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Research Article

Kinetics and Mechanism of Mn^{II} Catalyzed Periodate Oxidation of *p*-anisidine: Effect of pH

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Abstract

The stoichiometry for the initial part of the reaction, Mn^{II} catalysed periodate oxidation of *p*-anisidine (PMA), has been found to be 1 mol of PMA consuming 2 mol of periodate ion. The kinetic-mechanistic study of reaction in acetone-water medium was made spectrophotometrically by noting the increase in the absorbance of reaction intermediate. 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 suggesting an ion-dipole type interaction. Free radical scavengers do not affect the reaction rate. A special type of rate-pH profile shows a maximum at pH = 7.0. This pH effect also suggests the involvement of at least three differently reactive reactant species in the reaction and this fact has been considered by us while deriving the rate law. Under pseudo first order conditions $[IO_4^-] >> [PMA]$ and in agreement with the derived rate law, the $1/k_{cat}$ versus $[H^+]$ plot passes through the minimum and the results can be fitted to the equation: $1/k_{cat} = (K_2 / kK_3K_4[H^+]) + \{(K_w + K_b K_2) / kK_3K_4K_w\} + K_b[H^+] / kK_3K_4K_w$ where kK_3K_4 is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$ and K_b is base dissociation constant of PMA. The experimental value of $[H^+]_{min}$ is in good agreement with the value calculated by using the derived rate law equation and is characteristic of the substrate involved relating to the base dissociation constant of PMA. The value of thermodynamic parameters have been evaluated. © 2014 BCREC UNDIP. All rights reserved

Keywords: Kinetics and mechanism; Mn^{II}; periodate; *p*-anisidine; 4-methoxy-1,2-benzoquinone

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1. Introduction

p-anisidine has been enlisted [1] as toxic in the toxic release inventory of US EPA, 2001 and placed in group 3 of international agency for research on cancer which includes the chemicals that are not classifiable as to carcinogenicity in humans. Reports are available on the kinetic-mechanistic studies for the uncatalysed non-Malapradian periodate oxidation of aromatic amines [2-10]. Some of the recent reports include the Mn^{II} catalyzed periodate oxidation of 2,4-xylidine [11], 2,6-xylidine [12], *N*-methylaniline [13], *p*-toluidine [14] and 4-chloro, 2-methyl aniline [15]. The kinetic-mechanistic studies have been made on Mn^{II} catalyzed periodate oxidation of *p*-anisidine (PMA) in acetone-water medium and the results of these studies are being presented and discussed in this paper. Special effect of pH on

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the rate of reaction has been observed in terms of rate-pH profile giving a maximum at a pH. We have proved in this communication that this maximum is characteristic of the substrate involved and relates to the base dissociation constant of *p*-anisidine. This pH effect also suggests the involvement of at least three differently reactive reactant species in the reaction and this fact has been considered by us while deriving the rate law. The studies are important as these may provide conditions required for developing methods for detection and treatment of *p*-anisidine.

2. Materials and Methods

2.1. Reagents and Chemicals

Acetone (E. Merck) (CAS No. 67-64-1), *p*–anisidine (Aldrich) (CAS No. 104-94-9), manganese sulphate monohydrate (Aldrich) (CAS No. 10034-96-5), sodium metaperiodate (Loba Chemie) (CAS No. 7790-28-5), and all other chemicals of analytical 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.

2.2. Kinetics 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 PMA, Mn^{II} and buffer and maintained at the desired temperature (± 0.1 ^{0}C).

The progress of the reaction was followed by recording the absorbance on Shimadzu double

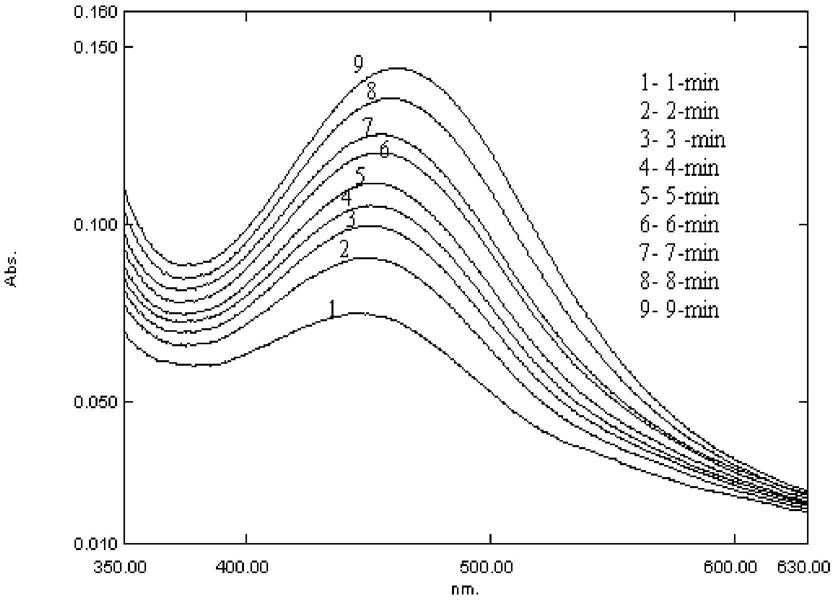


Figure 2. Rapid UV-VIS scan of reaction solution at different time at $[NaIO_4] = 4.0 \times 10^{-4}$ mol dm^{-3}, [PMA] = 4.0×10^{-5} mol dm^{-3}, $[Mn^{II}] = 7.28 \times 10^{-7}$ mol dm^{-3}, pH = 7.0, Acetone = 5.0 % (v/v), Temp. = 35.0 ± 0.1 ^{o}C.

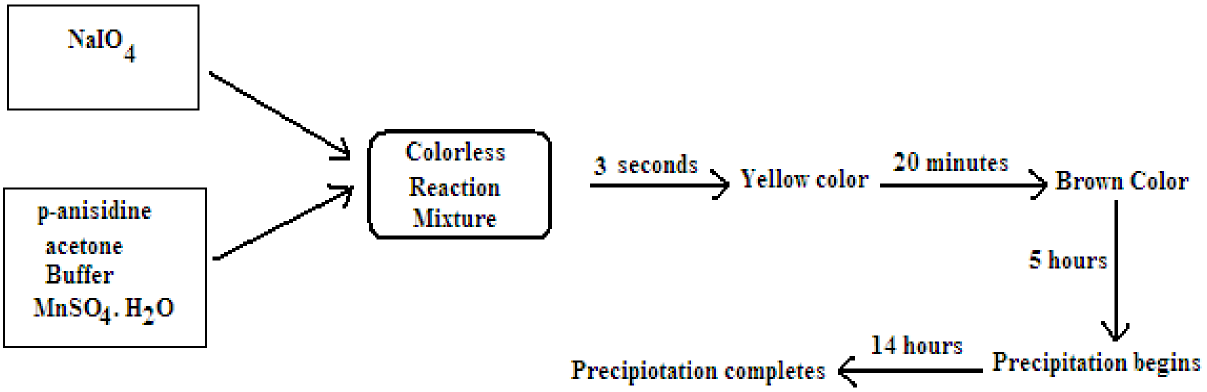


Figure 1. Color changes observed during the Mn^{II} catalysed periodate oxidation of p-anisidine

beam spectrophotometer (UV-1800), at 455 nm, i.e., the λ_{max} of the reaction intermediate 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. Guggenheim's method was used for evaluation of pseudo first order rate constants, k_{obs}.

2.3. Product Analysis

Reaction mixture containing oxidant in excess was left for fourteen hours to ensure completion of the reaction. Initially, the solution turned yellow, thereafter brown and finally the solid product settled down on standing. The observed changes are given in Figure 1. Reaction mixture was filtered and the filtrate was extracted with petroleum ether (40-60 °C) (CAS No. 8032-32-4, Analytical reagent grade, CDH, India). The extract was evaporated at room temperature (30±2 °C) to get a scarlet colored product which was found to be single when subjected to thin layer chromatography (TLC) using plate thickness of 0.5 mm, silica gel 'G' as adsorbent, chloroform+ acetone+ benzene in the ratio 4:6:4 ml used as eluent and 30 minutes as the time for development. It was recrystallised in ether and characterized as 4-methoxy-1,2-benzoquinone on the basis of positive test for quinine [17], M.P. 87 °C (literature value 88 °C [18]), UV spectrum (in $CHCl_3$ giving absorption maxima at 400 nm, which suggested the presence of quinonoid structure in the compound (literature values 406.5 nm, 4-methoxy-1, 2-benzoquinone [19]). The IR spectrum of this compound (in KBr) showed the presence of bands at 2976 cm^{-1} (s) (due to ring C−H stretch), 1674 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 methoxy group [20-23]), 3280 cm^{-1} (s) (may be due to overtones of C=O stretch). Further, the bands at 1520 cm^{-1} (s) and 1400 cm^{-1} (s) may be due to C==C ring stretch. The bands at 1238 cm^{-1} (m) to 1040 cm^{-1} (m) may be due to the asymmetric and symmetric C−O−C stretch and at 746 cm^{-1}(s)(m) and 824 cm^{-1} (m) (due to out of plane C=C and C−H bending mode). The observed values are in good agreement with those reported / expected for 4-methoxy-1,2-benzoquinone.

2.4. Stoichiometry

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 behavior up to 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. The results indicated the stoichiometry to be 1 mol PMA: 2 moles $NaIO_4$ for the reaction as in Eq. (1).

$$CH_3OC_6H_4NH_2 + 2IO_4^- + 2H^+ \xrightarrow{Mn^{II}} CH_3OC_6H_3O_2 + 2HIO_3 + NH_3 \qquad (1)$$

3. Results and Discussion

3.1. Preliminary Observations

On mixing the reactants, the solution turned light yellow within 3 seconds of mixing. As already shown in Figure 1, this color changes in to brown and finally the product is obtained on keeping for long time. 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 intermediate, C_4, to be 455 nm (Figure 2). The UV-VIS spectra of IO_4^- , PMA and Mn^{II} indicated these to show no absorption in visible region. Hence, for following the kinetics the absorbance changes were recorded at 455 nm at which only the intermediate C_4 absorbs.

3.2. 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 con-

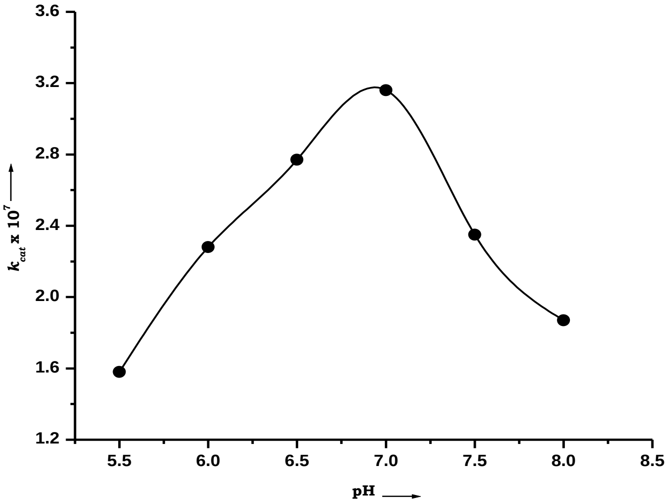


Figure 3. Effect of pH on reaction rate (Rate constant - pH-profile) [PMA] × 10^5 = 4.0 M, [$NaIO_4$] × 10^4 = 4.0 M, Temp. = 35± 0.1 °C, acetone = 5.0 % (v/v), [Mn(II)] × 10^7 = 7.28 M, λ_{max} = 455 nm.

stants, k_{obs}. Under these conditions, the kinetics was defined by the rate law (2):

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

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 $[PMA]_0$ represent respectively, the initial concentrations of periodate and PMA out of which later one is taken in excess. In the absence of Mn^{II}, no significant reaction occurred. The values of kcat obtained for different $[Mn^{II}]$, $[IO_4^-]_0$ and $[PMA]_0$ are seen to be in good agreement and consistent with the rate law (2) (Table 1).

Table 2. Thermodynamic Parameters. [PMA] × 10^5= 4.0 M, Mn (II)] × 10^7 = 7.28 M, [$NaIO_4$] × 10^4 = 4.0 M, acetone = 5.0 % (v/v), pH = 7.0, λ_{max} = 455 nm.

Temp. (± 0.1 °C)	k_{cat} × 10^{-7} ($dm^6\,mol^{-2}\,s^{-1}$)	ΔE ($kJ\,mol^{-1}$)	A × 10^{-11} ($dm^3mol^{-1}s^{-1}$)	$\Delta S^{\#}$ ($J\,mol^{-1}\,K^{-1}$)	$\Delta H^{\#}$ ($kJ\,mol^{-1}$)	$\Delta F^{\#}$ ($kJ\,mol^{-1}$)
35.0	3.16	21.08	1.20	148.66	18.45	65.36
40.0	3.71					
45.5	4.08					
50.0	4.63					

Table 1. Effect of different factors on the reaction rate at 35.0 ± 0.1 °C

[NaIO4]×10^4 (mol dm^{-3})	[PMA] ×10^5 (mol dm^{-3})	Mn^{II}×10^7 (mol dm$_{-3}$)	Acetone %(v/v)	pH	k_{obs} × 10^3 (s^{-1})	k_{cat} ×10^{-7} ($dm^6\,mol^{-2}\,s^{-1}$)
4.0	4.0	7.28	5.0	7.0	9.21	3.2
5.0	4.0	7.28	5.0	7.0	11.59	3.2
6.0	4.0	7.28	5.0	7.0	13.74	3.2
7.0	4.0	7.28	5.0	7.0	16.12	3.2
8.0	4.0	7.28	5.0	7.0	18.27	3.1
9.0	4.0	7.28	5.0	7.0	20.73	3.2
0.4	40.0	7.28	5.0	7.0	8.83	3.0
0.4	45.0	7.28	5.0	7.0	10.06	3.1
0.4	50.0	7.28	5.0	7.0	10.75	3.0
0.4	55.0	7.28	5.0	7.0	11.90	3.0
0.4	60.0	7.28	5.0	7.0	12.97	3.0
0.4	65.0	7.28	5.0	7.0	13.97	3.0
4.0	4.0	3.28	5.0	7.0	4.22	3.2
4.0	4.0	5.28	5.0	7.0	6.91	3.3
4.0	4.0	7.28	5.0	7.0	9.21	3.2
4.0	4.0	9.28	5.0	7.0	11.59	3.1
4.0	4.0	7.28	5.0	5.5	4.61	1.6
4.0	4.0	7.28	5.0	6.0	6.65	2.3
4.0	4.0	7.28	5.0	6.5	8.06	2.8
4.0	4.0	7.28	5.0	7.0	9.21	3.2
4.0	4.0	7.28	5.0	7.5	6.83	2.4
4.0	4.0	7.28	5.0	8.0	5.45	1.9
4.0	4.0	7.28	2.5	7.0	11.05	3.8
4.0	4.0	7.28	5	7.0	9.21	3.2
4.0	4.0	7.28	7.5	7.0	7.68	2.6
4.0	4.0	7.28	10.0	7.0	5.53	2.2

k_{obs} is the pseudo first order rate constant. k_{cat} is the overall rate constant for Mn^{II} catalysed pathway. k_{obs} and k_{cat} are related as given in Equation (2).

3.3. Effect of pH, Dielectric Constant of the Medium, and Free Radical Scavengers

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 5.5-8.0. k_{cat} versus [H$^+$] plot indicates a maximum at pH = 7.0 (Table 1, Figure 3).

An increase in the acetone (2.5 - 10 %) led to a decrease in the rate (42 %). For the reaction between an ion and a dipole, the Laidler as well as Amis equation [27], suggests a linear relationship between log k_{cat} and l/D. Further, according to Amis, the slope is negative if the reacting ion is anion. A plot between log k_{cat} vs l/D was found to be linear (Figure 4), with negative slope indicating that the reaction is an ion-dipolar type involving a direct bimolecular attack of *p*-anisidine on $H_4IO_6^-$ or IO_4^- (i.e. periodate monoanion which has been assumed to be the reactive species in the pH range in which the present studies were made, based on the evidences already available in literature [2, 26]). Also, the negative slope is in accordance with Amis equation for ion-dipolar type reaction.

Free radical scavengers, like acrylamide, allyl acetate and allyl alcohol had no effect on the reaction rate indicating no involvement of free radicals in the reaction mechanism.

3.4. Effect of Temperature and Evaluation of Thermodynamic Parameters

The rate constants were determined at four different temperatures (35-50 °C) Arrhenius plot was a staright line (Figure 5). 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 by using commonly known equations and these are given in Table 2. 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.

3.5. Special Features of the Reaction

Some important features of this reaction are as follows. Firstly, faster color 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 PMA into a 4-methoxy-1,2-benzoquinone. Secondly, the kinetic order of one in periodate against the requirement of two periodate molecules for each PMA molecule in the stoichiometry (Equation 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

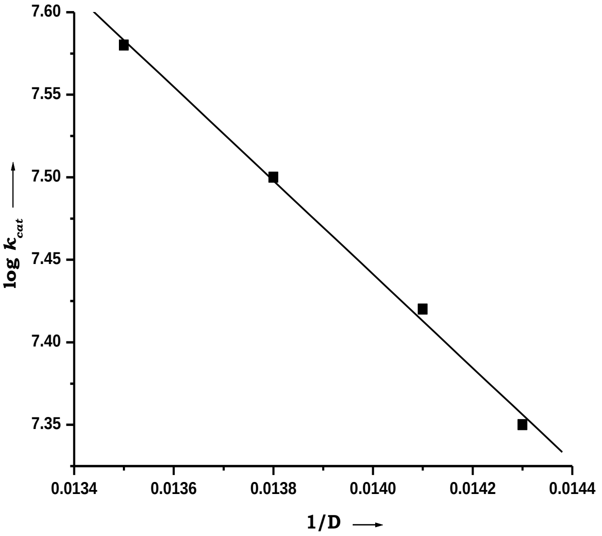


Figure 4. Effect of Dielectric constant on reaction rate at [NaIO$_4$] ×10^4 =4.0 M, [PMA] ×10^5 = 4.0 M, [Mn(II)] ×10^7 = 7.28 M, pH = 7.0, Temp. = 35±0.1 °C, λ_{max} = 455 nm

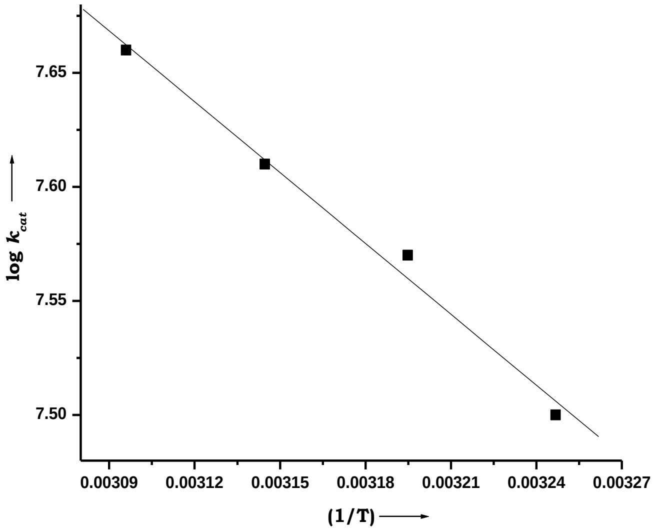


Figure 5. Arrhenius plot [NaIO$_4$] × 10^4 =4.0 M, [PMA] × 10^5 =4 .0M, pH = 7.0, acetone = 5.0% (v/v), λ_{max} = 455 nm, [Mn(II)] × 10^7 = 7.28 M

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, k_{cat} versus pH plot indicates the presence of at least three differently reactive reactant species (which is periodate in this system) in the pH region chosen for study [25]. 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 PMA 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 [26] given below:

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

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

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 Equation (5):

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

In the reaction mechanism proposed later, species $H_4IO_6^-$ has been considered reactive. In aqueous solution, PMA, undergoes the following acid-base equilibrium with $K_b = 22.9 \times 10^{-10}$ [24] in Equation (6).

$$CH_3OC_6H_4NH_2 + H_2O \rightleftarrows CH_3OC_6H_4N^+H_3 + OH^- \quad (6)$$

Since in the studied pH-range, both $CH_3OC_6H_4NH_2$ and $CH_3OC_6H_4N^+H_3$ exist, these species have been taken into account. From equilibrium (6), the equilibrium or free concentration of amine, [PMA], is given by Equation (7).

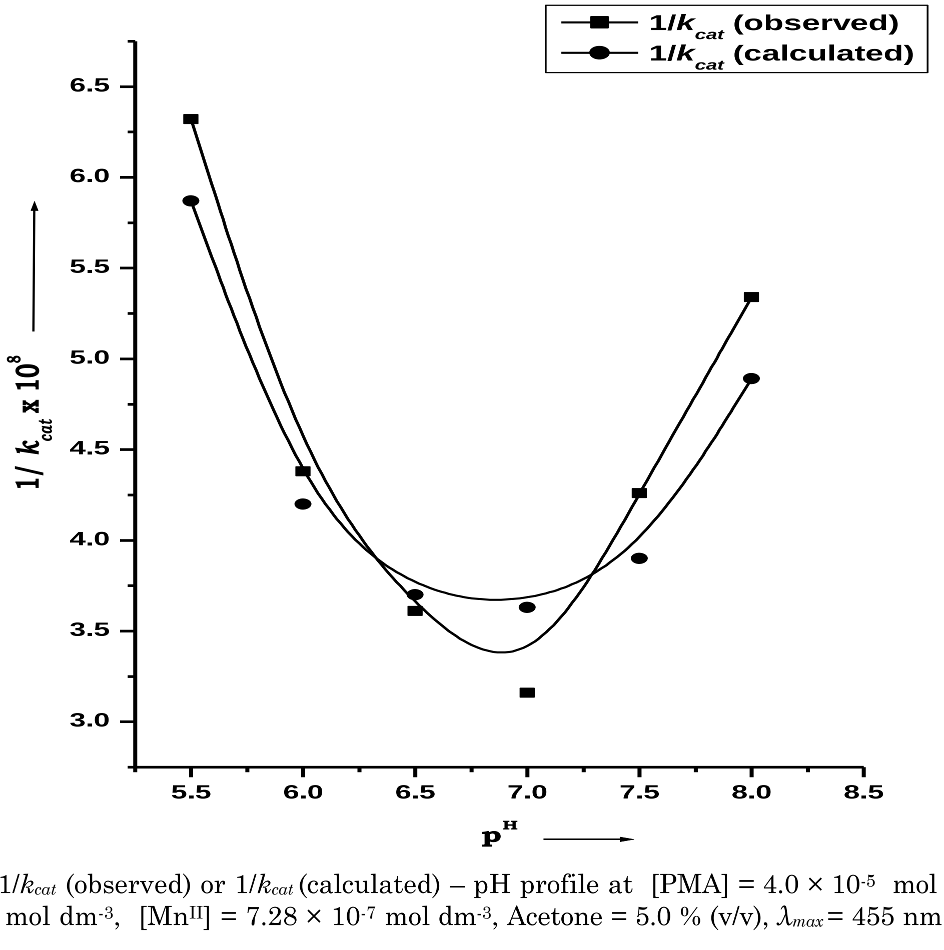


Figure 6. $1/k_{cat}$ (observed) or $1/k_{cat}$ (calculated) – pH profile at [PMA] = 4.0×10^{-5} mol dm^{-3}, [$NaIO_4$] = 4.0×10^{-4} mol dm^{-3}, [Mn^{II}] = 7.28×10^{-7} mol dm^{-3}, Acetone = 5.0 % (v/v), λ_{max} = 455 nm, Temp. = 35 ± 0.1 ^{0}C.

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

where $[PMA]_0$ is the total concentration of $CH_3OC_6H_4NH_2$.

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

$$CH_3OC_6H_4NH_2 + Mn^{2+} \overset{K_3}{\rightleftarrows} [C_1] \qquad (8)$$

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

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

$$[C_3] + H_4IO_6^- + H^+ \rightarrow [C_4] + H_2O + HIO_3 \text{ (fast)} \qquad (11)$$

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.

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

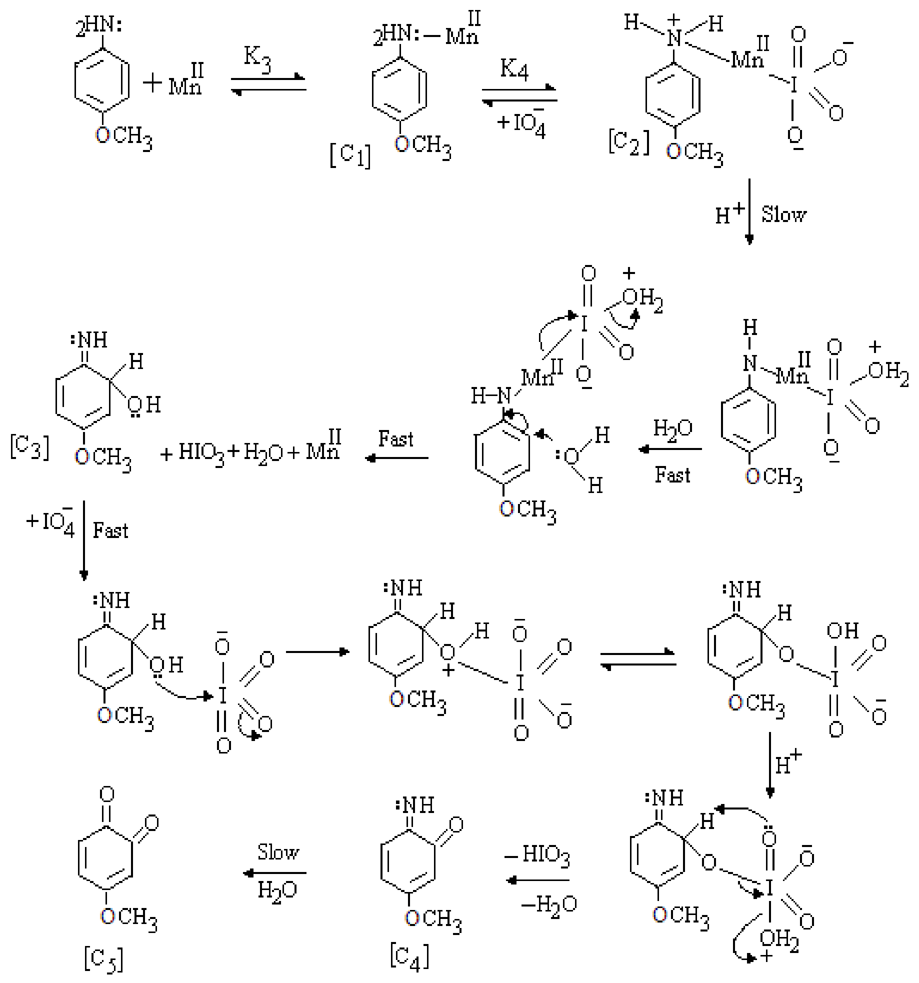
The proposed mechanism in Equations (8-11) leads to the rate law (13).

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

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

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

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



SCHEME - I

Equation (15).

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[PMA]_0[IO_4^-]_0\,[H^+] \,/\, \{K_2K_w+(K_w+K_b K_2)[H^+]+K_b[H^+]^2\} \quad (15)$$

On comparing Equations (2) and (15), we get:

$$k_{cat} = k\,K_3K_4K_w[H^+] \,/\, \{K_2\,K_w + (K_w + K_b\,K_2)[H^+] + K_b\,[H^+]^2 \quad (16)$$

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

$$1/k_{cat} = (K_2 \,/\, kK_3K_4\,[H^+]) + \{(K_w+ K_b\,K_2) \,/\, kK_3K_4\,K_w\} + K_b[H^+] \,/\, kK_3K_4K_w \quad (17)$$

The k_{cat} and pH data were fitted to Equation (17) and the best fit value of composite rate constant kK_3K_4 was found to 2.94×10^7 $dm^6\,mol^{-2}\,s^{-1}$. The plot comprising of the experimental data and calculated data is shown in Fig. 6. In this case, all experimental values are in good agreement and fall on the calculated line which confirms the applicability of Eq. (17) in the studied pH range i.e. 5.0-8.0.

On differentiating $1/k_{cat}$ with respect to $[H^+]$ in Equation (17), 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. This minimum can be seen in the experimental curve (Figure 6). 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, we obtain:

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

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

$$[H^+]_{min} = 1.0\times10^{-7}\ mol\ dm^{-3}$$

It is noteworthy that the calculated value of $[H^+]_{min}$ is in satisfactory agreement with the experimental value of $[H^+]_{min}$ of 1.0×10^{-7} mol dm^{-3} obtained from k_{cat} versus pH plot (Figure 3). This goes in strong support of the derived rate law and the proposed mechanism.

3.6. Molecular Mechanism

The detailed mechanism for the reaction is given in Scheme-I wherein IO_4^- has been assumed as the oxidizing species in the light of the fact that the present studies were carried out in the pH range in which periodate monoanion is the reactive species [2, 25]. The first step in the proposed mechanism is the bimolecular reaction between p-anisidine and Mn^{II} to form an intermediate C_1, which, in turn, is attacked by periodate ion to form an intermediate ternary complex C_2. 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. The catalytic role of Mn^{2+} appears to be due to the formation of a ternary complex, $[(PMA)Mn(H_4IO_6)]^+$, in which manganese helps in electron transfer. Further the proposed 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 [7,8]. 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 intermediate C_2 is unstable and attacked by water molecule to give intermediate C_3. C_3 is attacked by another periodate molecule in fast step to give quinoneimine C_4. The overall reaction appears to involve several steps and possibly several transient intermediates, in addition to comparatively stable one C_4.

The kinetic order of one in periodate against the requirement of two periodate molecules for each PMA molecule in the stoichiometry 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. The last step seems to be the hydrolysis of C_4 to give the benzoquinone C_5, as the final product of oxidation separated and identified as 4-methoxy-1,2-benzoquinone. The observation that free radical scavengers have no effect on reaction rate rules out the involvement of free radicals in the oxidation mechanism.

4. Conclusion

Mn^{II} catalysed periodate oxidation of *p*-anisidine (PMA) is first order in reactants and catalyst each. A decrease in dielectric constant of the medium results in decrease in the rate of reaction suggesting thereby, the ion-dipole type of reaction. Free radical scavengers do not affect the reaction rate. One mol of PMA reacts with two moles of periodate during the initial part of reaction. The main reaction product is

4-methoxy-1,2-benzoquinone. Results under pseudo-first order conditions, $[IO_4^-] >> [PMA]$, are in agreement with the derived rate law. In agreement with the rate law the $1/k_{cat}$ versus pH plot passes through a minimum. Rate-pH profile shows a maximum at a pH of 7.0. This value is characteristic of the substrate and relates to its base dissociation constant by $[H^+]_{min} = (K_2\ K_w\ /\ K_b)^{1/2}$. This pH effect also suggests the involvement of at least three differently reactive reactant species in the reaction.

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