.0	7.0	7.28	5.0	4.0	6.5	10.59	2.1
7.0	7.0	7.28	5.0	6.0	6.5	10.82	2.1
7.0	7.0	7.28	5.0	8.0	6.5	11.05	2.2
7.0	7.0	7.28	5.0	-	6.5	12.36	2.4
7.0	7.0	7.28	10.0	-	6.5	11.21	2.2
7.0	7.0	7.28	15.0	-	6.5	9.98	2.0
7.0	7.0	7.28	20.0	-	6.5	8.75	1.7

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

The effect of pH was examined in the range 4.5-8.0. $1/k_{cat}$ versus pH plot indicates a maximum at pH = 6.5 (Table 1, Fig. 2). An increase in ionic strength, μ, with the help of sodium chloride $\{(2–8)\times10^{-3}$ mol $dm^{-3}\}$ led to slight increase in the rate (6.7%) and an increase in the acetone led to a decrease in the rate. Free radical scavengers, viz., acrylamide and allyl alcohol had no effect on the reaction rate.

The rate constants were determined at four different temperatures (35.0 to 50.0°C) under the conditions, [ANIS] = 7.0×10^{-4} mol dm^{-3}, $[NaIO_4] = 7.0 \times 10^{-5}$ mol dm^{-3}, $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, Acetone = 5.0 % (v/v), pH = 6.5, λ_{max} = 490 nm. The values of different thermodynamic parameters viz. activation energy (ΔE), entropy of activation ($\Delta S^{\#}$), Arrhenius frequency factor (A), free energy of activation ($\Delta G^{\#}$) and enthalpy of activation ($\Delta H^{\#}$) were found as ΔE = 9.95 kJ mol^{-1}, $A = 1.18 \times 10^8$ dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -99.18$ J mol^{-1} K^{-1}, $\Delta G^{\#}$ = 38.62 kJ mol^{-1} and $\Delta H^{\#}$ = 7.33 kJ mol^{-1}. The value of $\Delta G^{\#}$ was temperature dependent. A high negative value of $\Delta S^{\#}$ is suggestive of solvent interactions and the probability that the transition state may be solvated. Small value of activation energy is characteristic of catalyzed reaction.

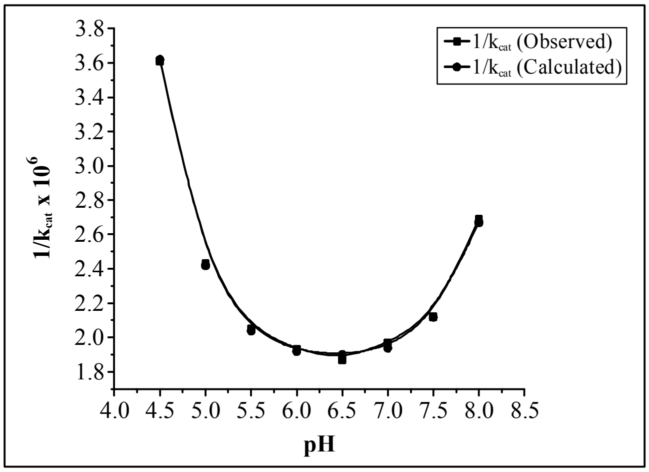


Fig. 2: $1/k_{cat}$ (observed) or $1/k_{cat}$(calculated) – pH profile at $[NaIO_4] = 3.0 \times 10^{-4}$ mol dm^{-3}, $[ANIS] = 3.0 \times 10^{-3}$ mol dm^{-3},$[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, Acetone = 5.0 % (v/v), λ_{max} = 490 nm, Temp. = 35.0 ± 0.1 ^{0}C

Some important features of this reaction are as follows. Firstly, 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 ANIS into a methoxy-1, 4-benzoquinone. Secondly, the kinetic order of one in periodate against the requirement of two periodate molecules for each ANIS 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. Thirdly, $1/k_{cat}$ versus $[H^+]$ plot 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.

In aqueous solutions, periodate exists in following equilibria (3-4).

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, K_1 = 2.3 \times 10^{-2} \quad \ldots(3)$$

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

The value of K_1 indicates that in the pH range 4.5-9 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, o-anisidine[22], undergoes the following acid-base equilibrium with $K_b = 3.0 \times 10^{-10}$.

$$CH_3OC_6H_4NH_2 + H_2O \rightleftharpoons CH_3OC_6H_4N^+H_3 + OH^- \quad ...(5)$$

Since in the studied pH-range both, $CH_3OC_6H_4NH_2$ and $CH_3OC_6H_4N^+H_3$ exist, these species have been taken into account. The pH effect may be explained by assuming the $CH_3OC_6H_4NH_2$ and $H_4IO_6^-$ to be reactive.

Based on the observed kinetics rate law (Eq. 2) and pH-dependence, the following mechanism is proposed.

$$CH_3OC_6H_4NH_2 + Mn^{2+} \overset{K_3}{\rightleftharpoons} [C_1] \quad ...(6)$$

$$[C_1] + [IO_4^-] \overset{K_4}{\rightleftharpoons} [C_2] \text{ (fast)} \quad ...(7)$$

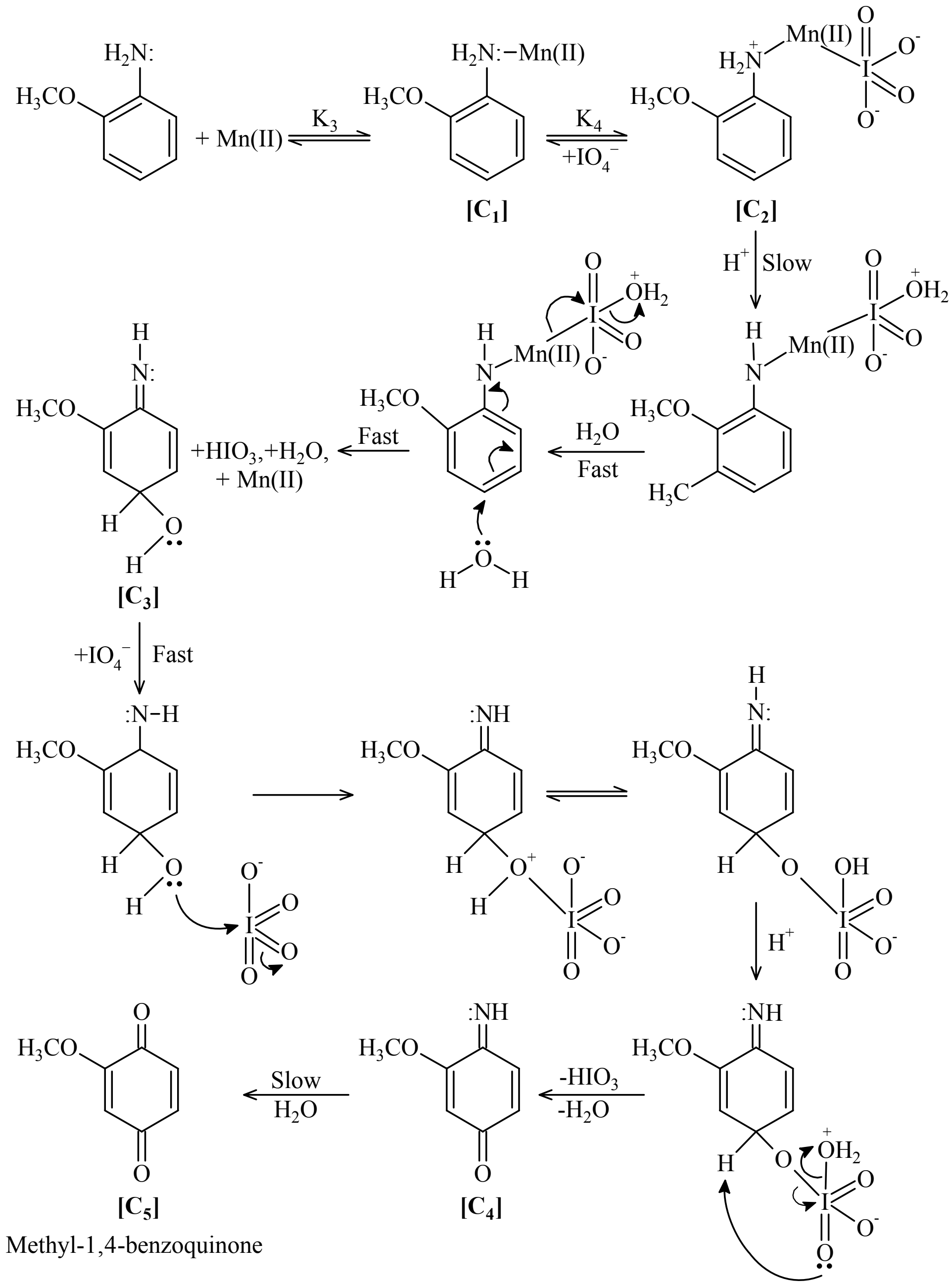
$$[C_2] + H^+ \xrightarrow{k} [C_3] + HIO_3 + Mn^{2+} \text{ (slow)} \quad ...(8)$$

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

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.

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

In the mechanism for simplicity, $H_4IO_6^-$ has been written as IO_4^-. 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, $[(ANIS)Mn(H_4IO_6)]^+$, in which Mn acts as a conduit for electron transfer. Further the proposed gross mechanism matches the kinetic and product studies, as given in **Scheme 1**. The formation of a charged intermediate complex C_2 by the attack of IO_4^- on the nitrogen of anilino group and stabilization of positive charge on nitrogen of this group, has already been established and supported by LFER studies for the uncatalyzed periodate oxidation of few aromatic amines[5,6]. In addition, a high negative value of entropy of activation and the effect of dielectric constant on the reaction rate support the involvement of solvation effects in this reaction.



Scheme 1

The proposed mechanism (6-9) leads to the rate law (11).

$$d[C_4]/dt = kK_3K_4\ [Mn^{II}][IO_4^-]\ [CH_3OC_6H_4NH_2] \qquad ...(11)$$

On substituting the values of concentrations of the reactive species [$CH_3OC_6H_4NH_2$] and [IO_4^-] in terms of equilibria (3-4) and (5), respectively, in Eq. (2), the complete rate law including [H^+] - dependence becomes:

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

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).

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

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

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

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

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

The k_{cat} and pH data were fitted to Eq. (15) and the best fit value of composite rate constant kK_3K_4 was found to 5.38×10^5 dm^6 mol^{-2} s^{-1}. The plot comprising of the experimental data and calculated data is shown in Fig. 2. In this case, all experimental values are in good agreement and fall on the calculated line, which confirms the applicability of Eq. (15) in the studied pH range i.e. 4.5-8.0.

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. This minimum can be seen in the experimental curve (Fig. 2). 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,

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

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

$$[H^+]_{min} = 3.80 \times 10^{-7}\ mol\ dm^{-3}$$

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 pH plot (Fig. 2) and this provides strong support to the proposed mechanism.

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