

Manganese(II) catalyzed oxidation of 2,4-xylydine by periodate – A kinetic-mechanistic study

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Abstract : The kinetics of the periodate oxidation of 2,4-xylydine (XYL) in acetone-water medium has been followed by monitoring the increase in the absorbance of reaction intermediate, C₄, and the main reaction product 3,5-dimethyl-1,2-benzoquinone. Results under pseudo-first order conditions, [IO₄⁻] >> [XYL], are in agreement with the rate law :

$$d[C]/dt = kK_3K_4K_w[Mn^{II}] [S] [IO_4^-]_0 [H^+] / \{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\}$$

where kK_3K_4 is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of H₄IO₆⁻ and K_b is base dissociation constant of 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 : $E_a = 4.9 \text{ kcal mol}^{-1}$, $A = 8.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $\Delta S^\ddagger = -47.2 \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta G^\ddagger = 18.9 \text{ kcal mol}^{-1}$ and $\Delta H^\ddagger = 4.3 \text{ kcal mol}^{-1}$.

Keywords : Kinetics, Mn^{II} catalysed, periodate oxidation, 2,4-xylydine, 3,5-dimethyl-1,2-benzoquinone.

Introduction

There are only few reports available on the kinetic studies for the Mn^{II} catalyzed non-Malapradian periodate oxidation of aromatic amines¹⁻⁴. Recent reports include the Mn^{II} catalyzed oxidation of neutral red⁵ by periodate and oxidation of acridine yellow by chloramine-T⁶. In continuation to our earlier studies on periodate oxidation⁷⁻¹⁰, the results of Mn^{II} catalysed oxidation of 2,4-xylydine (XYL) in acetone-water medium are presented in this communication.

Experimental

Reagents and chemicals :

Sodium metaperiodate (Loba Chemie), 2,4-xylydine (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 buffer¹¹, 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 NaIO₄ solution of known concentration to the reaction mixture containing the XYL, Mn^{II} and buffer and maintained at the desired temperature (± 0.1 °C).

The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV Pharmaspec-1700), at 474 nm, i.e. the λ_{max} of the orange 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.

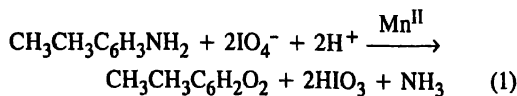
Product analysis :

Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially, the solution turned orange, thereafter yellow 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 orange residue that was dissolved in petroleum ether. The extracted portion was subjected to TLC (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 50 min as the time for development). Two components of red and yellow colours were separated in major and minor amounts, respectively. Yellow colored compound could not be collected in sufficient amount. Red colored compound was collected by preparatory TLC and recrystallized in diethyl ether to get solid red needles. It was characterized as 3,5-dimethyl-1,2-benzoquinone on the basis of positive test for quinone¹², m.p. 69 °C (literature value 68 °C¹³), UV spectrum in CHCl₃ giving absorption maxima at 255, 515 and 560 nm, which suggested the presence of quinonoid structure in the compound (literature values 260, 510 and 558 nm for 3,5-dimethyl-1,2-benzoquinone¹⁴). The IR spectrum of this compound (in KBr) showed the presence of bands at 2738 cm⁻¹ (s) (due to ring C-H stretch), 1660 cm⁻¹ (s) (indicating the presence of C=O on benzoquinone pattern with the possibility that the position of this band is lowered due to +I effect of methyl group¹⁵), 3250 cm⁻¹ (s) (may be due to overtones of C=O stretch as the frequency is about twice that of C=O stretch) and 2713 cm⁻¹ (s) (due to isolated C-H stretching). Further, the bands at 1386 cm⁻¹ (s), 1354 cm⁻¹ (s) may be due to C=C ring stretch. The bands at 1212 cm⁻¹ (m) to 1090 cm⁻¹ (m) may be due to the in-plane C-H bending and at 702 cm⁻¹ (s) (m) and 668 cm⁻¹ (m) (due to out-of-plane C=C bending mode). The observed values are in good agreement with those reported/expected for 3,5-dimethyl-1,2-benzoquinone.

Stoichiometry :

Stoichiometry of the reaction was determined by allowing a known excess of NaIO₄ to react with substrate. After completion of the reaction, the precipitated product was filtered out and in the filtrate unconsumed NaIO₄ was determined iodimetrically. The results indicated the stoichiometry to be 1 mol XYL : 2 moles periodate for the reaction as in eq. (1).



Results

Preliminary observations :

On mixing the reactants, the solution becomes orange which later changes in to yellow. 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 orange solution showed the λ_{max} of the intermedi-

ate, C₄, to be 474 nm (Fig. 1). The UV-Vis spectra of IO₄⁻, XYL and Mn^{II} indicated the to show no absorption in visible region. Hence, for following the kinetics the absorbance changes were recorded at 474 nm at which only the intermediate C₄ absorbs.

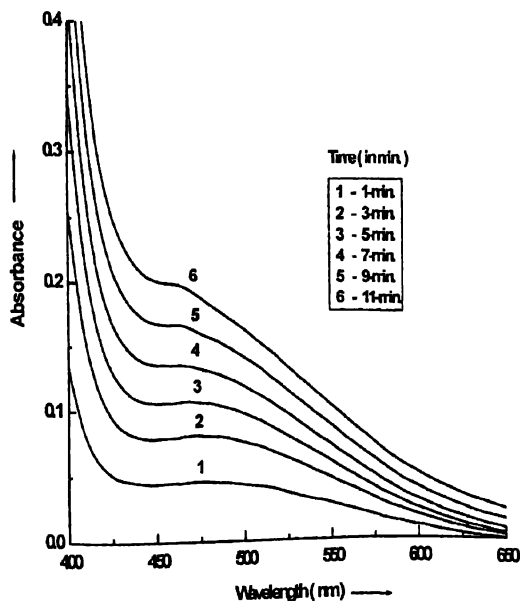


Fig. 1. Rapid UV-Vis scan of reaction solution at different time at pH = 7.0, acetone = 10% (v/v) and temp. = 30 °C, [NaIO₄] = 1.4 × 10⁻², [XYL] = 1.0 × 10⁻³ and [Mn^{II}] = 2.0 × 10⁻⁷ mol dm⁻³.

Rate law :

The kinetics was studied under pseudo 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).

$$d[C]/dt = k_{\text{cat}} [S] [\text{IO}_4^-]_0 [\text{Mn}^{\text{II}}] \quad (2)$$

where $k_{\text{obs}} = k_{\text{cat}} [\text{IO}_4^-]_0 [\text{Mn}^{\text{II}}]$ and k_{cat} is the rate constant for Mn^{II} catalysed pathway. [IO₄⁻]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}], [IO₄⁻]₀ and [S] are seen to be in good agreement and consistent with the rate law (2) (Table 1, Fig. 2).

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

The effect of pH was examined in the range 4.5–9.0.

Table I. Values of k_{obs} and k_{cat} at 30 ± 0.1 °C

[NaIO ₄] (M)	[XYL] (M)	10 ⁷ [Mn ^{II}] (mol dm ⁻³)	Acetone (% v/v)	10 ³ [NaCl] (mol dm ⁻³)	pH	10 ³ k_{obs} (s ⁻¹)	10 ⁷ k_{cat} (dm ⁶ mol ⁻² s ⁻¹)
0.020	0.0005	2.0	10	-	7.0	4.4	0.11
0.020	0.0010	2.0	10	-	7.0	4.8	0.12
0.020	0.0015	2.0	10	-	7.0	5.3	0.14
0.020	0.0020	2.0	10	-	7.0	5.6	0.14
0.010	0.001	2.0	10	-	7.0	2.3	0.14
0.012	0.001	2.0	10	-	7.0	3.2	0.14
0.014	0.001	2.0	10	-	7.0	3.7	0.14
0.016	0.001	2.0	10	-	7.0	4.0	0.13
0.018	0.001	2.0	10	-	7.0	4.5	0.13
0.020	0.001	2.0	10	-	7.0	4.8	0.12
0.014	0.001	1.0	10	-	7.0	1.7	0.12
0.014	0.001	1.5	10	-	7.0	2.7	0.13
0.014	0.001	2.0	10	-	7.0	3.7	0.14
0.014	0.001	2.5	10	-	7.0	4.5	0.13
0.014	0.001	3.0	10	-	7.0	5.3	0.13
0.014	0.001	3.5	10	-	7.0	6.3	0.13
0.014	0.001	2.0	10	-	4.5	2.2	0.08
0.014	0.001	2.0	10	-	5.0	2.4	0.09
0.014	0.001	2.0	10	-	5.5	2.8	0.10
0.014	0.001	2.0	10	-	6.0	3.2	0.12
0.014	0.001	2.0	10	-	6.5	4.8	0.17
0.014	0.001	2.0	10	-	7.0	3.7	0.14
0.014	0.001	2.0	10	-	7.5	3.6	0.13
0.014	0.001	2.0	10	-	8.0	3.0	0.11
0.014	0.001	2.0	10	-	8.5	2.8	0.10
0.014	0.001	2.0	10	-	9.0	2.7	0.10
0.014	0.001	2.0	10	1.0	7.0	2.7	0.095
0.014	0.001	2.0	10	2.0	7.0	2.4	0.085
0.014	0.001	2.0	10	3.0	7.0	2.2	0.080
0.014	0.001	2.0	10	4.0	7.0	2.0	0.070
0.014	0.001	2.0	2.5	-	7.0	4.6	0.17
0.014	0.001	2.0	5.0	-	7.0	4.3	0.16
0.014	0.001	2.0	7.5	-	7.0	4.0	0.15
0.014	0.001	2.0	10.0	-	7.0	3.7	0.14

$1/k_{\text{cat}}$ versus $[\text{H}^+]$ plot indicates a minimum at $\text{pH} = 6.5$ (Table 1, Fig. 3). An increase in ionic strength, I , with the help of sodium chloride $\{(1-4) \times 10^{-3} \text{ mol dm}^{-3}\}$ and an increase in the acetone (2.5–10%) led to a slight decrease in the rate (~20%). Free radical scavengers, viz. acrylamide and allyl alcohol had no effect on the reaction rate.

By determining the rate constants at four different temperatures (30.0 to 45.0 °C), the values of different

thermodynamic parameters were found and these are given in Table 2.

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

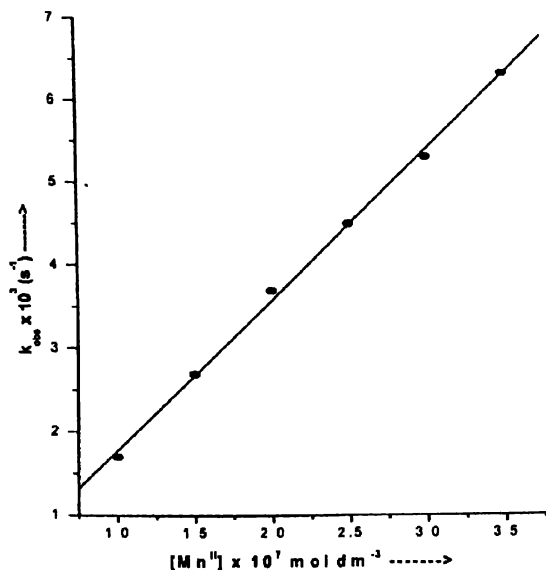


Fig. 2. Plot between k_{obs} and $[\text{Mn}^{\text{II}}]$ for the Mn^{II} catalysed periodate oxidation of 2,4-xylydine in acetone-water medium at $[\text{XYL}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{NaIO}_4] = 1.4 \times 10^{-2} \text{ mol dm}^{-3}$, acetone = 10% (v/v), pH = 7.0 and temp. = 30 °C.

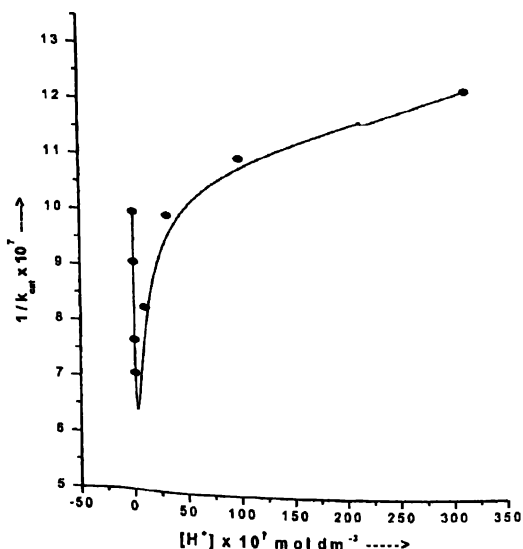
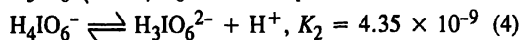
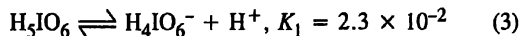


Fig. 3. Effect of $[\text{H}^+]$ on the rate of Mn^{II} catalysed periodate oxidation of 2,4-xylydine in acetone-water medium at acetone = 10% (v/v), pH = 7.0, temp. = 30 °C, $[\text{XYL}] = 1.0 \times 10^{-3}$, $[\text{NaIO}_4] = 1.4 \times 10^{-2}$ and $[\text{Mn}^{\text{II}}] = 2.0 \times 10^{-7} \text{ mol dm}^{-3}$.

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 XYL into benzoquinone. Secondly, the kinetic order of one in periodate against the requirement of two periodate molecules for each xylydine 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, $1/k_{\text{cat}}$ versus $[\text{H}^+]$ 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.

Construction of a mechanism requires discussion on the speciation of XYL and periodate. In aqueous solutions, periodate exists in the three forms governed by the equilibria (3-4).



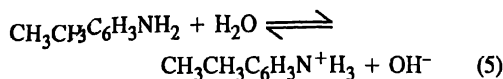
The value of K_1 indicates that in the pH range 4.5-9

Table 2. Activation parameters for Mn^{II} catalyzed periodate oxidation of 2,4-xylydine in acetone-water medium

$[\text{XYL}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{NaIO}_4] = 1.4 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] = 2.0 \times 10^{-7} \text{ mol dm}^{-3}$, acetone = 10.0% (v/v), pH = 7.0

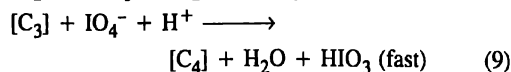
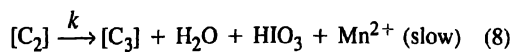
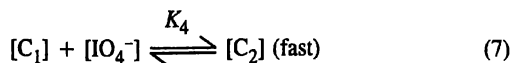
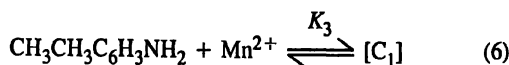
Temp. (°C)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^{-7} k_{\text{cat}}$ (dm ⁶ mol ⁻² s ⁻¹)	E_a (kcal mol ⁻¹)	A (dm ³ mol ⁻¹ s ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)
30	3.7	0.14	4.9	8.7×10^3	-47.2	18.9	4.3
35	4.2	0.16					
40	4.9	0.18					
45	5.5	0.20					

species H_5IO_6 shall be practically non-existent and hence only species $H_4IO_6^-$ and IO_4^- need to be considered for explaining observed pH-dependence. In aqueous solution, 2,4-xylidine, undergoes the following acid-base equilibrium with $K_b = 7.76 \times 10^{-10}$.

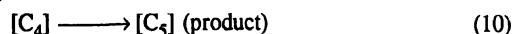


Since in the studied pH-range, both $CH_3CH_3C_6H_3NH_2$ and $CH_3CH_3C_6H_3N^+H_3$ exist, these species have been taken into account. The pH effect may be explained by assuming the $CH_3CH_3C_6H_3NH_2$ and $H_4IO_6^-$ to be reactive.

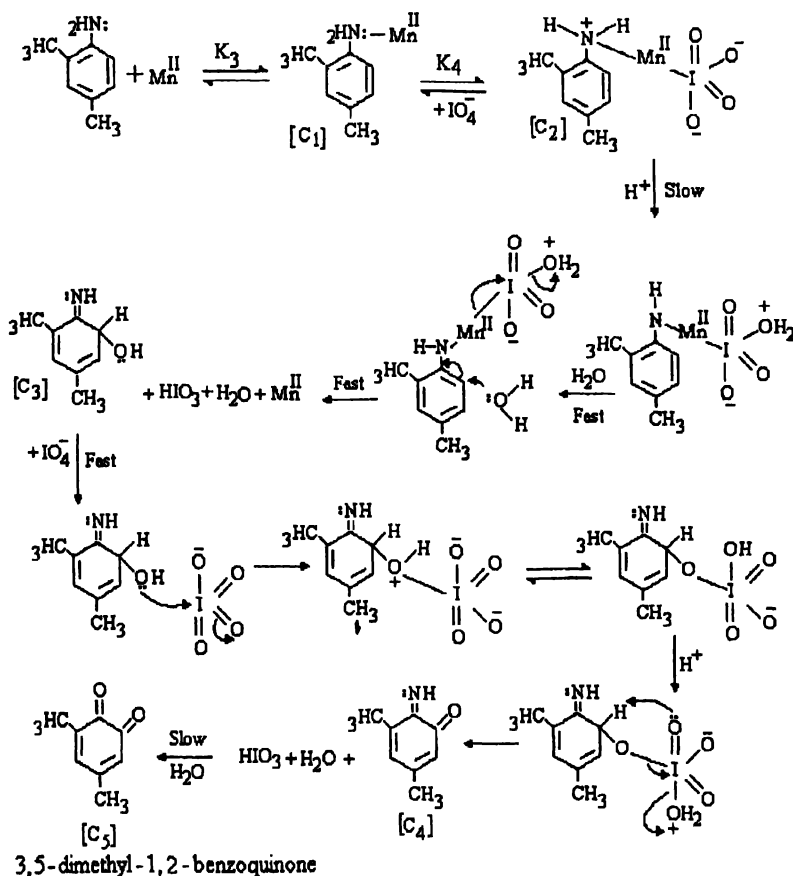
Based on the observed kinetics rate law (eq. (2)) and pH-dependence, the following mechanism is proposed.



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 .



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



Scheme 1

of Mn^{2+} appears to be due to the formation of a ternary complex, $[(XYL)Mn(H_4IO_6)]^+$, in which Mn acts as a conduit for electron transfer.

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

$$d[C_4]/dt = kK_3K_4[Mn^{II}][IO_4^-][CH_3CH_2C_6H_3NH_2] \quad (11)$$

On substituting the values of concentrations of the reactive species $[CH_3CH_2C_6H_3NH_2]$ and $[IO_4^-]$ in terms of equilibria (3-4) and (5), respectively, in eq. (2), the complete rate law including $[H^+]$ -dependence becomes :

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

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).

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[S][IO_4^-]_0 [H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\} \quad (13)$$

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

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

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

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

The nature of the rate law (15) shows that a plot of $1/k_{cat}$ versus $[H^+]$ shall pass through a minimum as discussed in a review by Gupta and Gupta¹⁷. 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 $d[1/k_{cat}]/d[H^+] = 0$ for obtaining hydrogen ion concentration at which the $1/k_{cat}$ vs $[H^+]$ profile will pass through minimum, we obtain,

$$[H^+]_{min} = (K_2K_w/K_b)^{1/2} \quad (16)$$

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

$$[H^+]_{min} = 2.4 \times 10^{-7} \text{ mol dm}^{-3}$$

It is noteworthy that the calculated value of $[H^+]_{min}$ is in

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

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