Mn^{II} Catalyzed Oxidation of 2,5-Xylidine by Periodate Ion – A Kinetic and Mechanistic Study

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Abstract

The kinetics of the periodate oxidation of 2, 5-Xylidine (2,5-XYL) 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 2, 5-dimethyl–1, 4–benzoquinone. Results under pseudo first order conditions, $[IO_4^-] \gg [2,5\text{-XYL}]$, are in agreement with the rate law: $d[C]/dt = kK_3K_4K_w [Mn^{II}] [2,5\text{-XYL}]_0 [IO_4^-]_0 [H^+] / \{K_2 K_w + (K_w + K_b K_2)[H^+] + K_b [H^+]^2\}$. 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 2,5-XYL. 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: $\Delta E = 5.69$ kJ mol^{-1}, $A = 6.52 \times 10^6$ dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -104.44$ J mol^{-1}K^{-1}, $\Delta G^{\#} = 35.56$ kJ mol^{-1} and $\Delta H^{\#} = 3.16$ kJ mol^{-1}.

Keywords: *Kinetics; Mn^{II} catalysed; Periodate oxidation; 2, 5-xylidine; 2, 5- dimethyl-1, 4–benzoquinone*

Introduction

There are some reports available in literature related to the uncatalysed [1-15] /Mn^{II} catalysed periodate oxidation of aromatic amines [16-29]. Also, there are some reports available which propose the ternary complex formation between periodate, 2, 4-xylidine [18], 2,3-xylidine [28] and Mn^{II} in some reactions catalysed by Mn^{II}. With CAS no. 90-04-0, 2, 5-xylidine 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 on the Mn^{II} catalysed periodate oxidation of 2, 5-xylidine (2,5-XYL) in acetone-water medium are being presented in the present communication.

Experimental

Reagents and chemicals

Sodium metaperiodate (CDH), 2, 5-xylidine (E. Merck), acetone (E. Merck), manganese sulphate monohydrate (CDH) and all other chemicals of E. Merck or CDH Analar grade were used after redistillation/ recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer [29,30] 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 2,5-XYL, Mn^{II} and buffer and maintained at the desired temperature ($\pm 0.1°C$). The progress of the reaction was followed by recording the absorbance on Schimadzu double beam spectrophotometer (UV - 1800), at 535 nm, i.e., the λ_{max} of the reaction intermediate / product 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 0.015 M $NaIO_4$ + 0.001 M 2,5D + 7.28×10^{-6} M Mn (II) +10.0 % (v/v) acetone, was prepared, shaken and set aside. It development of light pink colour changing into wine red and then brown followed by precipitation in about 24 hours. The reaction mixture was filtered after it and the filtrate was extracted with petroleum ether ($40 – 60°C$). The extract was evaporated at room temperature to get a solid residue that was dissolved in petroleum ether. The extracted portion was subjected to TLC with following parameters fixed by hit and trial: Plate thickness=0.5 mm, Adsorbant=Silica gel 'G', Eluent=Benzene, elution= 30 minutes. Three separated components, reddish, brown and yellow in colour. The red and brown components could not be collected in sufficient amount due to small yield. The yellow component was recrystallized in ethanol, obtained as yellow needles and characterized as 2,5-dimethyl-1,4-benzoquinone. The melting point of separated compound was found to be $126°C$ (Lit. $125°C$ for 2,5-dimethyl-1,4-benzoquinone [31]). This compound responded positive for a quinone [32]. The λ_{max} obtained for this compound in CCl_4 solvent were 250, 262, 310, 428, and 450 nm (literature values: 252, 259, 309, 425, and 445 nm for 2,5-dimethyl-1,4-benzoquinone [33]). The IR spectrum of compound (in KBr) showed the bands at 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 methyl group [34-35]), 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 1108 cm^{-1}(m) to 1166 cm^{-1}(m) may be due to the in plane C-H bending. The band at 831 cm^{-1} (m) (due to out of plane bending in case of two adjacent H-atoms) and 506 cm^{-1} (m) (may be due to out of plane C=C bending mode)[34]. The observed values are in good agreement with those reported/ expected for 2,5-dimethyl-1,4 -benzoquinone. Therefore, on the basis of these studies, this compound may be 2,5-dimethyl-1,4 -benzoquinone with the structure given below:
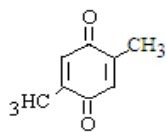
Stoichiometry

In order to determine the number of moles of periodate reacting with one mol of 2,5-XYL, graphical method was adopted. Oxidant was taken in excess. At suitable intervals of time, 5 ml of the reaction mixture was pipetted out and the product, either in turbid or in precipitated form, was extracted in chloroform. Now the reaction mixture was estimated for unreacted $NaIO_4$ iodometrically. It was taken as the point corresponding to the completion of the *first stage of the reaction* for which the kinetic studies were made. At inflexion point on the curve, the volume of periodate consumed to oxidize 5 ml of 0.001M 2,5-XYL was evaluated for two kinetic runs in which two different concentrations of $NaIO_4$ were used

Thus it can be concluded that 2 moles of periodate were consumed by each mol of 2,5-XYL for the first stage of the reaction Eq. (1).

$$(CH_3)_2C_6H_3NH_2 + 2IO_4^- + 2H^+ \xrightarrow{\quad Mn^{II} \quad} (CH_3)_2C_6H_2O_2 + 2HIO_3 + NH_3 \quad (1)$$
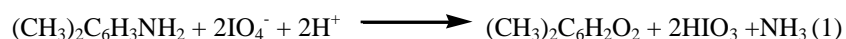
Results

Preliminary observations

On mixing the reactants, the solution turned light pink colour changing into wine red and then brown followed by precipitation in about 24 hours. 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 535 nm (FIG. 1). IO_4^-, 2,5-XYL 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 535 nm at which only the intermediate C_4 absorbs.

FIG. 1. **Rapid UV-VIS scan of reaction solution at different time at pH=5.5, $[NaIO_4]$=2.0 × 10^{-3} mol dm^{-3},[2,5-XYL]=4.0 × 10^{-4} mol dm^{-3}, $[Mn^{II}]$=3.28 × 10^{-6} mol dm^{-3}, acetone=5.0 % (v/v), Temp=30.0 ± 0.1°C.**
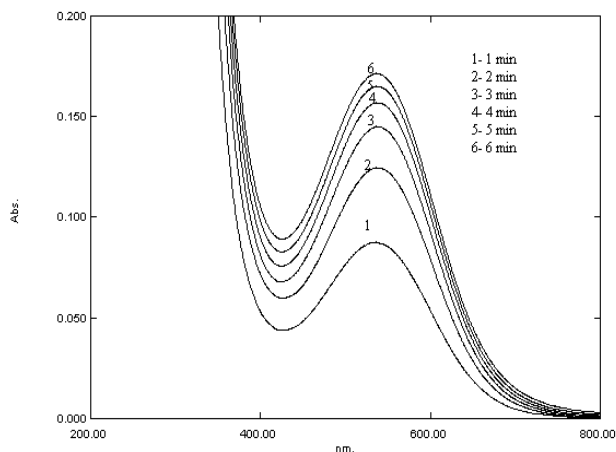
Rate Law

The kinetics was studied under pseudo order conditions by keeping 2,5-XYL 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).

$$d[C]/dt = k_{cat} [2,5\text{-XYL}]_0 [IO_4^-]_0 [Mn^{II}] \quad\text{...} \quad (2)$$

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 $[XYL]_0$ represent respectively, the initial concentrations of periodate and 2,5-XYL 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 $[2,5\text{-XYL}]_0$ are seen to be in good agreement and consistent with the rate law (2) (TABLE 1).

TABLE 1. **Effect of various factors on the reaction rate Temp.$=30.0 \pm 0.1^{\circ}$C**

$[NaIO_4] \times 10^5$ mol dm^{-3}	$[2,5\text{-XYL}] \times 10^5$ mol dm^{-3}	$[Mn^{II}]$ $\times 10^6$ mol dm^{-3}	Acetone (%V/V)	pH	$k_{obs} \times 10^2$ (s^{-1})	$k_{cat} \times 10^{-6}$ (dm^6 mol^{-2} s^{-1})
80.0	8.0	7.28	5.0	5.5	3.69	6.34
80.5	8.0	7.28	5.0	5.5	3.78	6.11
90.0	8.0	7.28	5.0	5.5	3.83	5.84
95.0	8.0	7.28	5.0	5.5	3.90	5.64
100.0	8.0	7.28	5.0	5.5	4.00	5.49
80.0	5.0	7.28	5.0	5.5	3.32	5.70
80.0	6.0	7.28	5.0	5.5	3.44	5.96
80.0	7.0	7.28	5.0	5.5	3.56	6.11
80.0	8.0	7.28	5.0	5.5	3.69	6.34
80.0	9.0	7.28	5.0	5.5	3.76	6.46
80.0	8.0	3.28	5.0	5.5	3.11	7.36
80.0	8.0	5.28	5.0	5.5	3.47	6.87
80.0	8.0	7.28	5.0	5.5	3.69	6.34
80.0	8.0	9.28	5.0	5.5	4.06	6.12
80.0	8.0	7.28	5.0	5.0	2.95	5.06
80.0	8.0	7.28	5.0	5.5	3.69	6.34
80.0	8.0	7.28	5.0	6.0	4.04	6.93
80.0	8.0	7.28	5.0	6.5	4.12	7.09
80.0	8.0	7.28	5.0	7.0	3.95	6.79
80.0	8.0	7.28	5.0	7.5	3.51	6.03
80.0	8.0	7.28	5.0	8.0	2.84	4.88
80.0	8.0	7.28	2.5	5.5	4.36	7.48
80.0	8.0	7.28	5.0	5.5	3.69	6.34
80.0	8.0	7.28	7.5	5.5	3.26	5.59
80.0	8.0	7.28	10.0	5.5	2.80	4.80

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

The effect of pH was examined in the range 5.0 – 8.0. $1/k_{cat}$ versus pH plot indicates a maximum at pH=6.5 (TABLE 1, Fig. 2). The effect of variation of ionic strength on rate of reaction was found to be non-significant. 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. By determining the rate constants at four different temperatures (25.0 to 40.0°C), the values of different thermodynamic parameters were found and these are given in **TABLE 2**.

FIG. 2. **Effect of pH on rate constatnt ($1/k_{cat}$(observed) and$1/k_{cat}$(calculated)) – pH plot) at [2,5-XYL]=8.0×10^{-5} mol dm^{-3}, [NaIO$_4$]=8.0 ×10^{-4} mol dm^{-3}, λ$_{max=}$535 nm, [Mn^{II}] =7.28×10^6 mol dm^{-3}, Acetone=5.0 % (V/V), Temp. =30.0 ± 0. 1°C.**
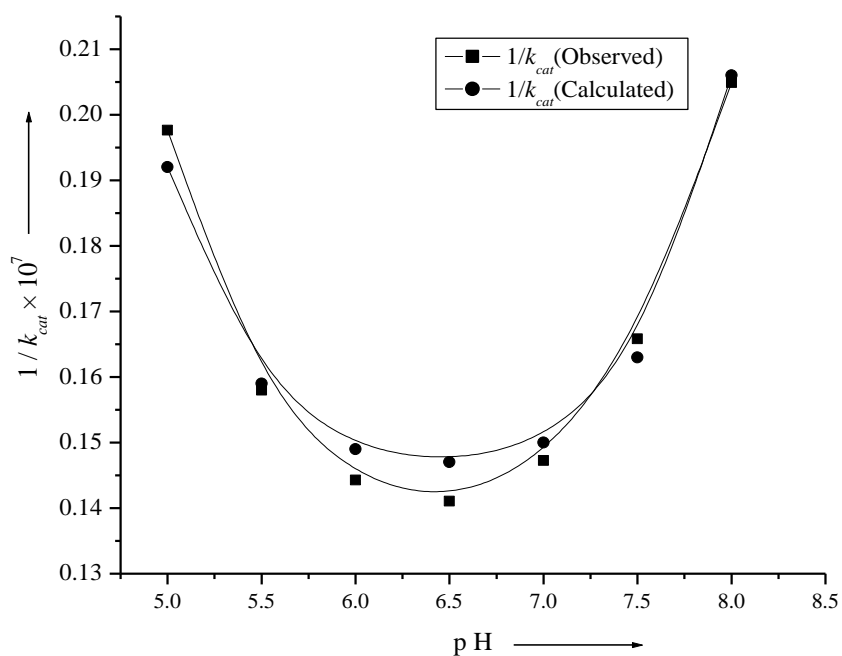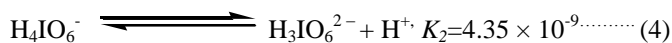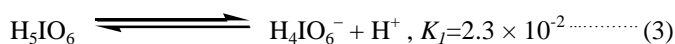

Discussion

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 2,5-XYL into a 2,5-dimethyl–1, 4–benzoquinone. Secondly, the kinetic order of one in periodate against the requirement of two periodate molecules for each 2,5-XYL 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 cannot 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.

TABLE 2. **Activation Parameters for Mn^{II} catalyzed periodate oxidation of 2, 5 -xylidine in acetone-water medium [2,5-XYL]=8.0 ×10^{-5} mol dm^{-3}, [NaIO$_4$]=8.0 ×10^{-4} mol dm^{-3}, [Mn^{II}]=7.28×10^{-6} mol dm^{-3}, Acetone=5.0% (V/V), pH=5.5, λ_{max}=535 nm.**

Temp. ($\pm 0.1°K$)	$k_{cat} \times 10^{-6}$ (dm^6 mol^{-2} s^{-1})	Temp. Coeff.	ΔE^* (kJ mol^{-1})	$A \times 10^{-6}$ (dm^3 mol^{-1} s^{-1})	$-\Delta S^{\#}$ (J mol^{-1} K^{-1})	$-\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta F^{\#}$ (kJ mol^{-1})
298	6.11	-----	-----	6.17	104.22	3.22	34.29
303	6.34	-----	5.31	6.39	104.38	3.18	34.80
308	6.56	1.07	5.54	6.62	104.52	3.13	35.32
313	6.82	1.08	6.23	6.88	104.63	3.09	35.84
Mean values		1.08	5.69	6.52	104.44	3.16	35.56

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

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

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \quad K_2 = 4.35 \times 10^{-9} \quad \text{..........(4)}$$
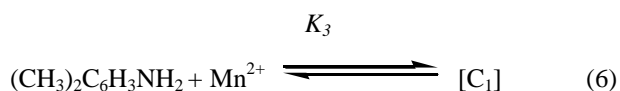
The value of K_1 indicates that in the pH range $5 - 8$ species H_5IO_6 shall be practically non-existent and hence only species $H_4IO_6^-$ and $H_3IO_6^{2-}$ need be considered for explaining observed pH - dependence. In aqueous solution, 2,5-XYL[36], undergo the following acid–base equilibrium with $K_b = 3.39 \times 10^{-10}$.
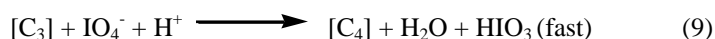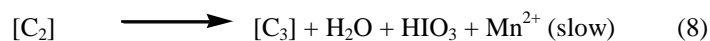
$$(CH_3)_2C_6H_3NH_2 + H_2O \rightleftharpoons (CH_3)_2C_6H_3N^+H_3 + OH^- \quad (5)$$
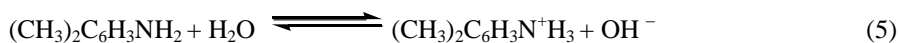
Since in the studied pH-range, both $(CH_3)_2C_6H_3NH_2$ and $(CH_3)_2C_6H_3N^+H_3$ exist, these species have been taken into account. The pH effect may be explained by assuming the $(CH_3)_2C_6H_3NH_2$ and $H_4IO_6^-$ to be reactive.

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

$$(CH_3)_2C_6H_3NH_2 + Mn^{2+} \xrightleftharpoons{K_3} [C_1] \quad (6)$$

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

k

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

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

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.

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

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, $[(2,5\text{-}XYL)Mn(H_4IO_6)]^+$, in which Mn acts as a conduit for electron transfer.

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

$$d[C_4]/dt = kK_3K_4[Mn^{II}][IO_4^-][2,5\text{-}XYL] \qquad (11)$$

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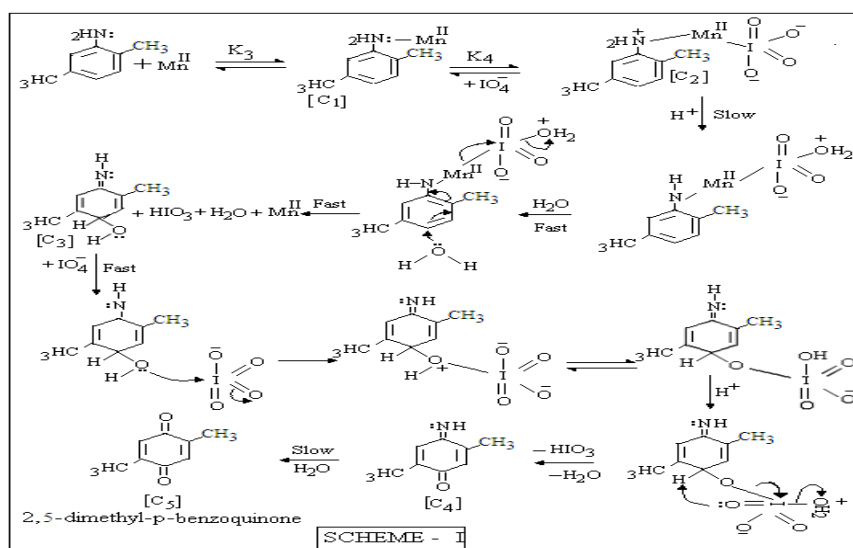
On substituting the values of concentrations of the reactive species $[2,5\text{-}XYL]$ and $[IO_4^-]$ in terms of equilibria (3-4) and (5), respectively, in eq. (2), the complete rate law including $[H^+]$ - dependence becomes:

$$d[C]/dt = kK_3K_4[Mn^{II}]\{([2,5\text{-}XYL][OH^-]/([OH^-]+K_b)\}\{([IO_4^-]_0[H^+]/(K_2+[H^+]))\} \qquad (12)$$

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

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[2,5\text{-}XYL][IO_4^-][H^+]/\{K_2K_w+(K_w+K_bK_2)[H^+]+K_b[H^+]^2\} \qquad (13)$$

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

$$k_{cat} = kK_3K_4K_w[H^+]/\{K_2K_w+(K_w+K_bK_2)[H^+]+K_b[H^+]^2\} \qquad (14)$$

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

$$1/k_{cat} = (K_2/kK_3K_4[H^+]) + \{(K_w+K_bK_2)/kK_3K_4K_w\} + K_b[H^+]/kK_3K_4K_w \qquad (15)$$

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 6.98×10^6 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. 5.0 - 8.0.

The nature of the rate law (15) shows that a plot of $1/k_{cat}$ versus $[H^+]$ shall pass through a minimum [37]. 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 (Fig. 3), we obtain,

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

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

$$[H^+]_{min}=3.58 \times 10^{-7} \text{ mol } dm^{-3}$$

FIG. 3. (**$1/k_{cats}$ vs. $[H^+]$ plot at $[2,5\text{-XYL}]=8.0\times10^{-5}$ mol dm^{-3}, $[NaIO_4]=8.0\times10^{-4}$ mol dm^{-3}, $\lambda_{max=}535$ nm, $[Mn^{II}]=7.28\times10^6$ mol dm^{-3}, Acetone=5.0 % (V/V),Temp. =30.0 ± 0. 1°C.**
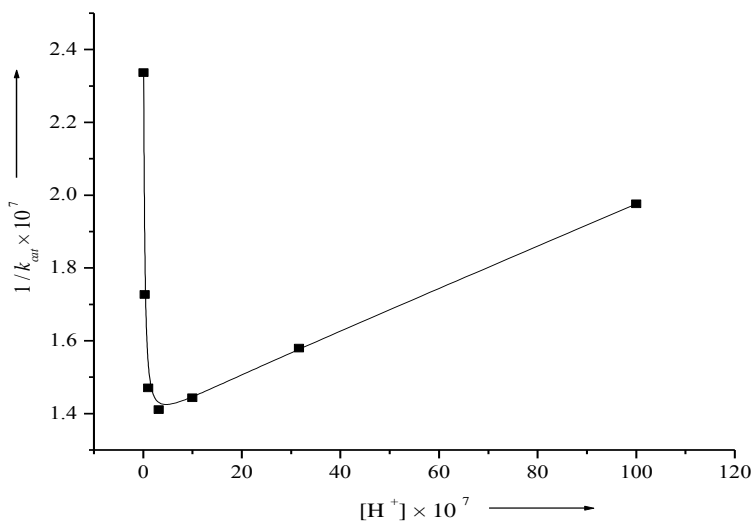
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