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Kinetics and Mechanism of Mn^{II} Catalyzed Periodate Oxidation of 2, 3-Xylidine in Acetone-Water Medium

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ABSTRACT

The main reaction product of the reaction between periodate and 2,3-xylidine catalysed by Mn^{II} in acetone-water medium is 2, 3-dimethyl-p-benzoquinone. One mol of 2, 3-xylidine (DMA) reacts with two moles of periodate during the initial part of reaction. The kinetics 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: $\Delta E = 24.21$ kJ mol^{-1}, $A = 1.15 \times 10^9$ dm^3 mol^{-1} s^{-1}; $\Delta S^\# = -148.22$ J mol^{-1} K^{-1}, $\Delta G^\# = 67.66$ kJ mol^{-1} and $\Delta H^\# = 21.63$ kJ mol^{-1}**.** Under pseudo first order conditions, $[IO_4^-] >> [2, 3\text{-DMA}]$, the rate law is given by:$d[C]/dt = kK_3K_4[Mn^{II}]K_w[DMA]_0[IO_4^-]_0\ [H^+]\ /\{K_2\ K_w + (K_w + K_b\ K_2)[H^+] + K_b[H^+]^2\}$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 DMA. $[DMA]_0$ and $[IO_4^-]_0$ are the total concentration respectively, of 2,3-xylidine and periodate. In agreement with the rate law the $1/k_{cat}$ versus pH plot passes through the minimum. Detailed molecular mechanism is discussed.

Keywords: Kinetics, Mn^{II}, periodate, 2,3-xylidine, 2,3-dimethyl-p-benzoquinone

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INTRODUCTION

Few kinetic-mechanistic studies have been made 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]. Present communication deals with the results of kinetic-mechanistic studies made on Mn(II) catalyzed periodate oxidation of 2, 3-xylidine (DMA) in acetone-water medium. The studies are important for their further expected use in developing methods for detection and treatment of the aromatic amines – the chemicals enlisted as toxic [15].

EXPERIMENTAL

Sodium metaperiodate (Loba Chemie), DMA (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.

On mixing the reactants, the solution becomes light yellow which later changes in to light orange 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 UV-VIS spectra of IO_4^-, 2, 3-DMA 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-2450) having high precision thermostatic control, at 470 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).

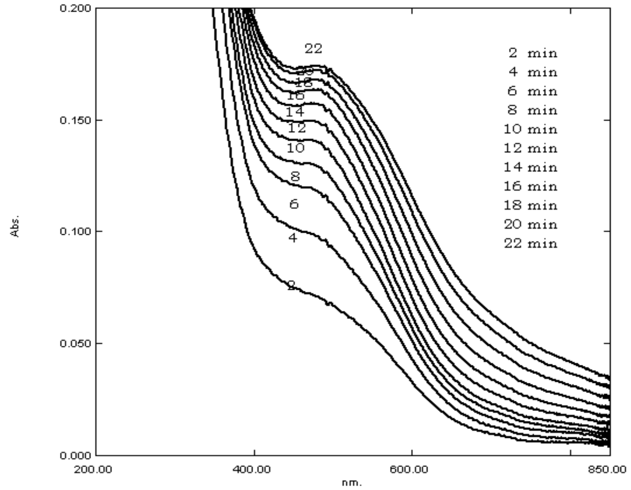


Figure 1: UV-VIS rapid scan

$[NaIO_4] = 2.0 \times 10^{-3}$ mol dm^{-3}, [2, 3-DMA] = 2.0×10^{-4} mol dm^{-3}, pH = 6.0, $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, acetone = 10.0 % (v/v), Temp = 35.0 ± 0.1ºC.

Reaction mixture containing oxidant in excess was prepared, shaken and set aside for 24 hours. It developed light yellow colour changing into light orange and then brown colour followed by the precipitation. 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 = Chloroform: Acetone: Benzene (10: 05: 85), Time for development = 30 minutes to get three separated components, reddish, violet and yellow in colour. The violet and red components could not be collected in sufficient amount due to small yield. The yellow coloured compound was collected by preparatory TLC, recrystallised in petroleum ether, obtained as yellow needles and characterized as 2, 3-dimethyl-*p*-benzoquinone on the basis of positive test for quinine [17], M.P. 58°C (literature value 56.6-57.5°C [18], and UV spectrum (in chloroform giving absorption maxima at 255, 260, 340 and 422 nm (literature values [19] 250, 257, 337 and 425 nm). The IR spectrum of this compound (in KBr) showed the presence of 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 [20]), 3250 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 [21-22]). Further, the bands at 1393 cm^{-1}(s) and 1492 cm^{-1} (s) (may be due to due to C= =C ring stretch), 1108 cm^{-1} (m) and 1166 cm^{-1}(m) (may be due to in plane C-H bending) and the bands at 831 cm^{-1}(m) (due to out plane bending in case of two adjascent H-atoms) and 506 cm^{-1}(m) (due to out of plane C=C bending mode). On the basis of these studies, the product may be 2, 3-dimethyl-*p*-benzoquinone.

RESULTS

Reaction Stoichiometry

Known excess of $NaIO_4$ was allowed to react with substrate and unreacted periodate was estimated iodimetrically. It was found that 1 mol of 2, 3-DMA consumes 2 moles of periodate for initial stage of the reaction as given below.

$$CH_3CH_3C_6H_3NH_2 + 2IO_4^- + 2H^+ \xrightarrow{Mn^{II}} CH_3CH_3C_6H_2O_2 + 2HIO_3 + NH_3 \qquad (1)$$

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).

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

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 $[DMA]_0$ 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 [DMA] are seen to be in good agreement and consistent with the rate law eq.(2).

Table 1: Effect of variation of concentration of reactants, $[Mn^{II}]$, pH and dielectric constant on the reaction rate at Temp. = 35.0 ± 0.1°C

$[NaIO_4]\times10^4$ mol dm^{-3}	[DMA] $\times10^4$ mol dm^{-3}	$Mn^{II}\times10^6$ mol dm^{-3}	Acetone %(v/v)	pH	$k_{obs}\times10^3$ s^{-1}	$k_{cat}\times10^{-5}$ dm^6 mol^{-2} s^{-1}
10.0	2.0	7.28	10.0	6.0	0.67	0.92
15.0	2.0	7.28	10.0	6.0	1.07	0.93
20.0	2.0	7.28	10.0	6.0	1.34	0.92
25.0	2.0	7.28	10.0	6.0	1.69	0.93
30.0	2.0	7.28	10.0	6.0	2.02	0.92
35.0	2.0	7.28	10.0	6.0	2.36	0.93
20.0	2.0	7.28	10.0	6.0	1.34	0.92
20.0	3.0	7.28	10.0	6.0	1.56	1.07
20.0	4.0	7.28	10.0	6.0	1.67	1.15
20.0	5.0	7.28	10.0	6.0	1.77	1.21
20.0	6.0	7.28	10.0	6.0	1.80	1.24
20.0	7.0	7.28	10.0	6.0	1.86	1.28
20.0	2.0	3.28	10.0	6.0	0.63	0.97
20.0	2.0	5.28	10.0	6.0	0.92	0.87
20.0	2.0	7.28	10.0	6.0	1.34	0.92
20.0	2.0	9.28	10.0	6.0	1.73	0.93
2.0	20.0	7.28	10.0	5.5	0.22	0.15
2.0	20.0	7.28	10.0	6.0	1.50	1.03
2.0	20.0	7.28	10.0	6.5	1.74	1.19
2.0	20.0	7.28	10.0	7.0	1.41	0.97
2.0	20.0	7.28	10.0	7.5	1.12	0.77
2.0	20.0	7.28	10.0	8.0	0.89	0.61
2.0	20.0	7.28	10.0	8.5	0.58	0.40
20.0	2.0	7.28	5.0	6.0	2.74	1.88
20.0	2.0	7.28	10.0	6.0	1.34	0.92
20.0	2.0	7.28	15.0	6.0	0.58	0.40
20.0	2.0	7.28	20.0	6.0	0.31	0.21

Effect of pH, Dielectric constant, free radical scavengers and temperature

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 8.5. 1/ k_{cat} vs pH plot indicates a minimum at pH = 6.5 (Fig. 2). Since the substrate is soluble only in acetone-water binary mixture, the kinetics had been studied in 10.0% (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 (5.0 – 20.0%) i.e. a decrease in dielectric constant (D) of the medium, led to a decrease in rate. Graphical plots between k_{cat} and 1/ D, were 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 (30.0 to 45.0°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 ΔE = 24.21 kJ mol^{-1}, $A = 1.15 \times 10^{9}$ dm^{3} mol^{-1} s^{-1}; $\Delta S^{\#} = -$ 148.22 J mol^{-1} K^{-1}, $\Delta G^{\#}$ = 67.66 kJ mol^{-1} and $\Delta H^{\#}$ = 21.63 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.

DISCUSSION

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 DMA into benzoquinone. Further, the kinetic order of one in periodate against the requirement of two periodate molecules for each DMA 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 I).

While proposing a suitable mechanism for the reaction under study, the speciation of DMA and periodate should be considered. In aqueous solutions, periodate is transformed into the three forms in water including orthoperiodic acid with equilibria and dissociation constants given below:

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

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

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)

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

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

In aqueous solution, DMA, undergoes the following acid – base equilibrium with K_b[24] = 5.0×10^{-10}.

$$CH_3CH_3C_6H_4NH_2 + H_2O \rightleftharpoons CH_3CH_3C_6H_4N^+H_3 + OH^- \qquad (6)$$

Since in the studied pH-range, both $CH_3CH_3C_6H_4NH_2$ and $CH_3CH_3C_6H_4N^+H_3$ exist, these species have been taken into account. From equilibrium (6), the equilibrium or free concentration of amine, [DMA], is given by Eq. (7).

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

Where $[DMA]_0$ is the total concentration of $CH_3CH_3C_6H_4NH_2$.

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.

$$CH_3CH_3C_6H_4NH_2 + Mn^{2+} \overset{K_3}{\rightleftharpoons} [C_1] \qquad (8)$$

$$[C_1] + [H_4IO_6^-] \overset{K_4}{\rightleftharpoons} [C_2] \text{ (fast)} \qquad (9)$$

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

$$[C_3] + H_4IO_6^- + H^+ \longrightarrow [C_4] + HIO_3 \text{ (fast)} \qquad (11)$$

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.

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

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, $[(DMA)Mn(H_4IO_6)]^+$, in which Mn helps in electron transfer. Further the proposed gross mechanism matches the kinetic and product studies, as given in scheme I. 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 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.

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

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

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

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

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

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[DMA]_0[IO_4^-]_0[H^+] /\{K_2K_w+(K_w+K_bK_2)[H^+]+K_b[H^+]^2\} \quad (15)$$

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). The plot comprising both the experimental data and calculated line are shown in the figure 2. Except the data pertaining to pH 5.5, all experimental k_{cat} values are in good agreement and fall on the calculated line. Looking to the complexity of the system, the Eq. (17) satisfactorily explains the observed kinetics at least in the pH range 6.0 to 8.5.

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 profile observed by us (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,

$$[H^+]_{min} = (K_2 K_w / K_b)^{1/2} \qquad (18)$$

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

$$[H^+]_{min} = 2.93 \times 10^{-7} \text{ mol dm}^{-3}$$

It is noteworthy that the calculated value of $[H^+]_{min}$ is in good agreement with the experimental value of $[H^+]_{min}$ of 3.16×10^{-7} mol dm^{-3} obtained from $1/k_{cat}$ versus pH plot (Fig. 2). It again supports to the proposed rate law and mechanism.

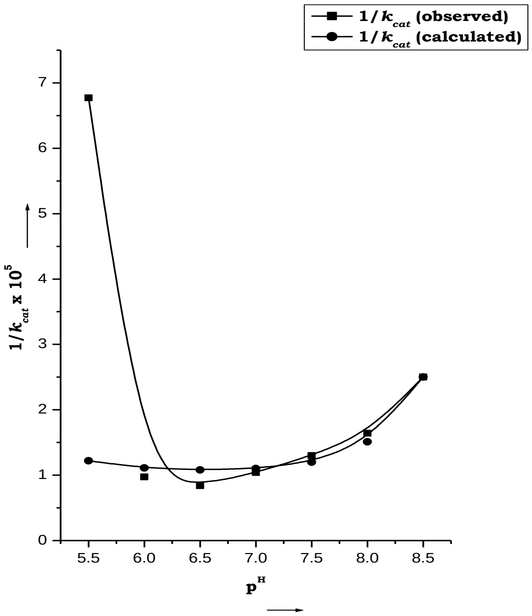
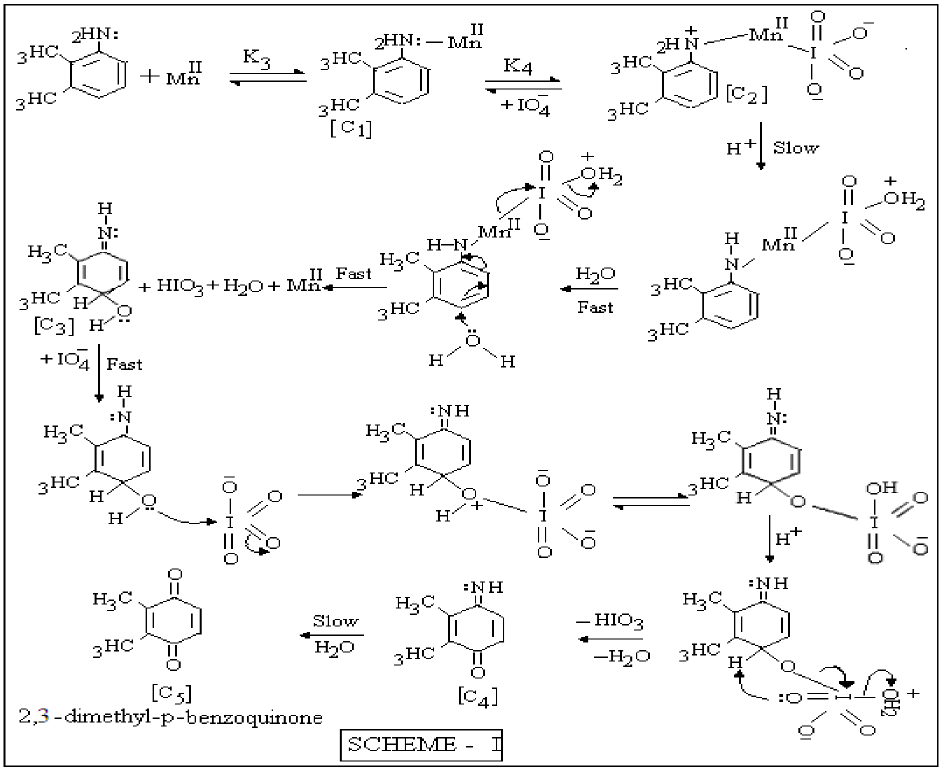


Figure 2: $1/k_{cat}$ (observed) or $1/k_{cat}$(calculated) vs pH plot

$[NaIO_4] = 2.0 \times 10^{-3}$ mol dm^{-3}, [DMA] = 2.0×10^{-4} mol dm^{-3}, $[Mn^{II}] = 7.28 \times 10^{-6}$ mol dm^{-3}, Acetone =10.0 %(v/v), λ_{max} = 470 nm, Temp = 35.0 ± 0.1 ^{0}C,



CONCLUSION

The main reaction product of the reaction between periodate and 2,3-xylidine catalysed by Mn^{II} in acetone-water medium is 2, 3-dimethyl-*p*-benzoquinone. One mol of 2, 3-xylidine reacts with two moles of periodate during the initial part of reaction. Under pseudo first order conditions, $[IO_4^-] >> [2, 3\text{-DMA}]$, the rate law is given by:

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

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 DMA. $[DMA]_0$ and $[IO_4^-]_0$ are the total concentration respectively, of 2,3-xylidine and periodate. In agreement with the rate law the $1/k_{cat}$ versus pH plot passes through the minimum. The proposed rate and mechanism are well supported by the experimental observations viz. evaluated entropy of activation, effect of dielectric constant of medium, main reaction product identified, and other kinetic features. Detailed molecular mechanism is discussed.

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