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Mn^{ii} Catalyzed Oxidation Of P-Bromoaniline By Periodate Ion: A Kinetic and Mechanistic Study.

RD Kaushik*[1], Jaspal Singh[1], Richa Saini[2], Kavita Rawat[1], and Ekata Kumari[3].

[1]Department of Chemistry, Gurukul Kangri University, Haridwar (Uttarakhand) India
[2]Department of Physics, Gurukul Kangri University, Haridwar (Uttarakhand) India
[3]Uttaranchal College of Science and Technology, Dehradun (Uttarakhand), India

ABSTRACT

The kinetics of the periodate oxidation of p-bromoaniline (PBA) in acetone-water medium has been followed by monitoring the increase in the absorbance of reaction intermediate, C_4, and the main reaction product is 4-bromo–1,2–benzoquinone. Results under pseudo first order conditions, $[IO_4^-] >> [PBA]$, are in agreement with the rate law: $d[C]/dt = kK_3K_4K_w [Mn^{II}] [PBA]_0 [IO_4^-]_0 [H^+] /\{K_2 K_w + (K_w + K_b K_2)[H^+] + K_b [H^+]^2\}$ 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 PBA. 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: $\Delta E = 11.434$ kJ mol^{-1},$A = 7.0217 \times 10^8$ dm^3 mol^{-1} s^{-1}; $\Delta S^\# = -106.803$ J $mol^{-1}K^{-1}$, $\Delta G^\# = 42.011$kJ mol^{-1} and $\Delta H^\# = 8.848$ kJ mol^{-1}.

Keywords: Kinetics, Mn^{II} catalysed, periodate oxidation, p–bromoaniline, 4- bromo-1,2-benzoquinone.

**Corresponding author*

INTRODUCTION

The kinetics and mechanism of the uncatalysed and Mn^{II} catalyzed non-Malapradian periodate oxidation of some aromatic amines has been the subject of study during the past few years. In these reports, a binary unstable intermediate complex formation between aromatic amine and periodate has been proposed in the reaction mechanism of uncatalysed reactions [1-16]. Also, there are some reports available which propose the ternary complex formation between periodate, aromatic amine and Mn^{II} in some reactions catalysed by Mn^{II} [17-28]. In present paper, the results and rate law have been found to differ widely from the earlier report on uncatalysed periodate oxidation of p-bromoaniline[2].

EXPERIMENTAL

Reagents and chemicals

Sodium metaperiodate (Loba Chemie), p-bromoaniline (Loba Chemie), 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 [29] was used for maintaining the pH.

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

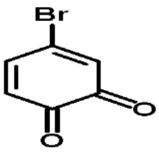
The progress of the reaction was followed by recording the absorbance on Schimadzu double beam spectrophotometer (UV - 2550), at 456 nm, i.e., the λ_{max} of the reaction intermediate / product absorbs. λ_{max} was not found to change with change in time under experimental conditions. Desired temperature was maintained with the help of a high precision thermostatic control.

Product analysis

Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially, the solution turned light yellow colour, thereafter wine red colour and then orange followed by precipitation in about 24 hours. The reaction mixture was extracted with petroleum ether, the extract was evaporated at room temperature to get a reddish-brown compound which were found to be TLC single (using plate thickness of 0.5 mm, silica gel 'G' as adsorbent, chloroform+ acetone+ benzene in the ratio 40:60:40 ml used as eluent and 40 minutes as the time for development). This compound was recrystallised in diethylether, obtained as red-brown plates and characterized as 4- bromo- 1, 2-benzoquinone**.** The melting point of separated compound was found to be 75^{o}C (Lit. 74-75^{o}C for 4-bromo-1,2-benzoqinone[30]).This compound responded positive test for a quinine [31, 32]. The absorption maxima for this compound in $CHCl_3$ solvent were 260, 475 and 490 nm, which suggested the presence of quinonoid structure in the compound [33]. The two longer wavelength bands are particularly characteristic of o- benzoquinones [2].

The IR spectrum of compound in KBr (Fig.-3) showed a strong band at 1712 cm^{-1}(s) due to C=O group on 1,2-benzoquinone pattern with lowering of position a little due to electronic effect of constituent [36], 3205 cm^{-1}(s) may be due to overtone of C=O stretch, 2642 cm^{-1} due to ring =C–H stretch [33], 1344 cm^{-1} and 1438 cm^{-1} due to (-C=C-) ring stretch, 1143 cm^{-1}(m) and 1027 cm^{-1}(m) in plane (=C–H) bending, 793 cm^{-1}(m) due to out of plane (=C-H) bending in case of two adjacent H-atoms[33], 744 and 638 cm^{-1}(m) due to (-C=C-) bending mode. Further the band at 547 cm^{-1}(s) was the characteristic of (C-Br) stretching [37, 38].

The ^{1}H NMR spectrum (in $CDCl_3$) showed signals at δ =7.091, s, (1H) and δ =6.658, d, (2 H) for the three protons attached to the ring. The UV-VIS, IR and H-NMR spectra match with the values reported in literature[2] for 4-bromo-1,2-benzoquinone. Therefore, the compound may be 4- bromo-1,2-benzoquinone with structure as follows



Stoichiometry

Stoichiometry of the reaction was determined by allowing a known excess of $NaIO_4$ to react with substrate. After completion of the reaction, the precipitated product was filtered out and in the filtrate unconsumed $NaIO_4$ was determined iodimetrically. The results indicated the stoichiometry to be 1 mol PBA: 2 moles $NaIO_4$ for the reaction as in eq. (1).

$$BrC_6H_4NH_2 + 2IO_4^- + 2H^+ \xrightarrow{Mn^{II}} BrC_6H_3O_2 + 2HIO_3 + NH_3 \quad \text{-----} (1)$$

RESULTS

Preliminary observations

On mixing the reactants, the solution turned light yellow colour, thereafter wine red colour and then Orange 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 rapid scan of the brown solution showed the λmax of the intermediate, C_4, to be 456 nm (Fig. 1). IO_4^- , PBA and Mn^{II} show no absorption in visible region as indicated by their UV-VIS spectra. Hence, for following the kinetics the absorbance changes were recorded at 456 nm at which only the intermediate C_4 absorbs.

Rate Law

The kinetics was studied under pseudo order conditions by keeping $NaIO_4$ 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).

$$d[C]/dt = k_{cat} [PBA]_0 [IO_4^-]_0 [Mn^{II}] \quad \text{------------} \quad (2)$$

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

Table-1: Effect of variation of concentration of reactants, $[Mn^{II}]$, pH and dielectric constant

$[NaIO_4]\times10^4$ (mol dm^{-3})	$[PBA]\times10^5$ (mol dm^{-3})	$[Mn(II)]\times10^6$ (mol dm^{-3})	Acetone (%v/v)	Temp. ±0.1	[NaCl] $\times10^3$ (mol dm^{-3})	pH	$k_{obs}\times10^3$ (s^{-1})	$k_{cat}\times10^5$ (dm^6 mol^{-2} s^{-1})
7.0	2.0	7.28	5.0	30.0	-	5.5	2.26	4.45
7.0	3.0	7.28	5.0	30.0	-	5.5	2.39	4.67
7.0	4.0	7.28	5.0	30.0	-	5.5	2.43	4.77
7.0	5.0	7.28	5.0	30.0	-	5.5	2.47	4.86
7.0	6.0	7.28	5.0	30.0	-	5.5	2.51	4.93
7.0	7.0	7.28	5.0	30.0	-	5.5	2.53	4.97
3.0	7.0	7.28	5.0	30.0	-	5.5	2.30	4.52
4.0	7.0	7.28	5.0	30.0	-	5.5	2.39	4.70
5.0	7.0	7.28	5.0	30.0	-	5.5	2.46	4.82
6.0	7.0	7.28	5.0	30.0	-	5.5	2.49	4.89
7.0	7.0	7.28	5.0	30.0	-	5.5	2.53	4.97

8.0	7.0	7.28	5.0	30.0	-	5.5	2.55	5.00
7.0	7.0	1.42	5.0	30.0	-	5.5	2.31	4.54
7.0	7.0	3.84	5.0	30.0	-	5.5	2.40	4.72
7.0	7.0	5.56	5.0	30.0	-	5.5	2.44	4.80
7.0	7.0	7.28	5.0	30.0	-	5.5	2.53	4.97
7.0	7.0	7.28	5.0	30.0	-	4.0	1.68	3.30
7.0	7.0	7.28	5.0	30.0	-	4.5	2.18	4.29
7.0	7.0	7.28	5.0	30.0	-	5.0	2.39	4.69
7.0	7.0	7.28	5.0	30.0	-	5.5	2.53	4.97
7.0	7.0	7.28	5.0	30.0	-	6.0	2.51	4.93
7.0	7.0	7.28	5.0	30.0	-	6.5	2.47	4.85
7.0	7.0	7.28	5.0	30.0	-	7.0	2.42	4.74
7.0	7.0	7.28	5.0	30.0	-	7.5	2.24	4.39
7.0	7.0	7.28	5.0	30.0	1.0	5.5	2.54	4.99
7.0	7.0	7.28	5.0	30.0	2.0	5.5	2.62	5.15
7.0	7.0	7.28	5.0	30.0	3.0	5.5	2.71	5.33
7.0	7.0	7.28	5.0	30.0	4.0	5.5	2.79	5.47
7.0	7.0	7.28	2.5	30.0	-	5.5	2.61	5.13
7.0	7.0	7.28	5.0	30.0	-	5.5	2.53	4.97
7.0	7.0	7.28	7.5	30.0	-	5.5	2.47	4.84
7.0	7.0	7.28	10.0	30.0	-	5.5	2.38	4.67
7.0	7.0	7.28	5.0	30.0	-	5.5	2.53	4.97
7.0	7.0	7.28	5.0	35.0	-	5.5	2.74	5.37
7.0	7.0	7.28	5.0	40.0	-	5.5	2.93	5.75
7.0	7.0	7.28	5.0	45.0	-	5.5	3.14	6.17

Temp. = 30.0 ± 0.1°C

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

The effect of pH was examined in the range 4.5 – 7.5. 1/ k_{cat} versus pH plot indicates a maximum at pH = 5.5 (Table–1, fig.2). An increase in the acetone led to a decrease in the rate. Free radical scavengers, viz., acrylamide and allyl alcohol had no effect on the reaction rate.

Table-2: Activation Parameters for Mn^{II} catalyzed periodate oxidation of p-bromoaniline in acetone-water medium

$[NaIO_4]\times10^4 = 7.0$ mol dm^{-3}, $[PBA]\times10^5 = 7.0$ mol dm^{-3}, $[Mn^{II}]\times10^6 = 7.28$ mol dm^{-3},
Acetone = 5.0% (v/v), pH = 5.5, λ_{max} = 456 nm

Temp. (±0.1) K	$k_{cat}\times10^{-5}$ (dm^6 mol^{-2} s^{-1})	Temp. Coeff.	ΔE (kJ mol^{-1})	A×10^{-8} (dm^3 mol^{-1} s^{-1})	-ΔS$^\#$ (J mol^{-1} K^{-1})	ΔH$^\#$ (kJ mol^{-1})	ΔF$^\#$ (kJ mol^{-1})
298	4.98	-----	-----	7.02	106.61	8.91	41.21
303	5.37	-----	11.79	7.03	106.72	8.87	41.74
308	5.75	1.16	11.08	7.02	106.88	8.83	42.28
313	6.17	1.15	11.43	7.02	107.01	8.79	42.81
Mean values		1.152 ± 0.57	11.43 ± 0.39	7.02 ± 0.004	106.80 ± 0.150	8.85 ± 0.047	42.01 ± 0.597

ΔE from graph: 11.40397 kJ mol^{-1}

The rate constants were determined at four different temperatures (35.0 to 50.0°C) under the conditions, [PBA] = 7.0×10^{-5} mol dm^{-3}, [NaIO$_4$] = 7.0×10^{-4} mol dm^{-3}, [Mn^{II}] = 7.28×10^{-6} mol dm^{-3}, Acetone = 5.0 % (v/v), pH = 5.5, λ_{max} = 456 nm. 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 as ΔE = 11.43 kJ mol^{-1}, A = 7.02×10^{8} dm^{3} mol^{-1} s^{-1}; $\Delta S^{\#}$ = – 106.80 J mol^{-1} K^{-1}, $\Delta G^{\#}$ = 42.01 kJ mol^{-1} and $\Delta H^{\#}$ = 8.85 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.

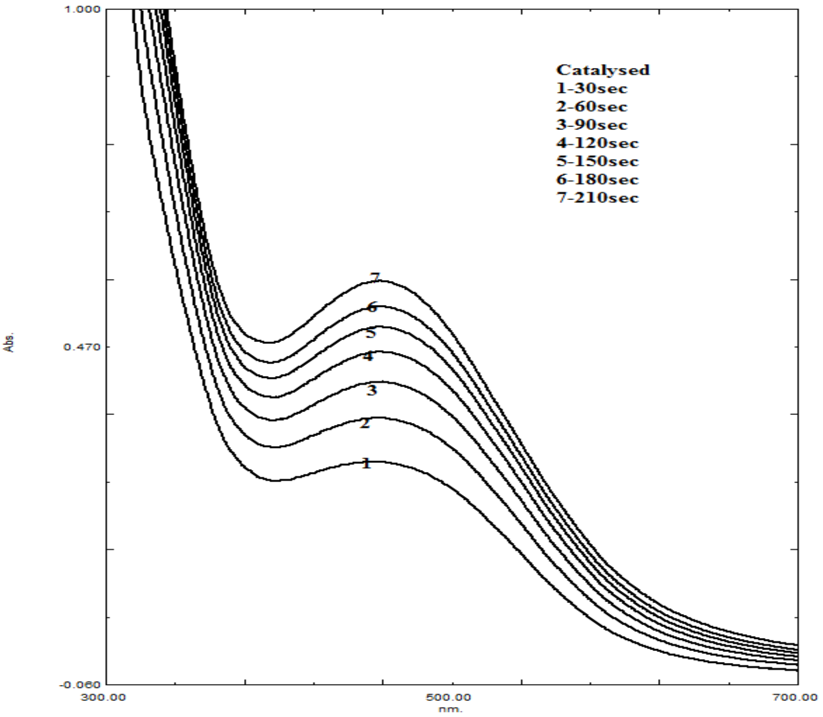


Fig 1: Rapid UV-VIS scan of reaction solution at different time at pH = 5.5, [NaIO4] = 2.0×10^{-3} mol dm^{-3}, [PBA] = 2.0×10^{-4} mol dm^{-3}, [Mn (II)] = 7.28×10^{-6} mol dm^{-3}, Acetone = 5.0 % (v/v), Temp = 30.0 ± 0.1^{0}C.

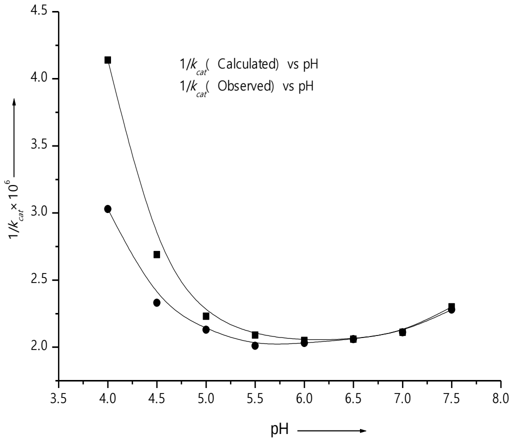


Fig 2: 1/k$_{cat}$ (observed) or 1/k$_{cat}$(calculated) – pH profile at [NaIO$_4$] = 7.0×10^{-4} mol dm^{-3}, [PBA] = 7.0×10^{-5} mol dm^{-3},[Mn^{II}] = 7.28×10^{-6} mol dm^{-3},Acetone = 5.0 % (v/v), λ_{max} = 456 nm,Temp = 30.0 ± 0.1 ^{0}C.

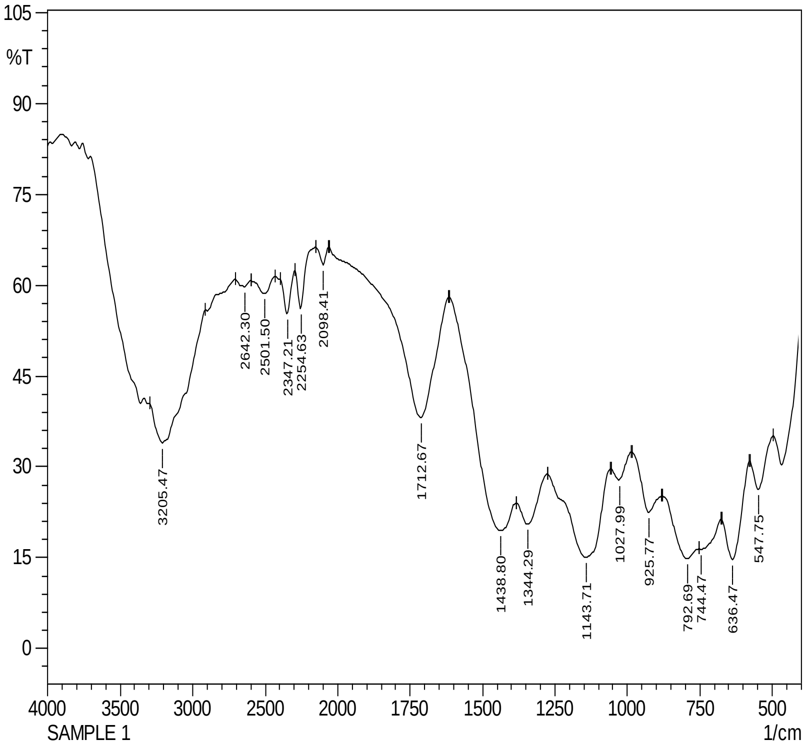
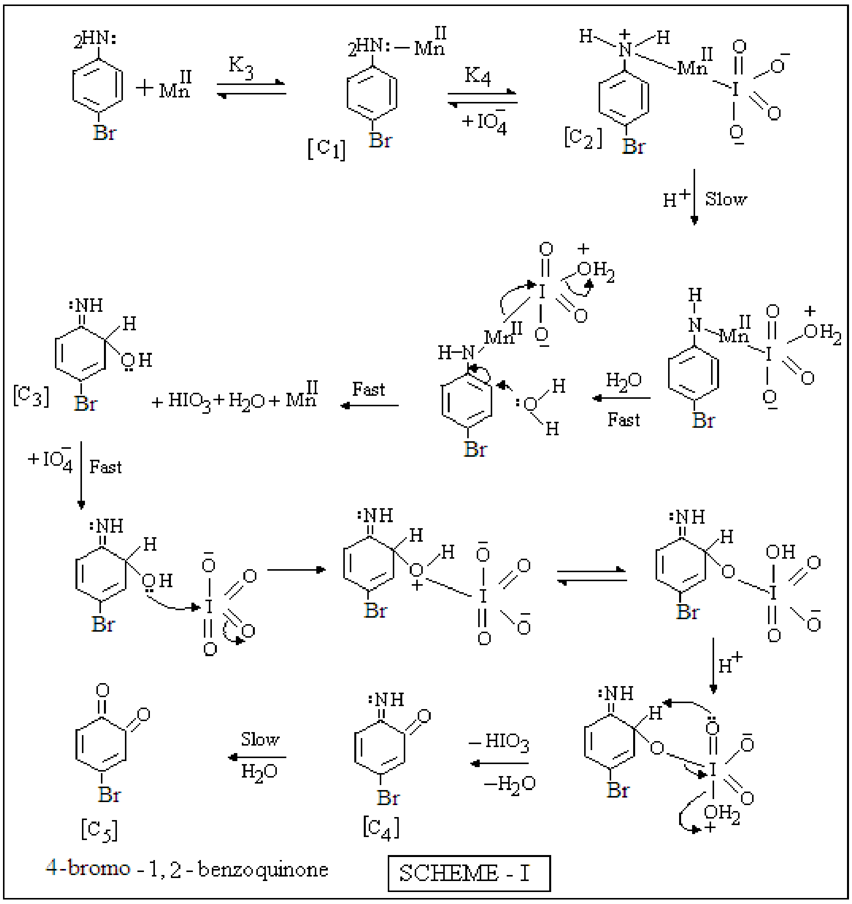


Figure 3: IR spectrum of 4-bromo-1, 2-benzoquinone



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 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 PBA into a 4-bromo–1,2–benzoquinone. Secondly, the kinetic order of one in periodate against the requirement of two periodate molecules for each PBA 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, $1/k_{cat}$ versus $[H^+]$ 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.

In aqueous solutions, periodate exists in following equilibria. (3–4).

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

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

The value of K_1 indicates that in the pH range 4.5 – 7.5 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. In aqueous solution, p-bromoaniline [39], undergoes the following acid – base equilibrium with $K_b = 1.05 \times 10^{-10}$.

$$BrC_6H_4NH_2 + H_2O \rightleftharpoons BrC_6H_4N^+H_3 + OH^- \qquad \text{----------} (5)$$

Since in the studied pH-range, both $BrC_6H_4NH_2$ and $BrC_6H_4N^+H_3$ exist, these species have been taken into account. The pH effect may be explained by assuming the $BrC_6H_4NH_2$ and $H_4IO_6^-$ to be reactive.

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

$$BrC_6H_4NH_2 + Mn^{2+} \overset{K_3}{\rightleftharpoons} [C_1] \qquad \text{-----}(6)$$

$$[C_1] + [IO_4^-] \overset{K_4}{\rightleftharpoons} [C_2] \text{ (fast)} \qquad \text{--------}(7)$$

$$[C_2] \xrightarrow{k} [C_3] + H_2O + HIO_3 + Mn^{2+} \text{ (slow)} \qquad \text{--------}(8)$$

$$[C_3] + IO_4^- + H^+ \longrightarrow [C_4] + H_2O + HIO_3 \text{ (fast)} \qquad \text{--------}(9)$$

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.

$$[C_4] \longrightarrow [C_5] \text{ (Product)} \qquad \text{--------}(10)$$

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 (Chart 1), the catalytic role of Mn^{2+} appears to be due to the formation of a ternary complex, $[(PBA)Mn(H_4IO_6)]^+$, in which Mn acts as a conduit for electron transfer.

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

$$d[C_4]/dt = kK_3K_4 [Mn^{II}][IO_4^-][BrC_6H_4NH_2] \qquad \text{--------}(11)$$

On substituting the values of concentrations of the reactive species [$BrC_6H_4NH_2$] and [IO_4^-] in terms of equilibria (3-4) and (5), respectively, in eq. (2), the complete rate law including [H^+] - dependence becomes:

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

On replacing the term, [OH^-][H^+], by K_w in numerator, and [OH^-] by K_w/ [H^+] in denominator, and on rearranging, the equation(12) becomes equation(13).

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[PBA]\ [IO_4^-]\ [H^+]\ /\{K_2\ K_w + (K_w + K_b\ K_2)[H^+] + K_b[H^+]^2\} \quad \text{--------}(13)$$

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

$$k_{cat} = k\ K_3K_4\ K_w[H^+]/\{K_2\ K_w + (\ K_w + K_b\ K_2\ )\ [H^+] + K_b\ [H^+]^2\} \quad \text{--------}(14)$$

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

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

The k_{cat} and pH data were fitted to Eq. 15 and the best fit Value of composite rate constant kK_3K_4 was found to 4.95×10^5 dm^6 mol^{-2} s^{-1}. The plot comprising of the experimental data and calculated data is shown in fig. 2. In this case, all experimental values are in good agreement and fall on the calculated line which confirms the applicability of Eq. 15 in the studied pH range i.e. 4.5 – 7.5.

The nature of the rate law (15) shows that a plot of $1/k_{cat}$ versus [H^+] shall pass through a minimum [40]. 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 $d[1/k_{cat}]\ /\ d[H^+]$ equal to zero for obtaining hydrogen ion concentration at which the $1/k_{cat}$ vs [H^+] profile will pass through minimum, we obtain,

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

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

$$[H^+]_{min} = 9.10 \times 10^{-7}\ mol\ dm^{-3}$$

It is noteworthy that the calculated value of $[H^+]_{min}$ is in satisfactory agreement with the experimental value of $[H^+]_{min}$ of 6.43×10^{-7} mol dm^{-3} obtained from $1/k_{cat}$ versus pH plot (Fig. 2) and this provides strong support to the proposed mechanism. The data presented in this paper, their interpretation, explanation of effect of pH on reaction rate, and the derived rate law that has been verified by experimental facts is different from what has earlier been reported in literature for uncatalysed periodate oxidation of p-benzoquinone.

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