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## Mn<sup>II</sup> Catalyzed Periodate oxidation of N, N-dimethyl-*p*-toluidine – A Kinetic and Mechanistic Study.

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### ABSTRACT

One mol of N,N-dimethyl-*p*-toluidine(DMT) 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 Mn<sup>II</sup> catalyzed periodate oxidation of DMT 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:  $\Delta E = 6.58 \text{ kJ mol}^{-1}$ ,  $A = 11.15 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ;  $\Delta S^\ddagger = -197.54 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger = 66.17 \text{ kJ mol}^{-1}$  and  $\Delta H^\ddagger = 3.84 \text{ kJ mol}^{-1}$ . Under pseudo first order conditions,  $[\text{IO}_4^-] \gg [\text{DMT}]$ , the rate law is given by:

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

Where  $kK_3K_4$  is the empirical composite rate constant,  $K_w$  is ionic product of water,  $K_2$  is acid dissociation constant of  $\text{H}_4\text{IO}_6^-$  and  $K_b$  is base dissociation constant of DMT. In agreement with the rate law the  $1/k_{cat}$  versus  $[\text{H}^+]$  plot passes through the minimum. Detailed molecular mechanism is given.

**Keywords:** N,N-dimethyl-*p*-toluidine, Mn<sup>II</sup>, periodate, 4-methyl-1,2-benzoquinone, Kinetics,

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## INTRODUCTION

Aromatic amines, many of which are enlisted as carcinogenic/ toxic due to their genotoxic or cytotoxic properties [1,2]. These are used as intermediates in the manufacture of plastics, dyes, drugs, explosives, rubber, epoxy polymers, azo dyes, aromatic polyurethane products and pesticides [3]. Therefore, studying their new reactions is always of interest for a chemist and biologist. In continuation to our reports on uncatalysed [4-8] and  $Mn^{II}$  catalysed periodate oxidation of some aromatic amines [9-15]. The results of kinetic-mechanistic studies made on  $Mn^{II}$  catalyzed periodate oxidation of N,N-dimethyl-p-toluidine (DMT) in acetone-water medium are presented and discussed in this paper.

## MATERIALS AND METHODS

All main chemicals line sodium metaperiodate (Loba Chemie), DMT(Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and other required 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<sup>16</sup> 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.

### Preliminary observations and study of kinetics

The UV-VIS spectra of  $IO_4^-$ , DMT 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 565 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).

### Product Analysis

Reaction mixture containing oxidant in excess was prepared, shaken and set aside for 30 hours. On mixing the reactants, the solution becomes violet which later changes in to dark-red. On keeping for long time, it finally shows precipitation and gives the product. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. 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 orange 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 = Chloroform: Acetone: Benzene (4: 6: 4), Time for development = 50 minutes. Two components of red and yellow colour were separated in major and minor amounts respectively with  $R_f$  values being 0.93 and 0.50 respectively. These  $R_f$  values were calculated by taking average of three parallel runs. Preparatory TLC was carried out to collect these components. The yellow coloured component, being in minor amount, could not be

collected in amount sufficient enough for carrying out characterisation studies. Only the red coloured component could be obtained in sufficient amount. It was recrystallised in ethyl alcohol as red needles and characterized as 4-methyl-1,2-benzoquinone on the basis of positive test for quinone [17], M.P. 69°C (literature value 68°C [18], and UV spectrum (in chloroform giving absorption maxima at 380 and 554 nm (literature values [19] 382 and 565 nm). The IR spectrum of this compound (in KBr) showed the presence of bands at 1632  $\text{cm}^{-1}$  (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]), 2924  $\text{cm}^{-1}$  (s) (may be due to overtones of C=O stretch as the frequency is about twice that of C=O stretch), 2738  $\text{cm}^{-1}$  (s) (due to isolated C-H stretching [21,22]). Further, the bands at 1386  $\text{cm}^{-1}$  (s) and 1354  $\text{cm}^{-1}$  (s) (may be due to C=C ring stretch), 1212  $\text{cm}^{-1}$  (m) and 1090  $\text{cm}^{-1}$  (m) (may be due to in plane C-H bending) and the bands at 702 and 668  $\text{cm}^{-1}$  (m) (due to out of plane C=C bending mode). The H-nmr spectrum of this compound in  $\text{CDCl}_3$  showed peaks at  $\delta = 7.220$ , D, (1H);  $\delta = 7.010$ , D, (1H);  $\delta = 6.550$ , S, (1H);  $\delta = 2.210$ , S, (3H). The latter may be due to three protons of  $-\text{CH}_3$  group attached to the ring while the former peaks may be due to the three protons of the ring in 4-methyl-1,2-benzoquinone.

## RESULTS

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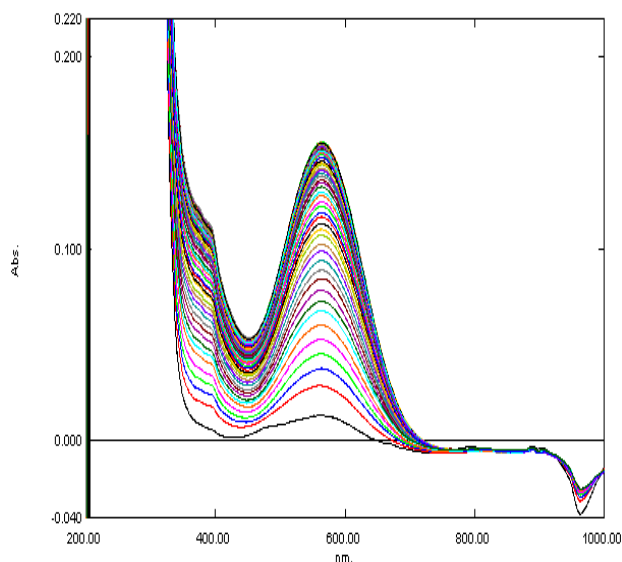


Figure 1: UV-VIS rapid scan at time interval of 60 seconds at  $[\text{NaIO}_4] = 8.0 \times 10^{-3}\text{ mol dm}^{-3}$ ,  $[\text{DMT}] = 3.0 \times 10^{-4}\text{ mol dm}^{-3}$ ,  $\text{pH} = 5.0$ ,  $[\text{MnII}] = 1.456 \times 10^{-7}\text{ mol dm}^{-3}$ , acetone = 10.0 % (v/v), Temp =  $35.0 \pm 0.1^\circ\text{C}$

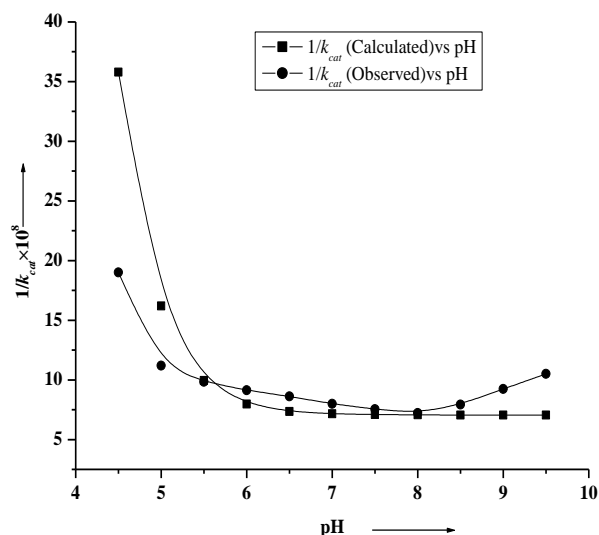


Figure 2:  $1/k_{cat}$  (observed) or  $1/k_{cat}$ (calculated) vs pH plot at  $[\text{NaIO}_4] = 8.0 \times 10^{-3}\text{ mol dm}^{-3}$ ,  $[\text{DMT}] = 3.0 \times 10^{-4}\text{ mol dm}^{-3}$ ,  $[\text{MnII}] = 1.456 \times 10^{-7}\text{ mol dm}^{-3}$ , Acetone = 10.0 % (v/v),  $\lambda_{max} = 565\text{ nm}$ , Temp =  $35.0 \pm 0.1^\circ\text{C}$ .

**Table 1: Effect of variation of concentration of reactants, [MnII], pH and dielectric constant on the reaction rate  
Temp. = 35.0 ± 0.1°C**

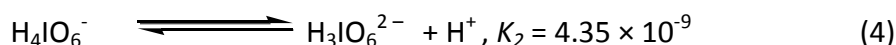
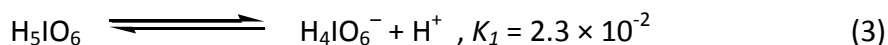
[NaIO <sub>4</sub> ] $\times 10^3$ mol dm <sup>-3</sup>	[DMT] $\times 10^4$ mol dm <sup>-3</sup>	Mn <sup>II</sup> $\times 10^7$ mol dm <sup>-3</sup>	Acetone %v/v	pH	$k_{obs}\times 10^3 s^{-1}$	$k_{cat}\times 10^{-7}$ dm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>
8.0	5.0	1.456	10.0	5.0	10.59	0.909
8.0	6.0	1.456	10.0	5.0	11.36	0.975
8.0	7.0	1.456	10.0	5.0	12.28	1.054
8.0	8.0	1.456	10.0	5.0	13.05	1.120
8.0	9.0	1.456	10.0	5.0	13.97	1.190
8.0	10.0	1.456	10.0	5.0	14.89	1.279
3.0	3.0	1.456	10.0	5.0	4.069	0.932
4.0	3.0	1.456	10.0	5.0	5.374	0.923
5.0	3.0	1.456	10.0	5.0	6.679	0.917
6.0	3.0	1.456	10.0	5.0	7.907	0.905
7.0	3.0	1.456	10.0	5.0	9.212	0.904
8.0	3.0	1.456	10.0	5.0	10.44	0.896
8.0	3.0	1.456	10.0	5.0	10.44	0.896
8.0	3.0	2.184	10.0	5.0	15.89	0.909
8.0	3.0	2.912	10.0	5.0	21.03	0.903
8.0	3.0	3.640	10.0	5.0	25.95	0.891
8.0	3.0	4.368	10.0	5.0	31.01	0.887
8.0	3.0	1.456	10.0	4.5	6.141	0.527
8.0	3.0	1.456	10.0	5.0	10.44	0.896
8.0	3.0	1.456	10.0	5.5	11.82	1.015
8.0	3.0	1.456	10.0	6.0	12.74	1.094
8.0	3.0	1.456	10.0	6.5	13.51	1.160
8.0	3.0	1.456	10.0	7.0	14.59	1.252
8.0	3.0	1.456	10.0	7.5	13.43	1.326
8.0	3.0	1.456	10.0	8.0	16.59	1.386
8.0	3.0	1.456	10.0	8.5	14.66	1.261
8.0	3.0	1.456	10.0	9.0	12.21	1.081
8.0	3.0	1.456	10.0	9.5	11.13	0.956
8.0	3.0	1.456	2.5	5.0	11.28	0.968
8.0	3.0	1.456	5.0	5.0	10.97	0.942
8.0	3.0	1.456	7.5	5.0	10.67	0.916
8.0	3.0	1.456	10.0	5.0	10.44	0.896

## DISCUSSION

As stated in the preliminary observations, the reaction appears to proceed in several steps and possibly several intermediates (including comparatively stable C<sub>4</sub>) are formed. The order is one in periodate against the requirement of two periodate molecules for initial stage in the stoichiometry (Eq. 1). It indicates the involvement of only one periodate in the rate determining step and second IO<sub>4</sub><sup>-</sup> ion to be consumed in a fast step leading to the formation of the intermediate, C<sub>4</sub>. Since the concentration of C<sub>4</sub> increases continuously with time and reaches a limiting value, its concentration cannot be in steady state. The 1/ *k<sub>cat</sub>* versus pH plot (Fig. 2), 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 [24]. No effect of free radical scavengers on reaction rate rules out the chances of free radical mechanism. High negative value of entropy of activation allows us to use the involvement of solvent while proposing a molecular mechanism for this reaction (Scheme-1).

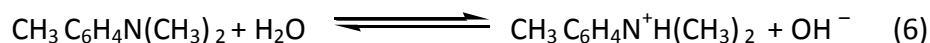
It is clear from the discussion made so far that the speciation of DMT and periodate is important in this reaction. In aqueous solutions, periodate is transformed into the three forms in water including orthoperiodic acid [25] with equilibria and dissociation constants [26, 27] given below:



The value of  $K_1$  indicates that in the pH range 4.5-9.5 species  $\text{H}_5\text{IO}_6$  shall be practically non-existent and hence only species  $\text{H}_4\text{IO}_6^-$  and  $\text{H}_3\text{IO}_6^{2-}$  need be considered for explaining observed pH - dependence. Based on this premise, the equilibrium or free concentration of  $\text{H}_4\text{IO}_6^-$ ,  $[\text{H}_4\text{IO}_6^-]$  shall be related to the total periodate concentration  $[\text{IO}_4^-]_0$  by Eq. (5)

$$[\text{H}_4\text{IO}_6^-] = [\text{IO}_4^-]_0 [\text{H}^+] / ([\text{H}^+] + K_2) \quad (5)$$

In the reaction mechanism proposed later, species  $\text{H}_4\text{IO}_6^-$  has been considered reactive. In aqueous solution, DMT, undergoes the following acid – base equilibrium with  $K_b = 1.2 \times 10^{-9}$ . [28].

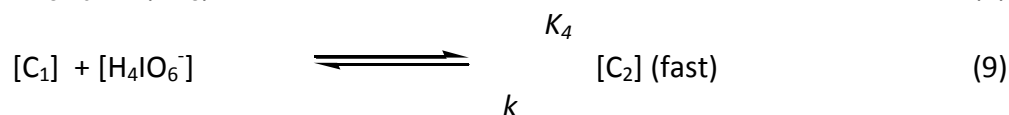
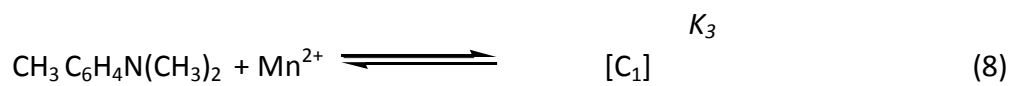
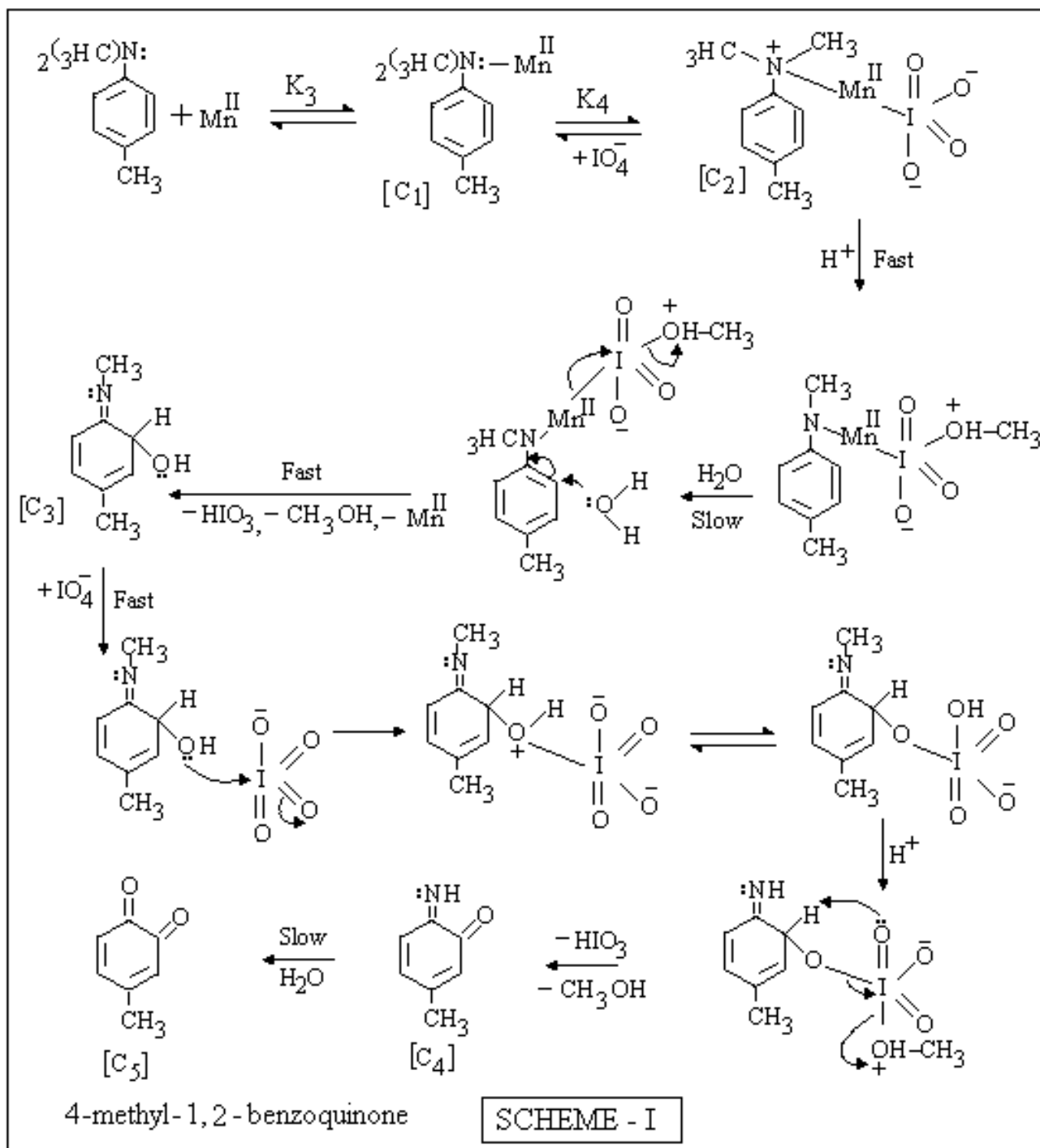


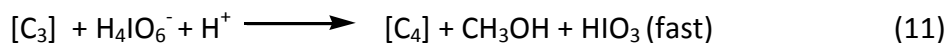
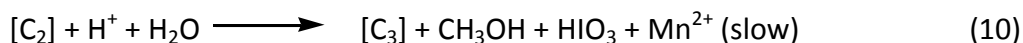
Since in the studied pH-range, both  $\text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$  and  $\text{CH}_3\text{C}_6\text{H}_4\text{N}^+\text{H}(\text{CH}_3)_2$  exist, these species have been taken into account. From equilibrium (6), the equilibrium or free concentration of amine, [DMT], is given by Eq. (7).

$$[\text{DMT}] = [\text{DMT}]_0 [\text{OH}^-] / \{[\text{OH}^-] + K_b\} \quad (7)$$

Where  $[\text{DMT}]_0$  is the total concentration of  $\text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ .

On this basis to explain the observed kinetics, rate law (Eq. 2), and pH- dependence, the following mechanism is proposed.





In steps (6 – 9), [C<sub>1</sub>], [C<sub>2</sub>], [C<sub>3</sub>] and [C<sub>4</sub>] are intermediates, out of which [C<sub>4</sub>] appears to undergo very slow reorganization/ hydrolysis to yield the reaction product, C<sub>5</sub>.



In the detailed mechanism (Scheme-1), the catalytic role of Mn<sup>2+</sup> appears to be due to the formation of a ternary complex, [(DMT)Mn(H<sub>4</sub>IO<sub>6</sub>)<sup>+</sup>], in which Mn helps in electron transfer.

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

$$d[C_4]/dt = kK_3K_4 [Mn^{II}][H_4IO_6^-][DMT] \quad (13)$$

On substituting the values of concentrations of the reactive species [DMT] and [H<sub>4</sub>IO<sub>6</sub><sup>-</sup>] from Eq. (5) and (7) in eq. (13), and taking H<sub>4</sub>IO<sub>6</sub><sup>-</sup> as IO<sub>4</sub><sup>-</sup> for simplicity [26], the complete rate law including [H<sup>+</sup>] - dependence becomes:

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

On replacing the term, [OH<sup>-</sup>][H<sup>+</sup>], by K<sub>w</sub> in numerator, and [OH<sup>-</sup>] by K<sub>w</sub>/ [H<sup>+</sup>] in denominator, and on rearranging, the equation(14) becomes equation(15).

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

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

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

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

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

The nature of the rate law (17) shows that a plot of 1/k<sub>cat</sub> versus [H<sup>+</sup>] or pH shall pass through a minimum<sup>10-13, 24</sup>. Differentiation of 1/k<sub>cat</sub> with respect to [H<sup>+</sup>] in Eq.(17), gives the values of d<sup>2</sup>[1/k<sub>cat</sub>] / d[H<sup>+</sup>]<sup>2</sup>. The positive value of second derivative suggests the plot of 1/k<sub>cat</sub> versus [H<sup>+</sup>] or pH to pass through a minimum. Thus, on setting d[1/k<sub>cat</sub>] / d[H<sup>+</sup>] equal to zero for obtaining hydrogen ion concentration at which the 1/k<sub>cat</sub> vs [H<sup>+</sup>] profile will pass through minimum, we obtain,

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



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

$$[H^+]_{\min} = 1.58 \times 10^{-8} \text{ mol dm}^{-3}$$

It is noteworthy that the calculated value of  $[H^+]_{\min}$  is in good agreement with the experimental value of  $[H^+]_{\min}$  of  $1.0 \times 10^{-8} \text{ mol dm}^{-3}$  obtained from  $1/k_{cat}$  versus pH plot (Fig. 2) and this provides good support to the proposed mechanism. The  $k_{cat}$  and pH data were fitted to Eqn. (17). The plots comprising both the experimental data and calculated line are shown in the Figure 2. Except the data pertaining to pH 4.5, all other experimental  $k_{cat}$  values are in satisfactory agreement with the calculated values. Looking to the complexity of the system, the Eq. (17) satisfactorily explains the observed kinetics at least in the pH range 5.0 to 9.5.

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