MnII CATALYZED PERIODATE OXIDATION OF N, N-DIETHYL-*m*-TOLUIDINE : A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

One mol of N, N-diethyl-*m*-toluidine (DET) reacts with two moles of periodate during the initial part of reaction. The main reaction product is 4-methyl-1, 2-benzoquinone. The kinetics of the MnII catalyzed periodate oxidation of DET in acetone-water medium has been followed by monitoring the increase in the absorbance of reaction intermediate. The reaction is first order in reactants and catalyst each. A decrease in dielectric constant of the medium results in decrease in the rate of reaction. Free radical scavengers do not affect the reaction rate. The values of thermodynamic parameters are: ΔE = 24.85 kJ mol^{-1}, A = 1.25 × 10^{10} dm^3 mol^{-1} s^{-1}; $\Delta S^{\#}$ = – 142.97 J mol^{-1} K^{-1}, $\Delta G^{\#}$ = 67.53 kJ mol^{-1} and $\Delta H^{\#}$ = 22.41 kJ mol^{-1}. Under pseudo first order conditions, [IO$_4^-$] >> [DET], the rate law is given by –

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

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$_4$IO$_6^-$ and K_b is base dissociation constant of DET. In agreement with the rate law the $1/k_{cat}$ versus [H$^+$] plot passes through the minimum. Detailed molecular mechanism is given.

Key words: Kinetics, MnII, Periodate, N, N-diethyl-*m*-toluidine, methyl-1,4-benzoquinone.

INTRODUCTION

Toxicity of aromatic amines is well known[1]. There is always a need of studying their oxidation and other reactions so that newer methods can be developed for detection and treatment of these chemicals. There are reports available on the kinetic-mechanistic studies

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of the uncatalysed[2-10] or catalysed[11-15] periodate oxidation of anilines. Present communication deals with the results of kinetic-mechanistic studies made on Mn^{II} catalyzed periodate oxidation of N,N-diethyl-m-toluidine (DET).

EXPERIMENTAL

All 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. Sodium metaperiodate (Loba Chemie), DET (Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) were used.

On mixing the reactants, the solution becomes a violet colour, which finally changed in to brownish red 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 UV-VIS spectra of IO_4^-, DET and Mn^{II} indicated these to show no absorption in visible region. Hence, for following the kinetics the absorbance changes were recorded on Shimadzu double beam spectrophotometer (UV Pharmaspec-1700) having high precision thermostatic control, at 536 nm (at which only the intermediate C_4 absorbs). Absorption maxima was not found to change with change in time under experimental conditions as shown by the rapid scan of the solution (Fig. 1).
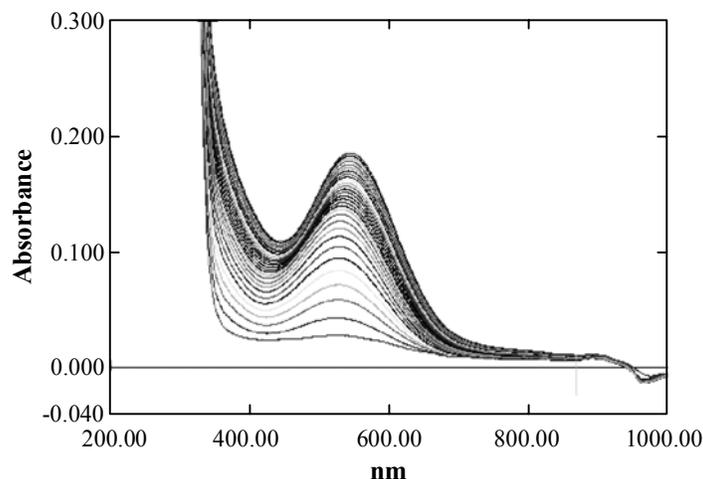
Fig. 1: UV-VIS rapid scan at time interval of 60 seconds at $[NaIO_4] = 8 \times 10^{-3}$ mol dm^{-3}, $[DMT] = 5.0 \times 10^{-4}$ mol dm^{-3}, pH = 7.0, $[Mn^{II}] = 2.912 \times 10^{-7}$ mol dm^{-3}, Acetone = 5.0% (v/v), Temp. = 35.0 ± 0.1ºC

Reaction mixture containing oxidant in excess was prepared, shaken and set aside for 30 hours. It developed a violet colour initially, which finally changed in to brownish red colour followed by precipitation. 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 dissolved in petroleum ether and found to be TLC single. The remaining part of the filtrate might be containing other products of this reaction that could not be separated and identified. The yellow component was collected by preparatory TLC, recrystallised in ethyl alcohol and characterized as methyl-1, 4-benzoquinone on the basis of positive test for quinone[17], melting point 68°C (literature value 69°C[18]), and UV spectrum (in ethyl alcohol giving absorption maxima at 250 (strong), 315, 430 and 445 nm (literature values 246 (strong), 312, 429 and 438 nm for methyl-1,4-benzoquinone[19]).

The IR spectrum of this compound (in KBr) showed the presence of bands at 1632 cm^{-1} (s) (indicating the presence of C=O on benzoquinone pattern with the possibility that the position of this band got lowered due to + I effect of methyl group[20]), 3280 cm^{-1} (s) (may be due to overtones of C=O stretch as the frequency is about twice that of C=O stretch), 2700 cm^{-1} (s) (due to isolated C–H stretching[21]). Further, the bands at 1514 cm^{-1} (s), 1457 cm^{-1} (s) and 1390 cm^{-1} (may be due to due to C=C ring stretch), 1250 cm^{-1} (m) and 11135 cm^{-1} (m) (may be due to in plane C-H bending) and the bands at at 665 cm^{-1} (m) and 518 cm^{-1} (m) (due to out of plane C=C bending mode). The H-nmr spectrum of this compound in CDCl$_3$ showed peaks at δ = 7.091, D, (2H); δ = 6.658, S, (1H); and δ = 2.156, S, (3H). A singlet at 2.156 may be due to –CH$_3$ group attached to the ring. The other signal in spectrum at δ = 6.658 and δ = 7.091 may be due to three protons of the ring in methyl-1, 4-benzoquinone.

RESULTS AND DISCUSSION

Stoichiometry

Known excess of NaIO$_4$ was allowed to react with substrate and unreacted periodate was estimated iodimetrically. log (a-x) versus time plot (where a-x is the concentration of unreacted periodate) followed the pseudo first order behaviour upto a point after which the inflexion was obtained. It was taken as the point corresponding to the completion of first stage of reaction for which the kinetics was studied. It was found that 1 mol of DET consumes 2 moles of periodate for initial stage of the reaction as given below :

$$CH_3C_6H_4N(C_2H_5)_2 + 2IO_4^- + 2H^+ + 2H_2O \xrightarrow{Mn^{II}} CH_3C_6H_3O_2 + 2HIO_3 +$$
$$NH_3 + 2C_2H_5OH \qquad ...(1)$$
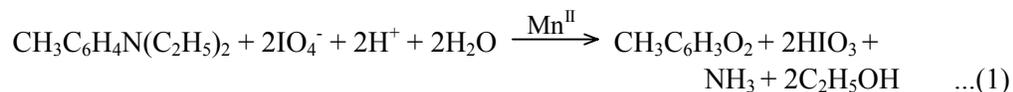
Another molecule of periodate may react in later stages of the reaction to give other reaction products.

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).

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

where $k_{obs} = k_{cat} [IO_4^-]_0 [Mn^{II}]$ and k_{cat} is the rate constant for Mn^{II} catalysed pathway. $[IO_4^-]_0$ and $[DET]_0$ represent the initial concentration of periodate and substrate. In the absence of Mn^{II}, no significant reaction occurred. The values of k_{cat} obtained for different $[Mn^{II}]$, $[IO_4^-]_0$ and $[DET]$ are seen to be in good agreement and consistent with the rate law Eq. (2).

Other factors influencing the rate of reaction

As the reacting species are differently protonated, it was considered necessary to study the effect of pH on the reaction rate and hence, the reaction was studied in the pH range 5.5 to 9.0. $1/k_{cat}$ vs pH plot indicates a minimum at pH = 7.5 (Fig. 2). Since the substrate is soluble only in acetone-water binary mixture, the kinetics had been studied in 5.0% (v/v) acetone-water mixtures. Because of this, it became necessary to examine the effect of varying proportion of acetone in binary reaction mixtures on reaction rate. An increase in the acetone (2.5-10%) i.e. a decrease in dielectric constant (D) of the medium, led to a decrease in rate. Graphical plot between k_{cat} and 1/D, was found to be straight line with negative slope. Further, Free radical scavengers, viz., acrylamide and allyl alcohol had no effect on the reaction rate, indicating thereby, no involvement of free radicals in the reaction.

The rate constants were determined at four different temperatures (35.0 to 50.0°C) as indicated earlier, 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 and the mean values are $\Delta E = 24.85$ kJ mol^{-1}, $A = 1.25 \times 10^{10}$ dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -142.97$ J mol^{-1} K^{-1}, $\Delta G^{\#} = 67.53$ kJ mol^{-1} and $\Delta H^{\#} = 22.41$ 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. Statistical analysis confirmed that the standard errors of $\Delta H^{\#}$ and $\Delta S^{\#}$ correlate and lead to the centre of temperature range used, as given by the relation[22]: $T_{av} = \sigma (\Delta H^{\#})/ \sigma (\Delta S^{\#})$.
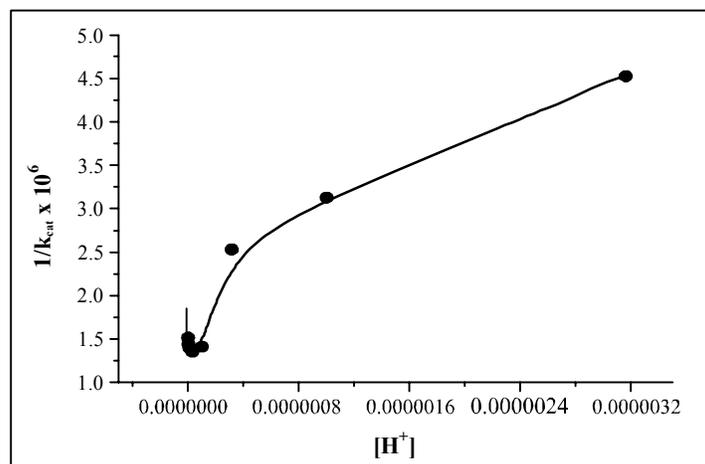
Fig. 2: $1/k_{cat}$ vs [H$^+$] plot at [NaIO$_4$] = 8 × 10^{-3} mol dm^{-3}, [DMT] = 5.0 × 10^{-4} mol dm^{-3}, pH = 7.0, [Mn^{II}] = 2.912 × 10^{-7} mol dm^{-3}, Acetone = 5.0 % (v/v), Temp. = 35.0 ± 0.1ºC, λ_{max} = 536 nm

The 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 DET into benzoquinone.

Further, the kinetic order of one in periodate against the requirement of two periodate molecules for each DET 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. Next important feature is the $1/k_{cat}$ versus pH plot [Fig. 2], which indicates the presence of at least three differently reactive species of reactant (which is periodate in this system) in the pH region chosen for study[23]. Finally, the observation that free radical scavengers have no effect on reaction rate rules out the involvement of free radicals in the oxidation mechanism. The high negative value of entropy of activation supports the involvement of solvation effects in this reaction as given in the proposed molecular mechanism (**Scheme 1**).
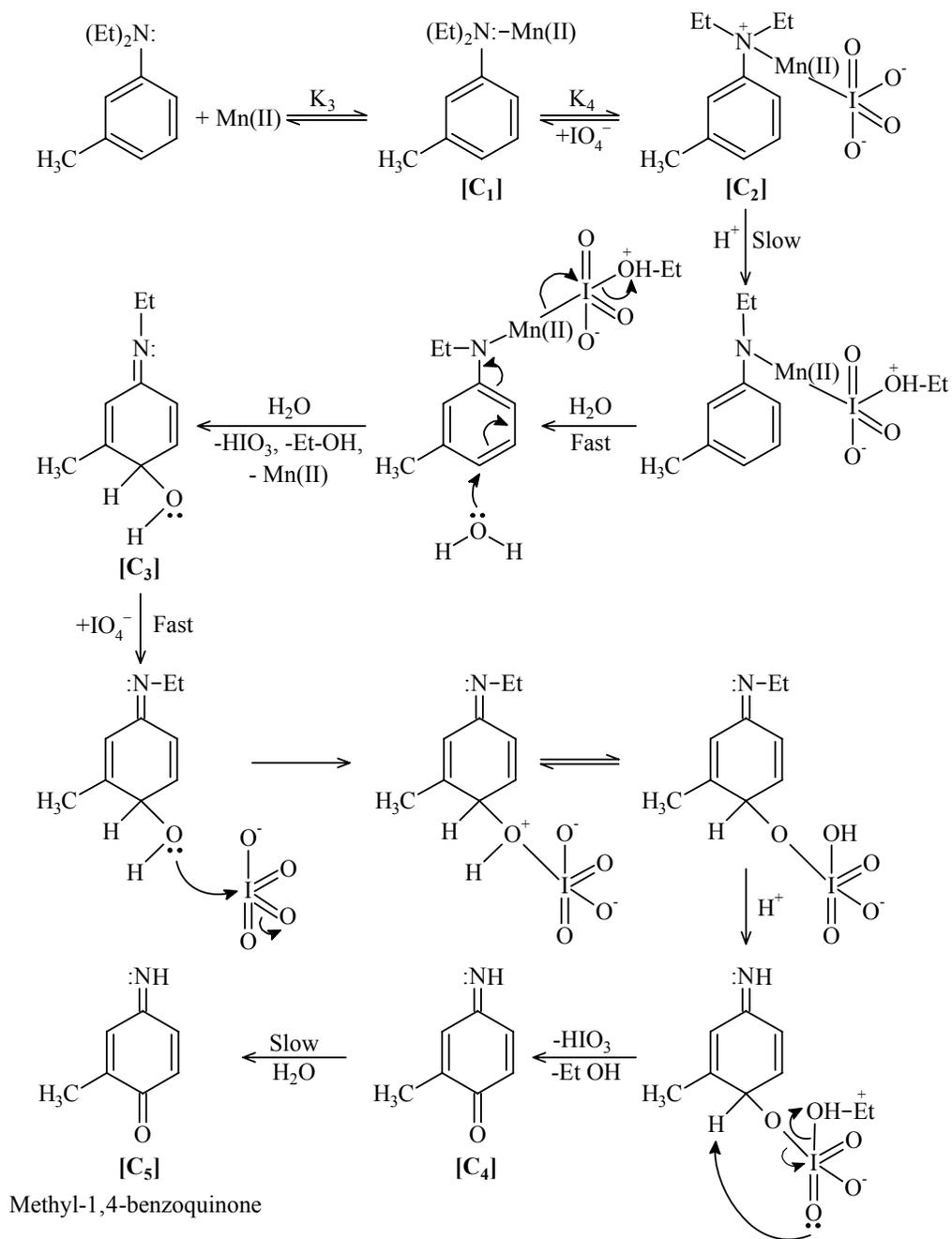
Scheme 1

While proposing a suitable mechanism for the reaction under study, the speciation of DET and periodate should be considered. In aqueous solutions, periodate is transformed into

the three forms in water including orthoperiodic acid[24] with equilibria and dissociation constants[25,26] given below:

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

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \; K_2 = 4.35 \times 10^{-9} \qquad \qquad ...(4)$$
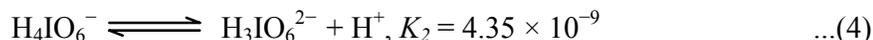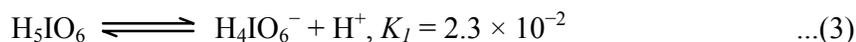
The value of K_1 indicates that in the pH range 4.5-9.5 species H_5IO_6 shall be practically non-existent and hence only species $H_4IO_6^-$ and $H_3IO_6^{2-}$ need be considered for explaining observed pH - dependence. Based on this premise, the equilibrium or free concentration of $H_4IO_6^-$, $[H_4IO_6^-]$ shall be related to the total periodate concentration $[IO_4^-]_0$ by Eq. (5)

$$[H_4IO_6^-] = [IO_4^-]_0 \, [H^+] / ([H^+] + K_2) \qquad \qquad ...(5)$$

In the reaction mechanism proposed later, species $H_4IO_6^-$ has been considered reactive.

In aqueous solution, DET, undergoes the following acid-base equilibrium with $K_b{}^{27} = 1.32 \times 10^{-7}$.

$$CH_3C_6H_4N(C_2H_5)_2 + H_2O \rightleftharpoons CH_3C_6H_4N^+H \, (C_2H_5)_2 + OH^- \qquad \qquad ...(6)$$

Since in the studied pH-range, both $CH_3C_6H_4N \, (C_2H_5)_2$ and $CH_3C_6H_4N^+H(C_2H_5)_2$ exist, these species have been taken into account. From equilibrium (6), the equilibrium or free concentration of amine, [DET], is given by Eq. (7).

$$[DET] = [DET]_0 \, [OH^-] / \{[OH^-] + K_b\} \qquad \qquad ...(7)$$

Where $[DET]_0$ is the total concentration of $CH_3C_6H_4N(C_2H_5)_2$.

To explain the observed pH – dependence, it is necessary to assume DMA and $H_4IO_6^-$ to be reactive speceies. On this basis to explain the observed kinetics, rate law (Eq. 2), and pH- dependence, the following mechanism is proposed.

$$CH_3 \, C_6H_4N(C_2H_5)_2 + Mn^{2+} \; \xrightleftharpoons{K_3} \; [C_1] \qquad \qquad ...(8)$$

$$[C_1] + [H_4IO_6^-] \; \xrightleftharpoons{K_4} \; [C_2] \text{ (fast)} \qquad \qquad ...(9)$$

$$[C_2] + H^+ + H_2O \; \xrightarrow{k} \; [C_3] + C_2H_5OH + HIO_3 + Mn^{2+} \text{ (slow)} \qquad ...(10)$$

$$[C_3] + H_4IO_6^- + H^+ \; \longrightarrow \; [C_4] + C_2H_5OH + HIO_3 \text{ (fast)} \qquad \qquad ...(11)$$
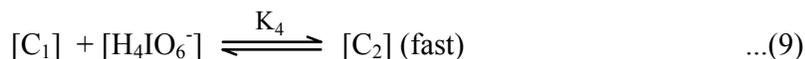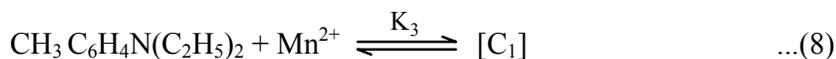
In steps (6-9), $[C_1]$, $[C_2]$, $[C_3]$ and $[C_4]$ are intermediates, out of which $[C_4]$ appears to undergo very slow reorganization/hydrolysis to yield the reaction product, C_5.

$$[C_4] \longrightarrow [C_5] \text{ (product)} \qquad \qquad …(12)$$

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, $[(DET)Mn(H_4IO_6)]^+$, in which Mn helps in electron transfer.

The proposed mechanism (8-11) leads to the rate law (13).

$$d[C_4]/dt = kK_3K_4 \, [Mn^{II}][\, H_4IO_6^- \,] \, [DET] \qquad \qquad …(13)$$

On substituting the values of concentrations of the reactive species [DET] and $[H_4IO_6^-]$ from Eq. (5) and (7) in eq. (13), and taking $H_4IO_6^-$ as IO_4^- for simplicity[26], the complete rate law including $[H^+]$ - dependence becomes:

$$d[C]/dt = kK_3K_4[Mn^{II}]\{([DET]_0 \, [OH^-]/([OH^-] + K_b)\} \, \{([IO_4^-]_0 \, [H^+]/(K_2 + [H^+])\} \quad …(14)$$

On replacing the term, $[OH^-][H^+]$, by K_w in numerator, and $[OH^-]$ by $K_w/ [H^+]$ in denominator, and on rearranging, the Eq.(14) becomes Eq. (15).

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[DET]_0[IO_4^-]_0 \, [H^+]/\{K_2 \, K_w +(K_w + K_b K_2)[H^+] + K_b[H^+]^2\} \quad …(15)$$

On comparing Eqs. (2) and (15), we get

$$k_{cat} = k \, K_3K_4 K_w[H^+]/\{K_2 \, K_w + (\, K_w + K_b K_2 \,) \, [H^+] + K_b \, [H^+]^2\} \qquad …(16)$$

Equation (16) on rearranging becomes Eq. (17).

$$1/k_{cat} = (K_2 / \, kK_3K_4 \, [H^+])+\{(K_w+ K_b K_2) / \, kK_3K_4 K_w\} + K_b[H^+] / \, kK_3K_4 K_w \qquad …(17)$$

The k_{cat} and pH data were fitted to Eqn. (17). All experimental k_{cat} values are in good agreement with the calculated values (Table 2), which provides support to the Eq. (17). Further, on differentiating $1/k_{cat}$ with respect to $[H^+]$ in, 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 $[H^+]$ or pH to pass through a minimum. This is in line with the experimental observation (Fig. 2). Furthermore, 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,

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

Table 1: Kinetic data at 35.0 ± 0.1°C

[NaIO$_4$] × 10^3 mol dm^{-3}	[DET] × 10^4 mol dm^{-3}	Mn^{II} × 10^7 mol dm^{-3}	Acetone % (v/v)	pH	k_{obs} × 10^3 s^{-1}	k_{cat} × 10^{-7} dm^6 mol^{-2}s^{-1}
8.0	5.0	2.912	5.0	7.0	1.65	0.0708
8.0	6.0	2.912	5.0	7.0	1.67	0.0802
8.0	7.0	2.912	5.0	7.0	2.07	0.0889
8.0	8.0	2.912	5.0	7.0	2.23	0.0957
8.0	9.0	2.912	5.0	7.0	2.36	0.1013
8.0	10.0	2.912	5.0	7.0	2.49	0.1069
3.0	5.0	2.912	5.0	7.0	0.67	0.0765
4.0	5.0	2.912	5.0	7.0	0.88	0.0758
5.0	5.0	2.912	5.0	7.0	1.08	0.0743
6.0	5.0	2.912	5.0	7.0	1.26	0.0726
7.0	5.0	2.912	5.0	7.0	1.51	0.0738
8.0	5.0	2.912	5.0	7.0	1.65	0.0708
8.0	5.0	2.912	5.0	7.0	1.65	0.0708
8.0	5.0	3.640	5.0	7.0	2.10	0.0721
8.0	5.0	4.368	5.0	7.0	2.46	0.0704
8.0	5.0	5.096	5.0	7.0	2.86	0.0702
8.0	5.0	5.824	5.0	7.0	3.15	0.0676
8.0	5.0	2.912	5.0	5.5	0.51	0.0221
8.0	5.0	2.912	5.0	6.0	0.75	0.0320
8.0	5.0	2.912	5.0	6.5	0.92	0.0395
8.0	5.0	2.912	5.0	7.0	1.65	0.0708
8.0	5.0	2.912	5.0	7.5	1.72	0.0738
8.0	5.0	2.912	5.0	8.0	1.67	0.0715
8.0	5.0	2.912	5.0	8.5	1.61	0.0692
8.0	5.0	2.912	5.0	9.0	1.54	0.0659
8.0	5.0	2.912	2.5	7.0	1.73	0.0743
8.0	5.0	2.912	5.0	7.0	1.65	0.0708
8.0	5.0	2.912	7.5	7.0	1.57	0.0674
8.0	5.0	2.912	10.0	7.0	1.49	0.0640

Table 2: Observed and calculated values of rate constants

pH	$k_{cat} \times 10^{-5}$ (observed)	$k_{cat} \times 10^{-5}$ (calculated)
5.5	2.21	2.15
6.0	3.20	3.33
6.5	3.95	4.10
7.0	7.08	7.14
7.5	7.38	7.45
8.0	7.15	7.05
8.5	6.92	7.00
9.0	6.59	6.74

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

$$[H^+]_{min} = 1.81 \times 10^{-8} \text{ mol dm}^{-3}$$

It is noteworthy and goes in favour of the derived rate law that the calculated value of $[H^+]_{min}$ is in good agreement with the experimental value of $[H^+]_{min}$ of 3.16×10^{-8} mol dm^{-3} obtained from $1/k_{cat}$ versus $[H^+]$ plot (Fig. 2).

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