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EVALUATION OF KINETIC PARAMETERS FOR $\mathbf{Mn^{II}}$ CATALYZED PERIODATE OXIDATION OF *m*-TOLUIDINE: A MECHANISTIC STUDY

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ABSTRACT

The reaction kinetics of oxidation of *m*-toluidine by periodate in the acetone-water medium in the presence of Mn^{II} as catalyst was investigated systematically by detecting the change in absorbance of the intermediate of reaction. Results manifest that the reaction was first order with respect to both reactant and catalyst. It has been found that the reaction rate is not affected by free radical scavengers. However, the dielectric constant decreases in the medium decrease the reaction rate. Consequently, $1/k_{cat}$ versus $[H^+]$ plot was found to be in accordance with the rate law. The thermodynamic parameters were evaluated and the mechanism of the reaction has been proposed.

Keywords: Kinetics, Mechanism, Mn^{II}, Periodate, m-Toluidine, 3-Methyl-p-benzoquinone

INTRODUCTION

Most of the aromatic amines are carcinogenic in nature but their oxidant products quinones are not carcinogenic. The detailed communications are present on the kinetic-mechanistic studies for the uncatalyzed/Mn^{II} catalyzed periodate oxidation of aromatic amines[1-17]. Detailed transcripts are also accessible on the kinetics and mechanism for the uncatalyzed periodates oxidation of *m*-toluidine[11]. It is significant enumerating the methods developed for detecting some aniline derivatives catalyzed by Mn^{II} employing the reactions of periodate[18,19]. The studies on formed ternary intermediate complex in the Mn^{II} catalyzed periodate oxidation and evaluation of stability constant is also reported[20-22]. The investigations are significant and furthermore, anticipate application in evolving techniques for identification and investigation of aromatic amines overexposure[23]. The findings of kinetic-mechanistic studies made on Mn^{II} catalyzed periodate oxidation of *m*-toluidine (*m*-Tol) are conferred and investigated in this report.

EXPERIMENTAL

Material and Methods

The Analytical Reagent grade chemicals were used for precision work. Sodium metaperiodate (Loba Chemie), *m*-toluidine (Alfa Aesar), acetone (E. Merck), manganese sulfate monohydrate (Aldrich) were used after redistillation/recrystallization. The solutions were prepared in triply distilled water and analytical grade solvents. The pH of the reaction medium was maintained by Thiel, Schultz and Koch buffer[24].

The calculated amounts of reactants were mixed, giving the pink color solution which changed to yellow-brown on long-overdue. These observations show the preliminary formation of intermediates preceding the final product. Further absorption maxima of IO_4^-, *m*-Tol, and Mn^{II} do not exhibit absorption in the visible region. Therefore, the absorption maxima catalyzed/uncatalyzed was recorded at 490 nm using

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Shimadzu double beam spectrophotometer (UV-2550) having high precision thermostatic control (TCC). In the rapid scan absorption spectra of the reaction mixture, no change in absorption maximum was found under experimental conditions as shown in Fig.-1.

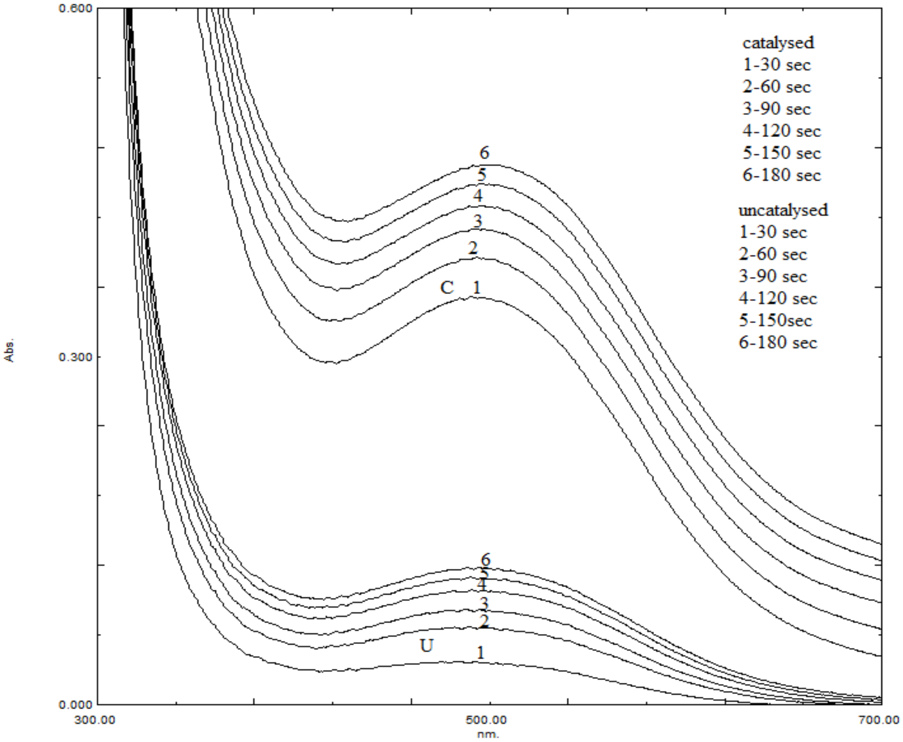


Fig.-1: Compression of UV-VIS rapid scan of uncatalyzed and catalyzed reaction at [*m*-Tol] ×10^4 =4.0 mol/m^3, [NaIO$_4$] ×10^3=4.0 mol/m^3, Acetone= 5.0 % (v/v), Temp. = 30.0 ± 0.1^{0}C, pH=5.5, for catalyzed reaction [Mn(II)] ×10^7 = 7.28 mol/m^3 only; U and C represent the uncatalyzed and catalyzed reaction respectively.

Product Analysis

The reaction mixture including oxidant in abundance was processed, agitated and retained for 24 hours. The change in color from pink to yellow-brown was observed which was further followed by precipitation. The filtrate was extracted with petroleum ether (40 - 60^{o}C) and concentrated at room temperature. TLC of the compound using Chloroform: Acetone: Benzene (10: 05: 85) as an eluent revealed the presence of two compounds. The final product was confirmed by the following characteristics positive test for quinone[25], melting point 67^{o}C (sublimes) (literature value 67-70^{o}C[26](sublimes)), and UV spectrum (absorption maxima in alcohol at 260, 320 and 435 nm respectively, where documented values[27] are 264, 312 and 429 nm). The IR spectrum showed the bands of this compound (in KBr) at 1665 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[28]), 3260 cm^{-1}(s) (maybe due to overtones of C=O stretch as the frequency is about twice that of C=O stretch), 2725 cm^{-1}(s) (due to isolated C–H stretching[29-30]). Further, the bands at 1380 cm^{-1}(s) and 1350 cm^{-1} (s) (maybe due to C=C ring stretch), 1384 cm^{-1} (s) (C-CH$_3$ bending) 1200 cm^{-1} (m) and 1100 cm^{-1}(m) (may be due to in-plane C-H bending) and the bands at 710 cm^{-1}(m)(s) and 660 cm^{-1}(m) (due to out of plane C=C bending mode). On the basis of the above observation, the major yellow colored product was identified as 3-methyl-*p*-benzoquinone.

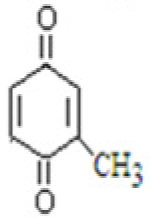
RESULTS AND DISCUSSION

Reaction Stoichiometry

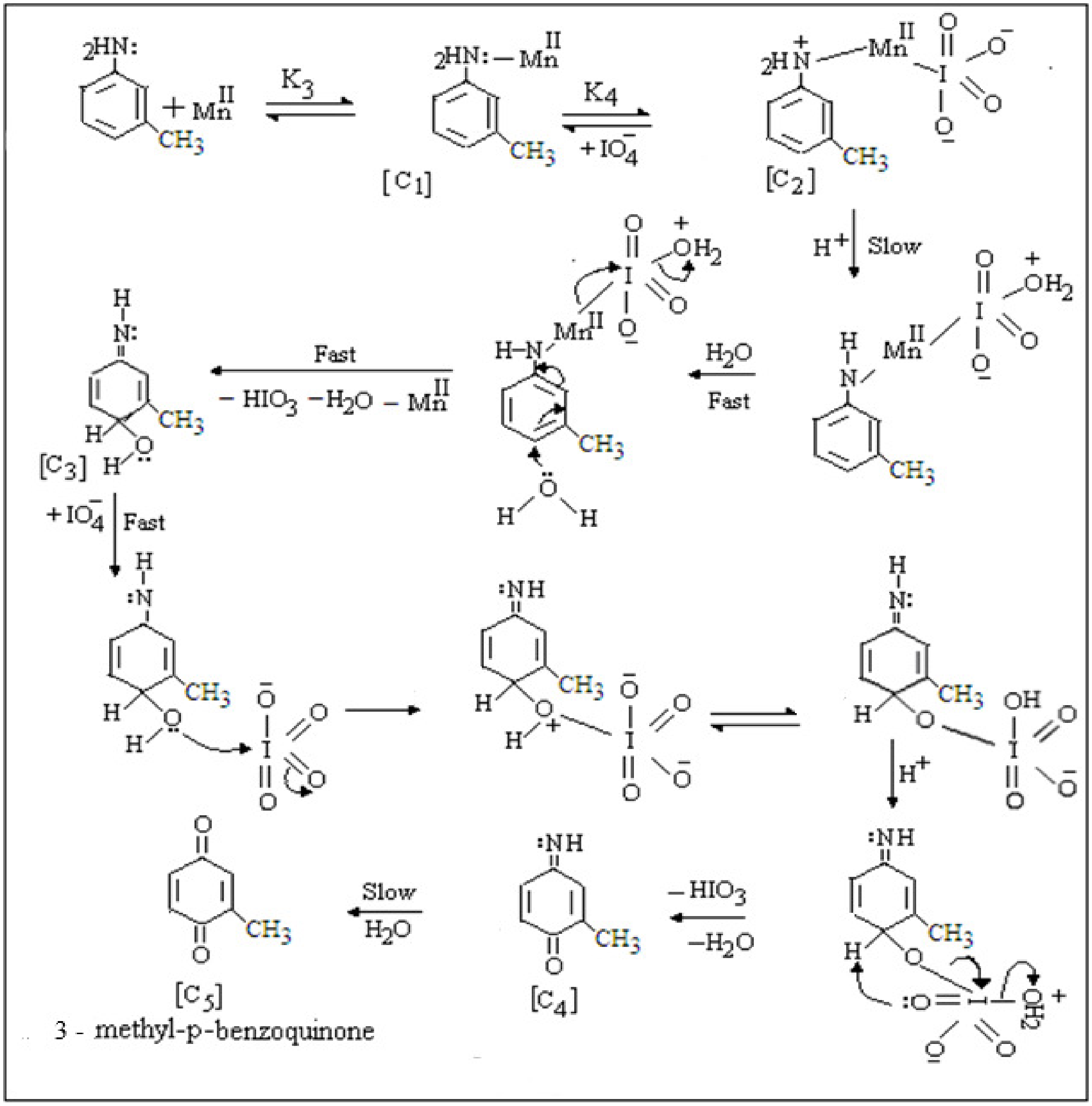
Iodimetric estimation of the substrate and unreacted periodate reacted with an excess of NaIO$_4$ was done. The pseudo-first-order behavior was observed in the plot between log (a-x) and time (where a-x is the concentration of unreacted periodate) to inflection point which is corresponding to the completion of the first stage of reaction for which the kinetics was studied. As given underneath, it was established that 2 moles of periodate for the initial stage of the reaction was consumed by 1 mol of *m*-Tol.

$$CH_3C_6H_4NH_2 + 2IO_4^- + 2H^+ \xrightarrow{Mn^{II}} CH_3C_6H_3O_2 + 2HIO_3 + NH_3 \qquad (1)$$

In afterward stages of the reaction, another molecule of periodate may react to give other reaction products.



[C5]
3 - methyl-p-benzoquinone



Scheme-1

Rate Law

The pseudo-order conditions were maintained for the kinetic study by keeping the periodate concentration in abundance. For the assessment of pseudo-first-order rate constants, k_{obs} Guggenheim's method was used. Hence, the rate law explained the kinetics (eqn.-2).

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

Where, $k_{obs} = k_{cat}\,[IO_4^-]_0\,[Mn^{II}]$,

k_{cat} = rate constant for Mn^{II} catalyzed pathway.

$[IO_4^-]_0$ and $[m\text{-Tol}]_0$ = the initial concentration of periodate and substrate.

In the absence of Mn^{II}, no momentous reaction occurred. The resultant values of k_{cat} for distinctive $[Mn^{II}]$, $[IO_4^-]_0$ and $[m\text{-Tol}]$ are found to be in excellent assertion and invariable with the rate law eq.(2) (Table-1).

Table-1: Effect of Variation of Concentration of Reactants, $[Mn^{II}]$, pH, Ionic Strength and Dielectric Constant on the Reaction Rate Constants

$[NaIO_4]\times10^5$ (mol/m^3)	[*m*-Tol]$\times10^5$ (mol/m^3)	[Mn(II)]$\times10^6$ (mol/m^3)	Acetone (v/v)%	[NaCl]$\times10^3$ (mol/m^3)	pH	Temp. ± 0.1^0C	$k_{obs}\times10^3$ (s^{-1})	$k_{cat}\times10^{-6}$ ($m^6mol^{-2}\,s^{-1}$)
50.0	9.0	7.28	5.0	-	5.5	30.0	5.99	1.65
60.0	9.0	7.28	5.0	-	5.5	30.0	7.39	1.69
70.0	9.0	7.28	5.0	-	5.5	30.0	8.70	1.71
80.0	9.0	7.28	5.0	-	5.5	30.0	10.0	1.72
90.0	9.0	7.28	5.0	-	5.5	30.0	11.4	1.73
100.0	9.0	7.28	5.0	-	5.5	30.0	12.7	1.74
70.0	9.0	7.28	5.0	-	5.5	30.0	8.70	1.71
70.0	10.0	7.28	5.0	-	5.5	30.0	8.84	1.73
70.0	11.0	7.28	5.0	-	5.5	30.0	8.87	1.74
70.0	12.0	7.28	5.0	-	5.5	30.0	9.01	1.76
70.0	13.0	7.28	5.0	-	5.5	30.0	9.04	1.77
70.0	14.0	7.28	5.0	-	5.5	30.0	9.06	1.78
70.0	9.0	3.28	5.0	-	5.5	30.0	3.45	1.65
70.0	9.0	5.28	5.0	-	5.5	30.0	6.21	1.68
70.0	9.0	7.28	5.0	-	5.5	30.0	8.70	1.71
70.0	9.0	9.28	5.0	-	5.5	30.0	11.22	1.73
9.0	70.0	7.28	2.5	-	5.0	30.0	6.63	1.30
9.0	70.0	7.28	2.5	-	5.5	30.0	8.70	1.71
9.0	70.0	7.28	2.5	-	6.0	30.0	9.65	1.89
9.0	70.0	7.28	2.5	-	6.5	30.0	9.91	1.94
9.0	70.0	7.28	2.5	-	7.0	30.0	9.69	1.90
9.0	70.0	7.28	2.5	-	7.5	30.0	8.88	1.74
9.0	70.0	7.28	2.5	-	8.0	30.0	7.06	1.38
70.0	9.0	7.28	5.0	1.0	5.5	30.0	8.70	1.71
70.0	9.0	7.28	5.0	2.0	5.5	30.0	8.81	1.73
70.0	9.0	7.28	5.0	3.0	5.5	30.0	8.91	1.74
70.0	9.0	7.28	5.0	4.0	5.5	30.0	8.95	1.76
70.0	9.0	7.28	2.5	-	5.5	30.0	8.99	1.76
70.0	9.0	7.28	5.0	-	5.5	30.0	8.70	1.71
70.0	9.0	7.28	7.5	-	5.5	30.0	8.41	1.65
70.0	9.0	7.28	10.0	-	5.5	30.0	8.23	1.62

Effect of pH, Ionic Strength, Dielectric Constant, Free Radical Scavengers and Temperature

The impact of pH on the rate of reaction was studied in the pH range 5.0 to 8.0, since the reacting species are differently protonated. The 1/ k_{cat} vs. pH plot indicate minimum pH at 6.5 (Fig.-3). Since, the solubility of the substrate is in 5.0% (v/v) acetone-water mixtures therefore, the kinetics had been studied in the same. Consequently, it became fundamental to analyze the consequence of varying ratio of acetone in a binary reaction mixture on the rate of reaction. Increments in the acetone (2.5-10.0%) i.e. lowering dielectric constant (D) of the medium, leading to lowering the rate. The graphical plots between k_{cat} vs. 1/ D, were found to be a straight line with a negative slope. It was also found that there was no involvement of free radical scavengers, namely, acrylamide and allyl alcohol on the reaction rate.

At four different temperatures (30.0 to 45.0°C) the rate constants and thermodynamic parameters (Table-2) viz. activation energy (ΔE) = 13.76 kJ mol^{-1}, entropy of activation ($\Delta S^{\#}$) = – 88.87J mol^{-1} K^{-1}, Arrhenius frequency factor (A) = 9.86× 10^{14} m^{3} mol^{-1} s^{-1}, free energy of activation ($\Delta G^{\#}$) = 38.77 kJ mol^{-1} and enthalpy of activation ($\Delta H^{\#}$) = 11.18 kJ mol^{-1} were recorded. The resultant $\Delta G^{\#}$ was found to be temperature dependent. The high negative value of $\Delta S^{\#}$ is suggestive of solvent interactions and the probability that the transition state may be solvated whereas a small value of ΔE is representing the catalyzed reaction. This analysis substantiates that the standard errors of $\Delta H^{\#}$ and $\Delta S^{\#}$ correlate and precede to the center of temperature range used, as stated by the relation[31]: $T_{av} = \sigma (\Delta H^{\#}) / \sigma (\Delta S^{\#})$.

Table-2: Evaluation of Kinetic parameters for periodate oxidation of *m*-toluidine [*m*-Tol] ×10^{5} = 9.0 mol/m^{3}, [NaIO$_4$] ×10^{4}= 7.0 mol/m^{3}, Acetone = 5.0 %(v/v), [Mn(II)] ×10^{6} = 7.28 mol/m^{3}, pH = 5.5, λ_{max} = 490 nm.

Temp.(°K)	k_{cat}×10^{-6}	Temp.	*Ea*	A×10^{-14} (m^{3}mol^{-1}s^{-1})	-$\Delta S^{\#}$	$\Delta H^{\#}$	$\Delta F^{\#}$
(±0.1°C)	(m^{6} mol^{-2}s^{-1})	Coff.	(kJ mol^{-1})		(Jmol^{-1}K^{-1})	(kJmol^{-1})	(kJmol^{-1})
303	1.7	-	-	14.2420	88.6670	11.2370	38.1033
308	1.8	-	13.9600	10.7290	88.8110	11.1950	38.5492
313	2.0	1.2000	14.8090	8.2107	88.8970	11.1530	38.9788
318	2.2	1.1800	12.4980	6.2699	88.0710	11.1120	39.4370
	Mean values	1.1913	13.7561	9.8600	88.870	11.1747	38.7671
		±0.009	±0.9544	±02.9600	±0.1498	±0.0465	±0.4954

Ea graphical value = 13.861 K.cal mol^{-1}

The fast change in the color of the reaction mixture in comparison to the product formed on retaining for long -overdue specify the formation of colored intermediate within minutes and the final product in hours. During the oxidation of *m*-Toluidine into benzoquinone, various steps are involved in the reaction including several transient intermediates along with a stable C_4 intermediate. The stoichiometry for each *m*-Tol molecule requires two periodate molecule, where one is the rate determining step and another is used up in the fast step suggesting the formation of intermediate C_4 (Eqn.-1). It has been found that the concentration of C_4 cannot be constant as it increases with time reaching a limiting value. The characteristic 1/ k_{cat} versus pH plot (Fig.-3) specify that in the pH region chosen for study[32] the presence of at least three reactive species of reactant (periodate as per this system) was found. It was observed that the reaction rate has no effect on free radical scavengers. As given in the proposed pathway (Scheme-1) the high negative value of entropy of activation suggests the inclusion of salvation effect.

The speciation of *m*-Tol and periodate should be contemplated while conversing a proficient mechanism for the reaction under study. The periodate is transformed into three forms in aqueous solutions containing orthoperiodic acid[33] with equilibria and dissociation constants[34, 35] given below:

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

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

The value of K_1 implies that in the pH range 5.0-8.0 species H_5IO_6 will be almost non-existing and therefore, only species $H_4IO_6^-$ and $H_3IO_6^{2-}$ are contemplated for elucidating the periodate observed pH dependence. Based on this condition, the equilibrium or free concentration of $H_4IO_6^-$, $[H_4IO_6^-]$ shall be related to the entire concentration $[IO_4^-]_0$ by Eq. (5)

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

The species $H_4IO_6^-$ has been considered reactive, as per the later conversed reaction mechanism. In aqueous solution, *m*-Tol undergoes the subsequent acid – base equilibrium with $K_b^{26} = 5.37 \times 10^{-10}$.

$$CH_3C_6H_4NH_2 + H_2O \rightleftharpoons CH_3C_6H_4N^+H_3 + OH^- \quad (6)$$

Since in the learned pH-range, both $CH_3C_6H_4NH_2$ and $CH_3C_6H_4N^+H_3$ exist, these species have been taken into the explanation. From equilibrium (6), the equilibrium or free concentration of amine, [*m*-Tol], is stated by Eq. (7).

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

Where, $[m\text{-Tol}]_0$ is the total concentration of $CH_3C_6H_4NH_2$.

To elucidate the pH – dependence, it is inevitable to presume *m*-Tol and $H_4IO_6^-$ to be reactive species. To interpret the observed kinetics on this base, rate law (Eq. 2), and pH- dependence, the subsequent pathway converses.

$$CH_3C_6H_4NH_2 + Mn^{2+} \overset{K_3}{\rightleftharpoons} [C_1] \quad (8)$$

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

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

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

Where, $[C_1]$, $[C_2]$, $[C_3]$ and $[C_4]$ are intermediates, finally $[C_4]$ rearrangement/ hydrolysis to yield the reaction product, C_5.

$$[C_4] \longrightarrow [C_5] \text{ (Product)} \quad (12)$$

The forming of intermediates $[C_1]$ and $[C_2]$ in a fast step having low values of equilibrium constants, K_3 and K_4, is supposed in the intended gross mechanism. In the detailed mechanism (Scheme-1), the catalytic role of Mn^{2+} appears due to ternary complex formation, $[(m\text{-Tol})Mn(H_4IO_6)]^+$, in which Mn aids in electron movement.

The discoursed mechanism (8-11) precedes to the rate law (13).

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

On replacing the values of concentrations of the reactive species [*m*-Tol] and $[H_4IO_6^-]$ from Eq. (5) and (7) in eq. (13), and taking $H_4IO_6^-$ as IO_4^- for simplicity[32], the concluding rate law containing $[H^+]$ - dependence becomes:

$$d[C]/dt = kK_3K_4[Mn^{II}]K_w[m\text{-Tol}]_0[IO_4^-]_0 [H^+] /\{K_2 K_w +(K_w + K_b K_2)[H^+] + K_b[H^+]^2\} \quad (14)$$

On comparison Eqs. (2) and (14), we get

$$k_{cat} = k K_3K_4 K_w[H^+]/\{K_2 K_w + (K_w + K_b K_2) [H^+] + K_b [H^+]^2\} \quad (15)$$

Rearrangement of Eq. (15) becomes Eq. (16).

$$1/k_{cat} = (K_2 / kK_3K_4 [H^+]) + \{(K_w + K_b K_2) / kK_3K_4 K_w\} + K_b[H^+] / kK_3K_4 K_w \quad (16)$$

The k_{cat} and pH data were substituted to Eqn. (17). The plot encircling both the experimental data and calculated line are shown in the Fig.-2.

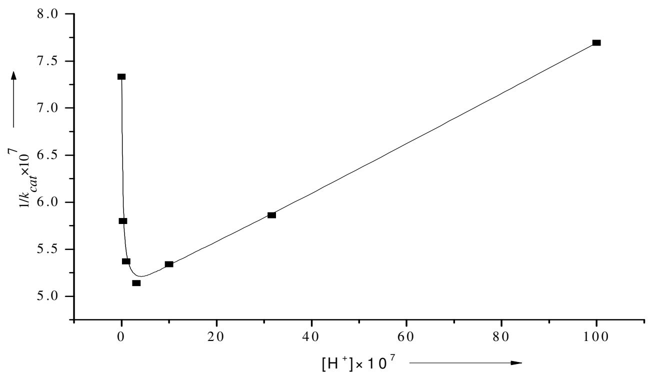


Fig-2: Effect of pH on Rate Constant ($1/k_{cat}$ vs $[H^+]$ plot) at [m-Tol] × 10^5=9.0 mol/m^3, [$NaIO_4$] × 10^4 = 7.0 mol/m^3, Acetone=5.0 % (v/v), [Mn(II)] × 10^6 = 7.28 mol/m^3, Temp. = 30.0 ± 0.1^{0}C, λ_{max} = 490 nm.

All experimental k_{cat} values were found to be in excellent concurrence and subside on the calculated line. Looking at the intricacy of the system, the Eq. (17) satisfactorily elucidates the observed kinetics in the pH range 5.0 to 8.0.

The nature of the rate law (17) discloses that a plot of $1/k_{cat}$ versus $[H^+]$ or pH must surpass through a minimum[17,32]. On differentiating $1/k_{cat}$ w.r.t $[H^+]$, we get the values of $d^2[1/k_{cat}] / d[H^+]^2$. The value of the second derivative is found to be positive showing the plot of $1/k_{cat}$ versus $[H^+]$ or pH to pass through a minimum. Thus, on putting $d[1/k_{cat}] / d[H^+]$ equitable to zero for getting hydrogen ion concentration at which the $1/k_{cat}$ vs $[H^+]$ outline will pass through minimum (Fig.-2), we get,

$$[H^+]_{min} = (K_2 K_w / K_b)^{1/2} \quad (17)$$

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

$$[H^+]_{min} = 2.85 \times 10^{-7} \text{ mol/m}^3$$

It is notable that the calculated value of $[H^+]_{min}$ is in excellent concurrence with the experimental value of $[H^+]_{min}$ of 3.16×10^{-7} mol dm^{-3} obtained from $1/k_{cat}$ vs. pH plot (Fig. 3) and this stipulates excellent support to the conversed pathway.

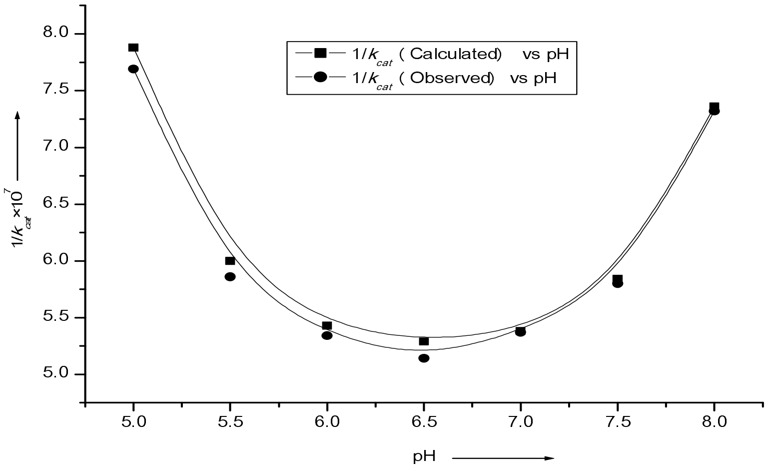


Fig.-3: $1/k_{cat}$ (Calculated) or $1/k_{cat}$ (Observed) vs. pH at [m-Tol] ×10^5=9.0 mol/m^3, [$NaIO_4$] ×10^4 = 7.0 mol/m^3, Acetone=5.0 % (v/v), [Mn(II)] × 10^6 = 7.28 mol/m^3, Temp. = 30.0±0.1^{0}C, λ_{max}= 490 nm.

CONCLUSION

The methods developed by us are cost effective; include the application of simple equipment and easily available chemicals. This method is improved than some of the beforehand detailed methods in terms of the easiness of the process involved. Moreover, this method is less time consuming as no pretreatment of the specimens etc. are involved except in cases where some rare interferants are present as already investigated. As a consequence, this method has substantial probability in trace mechanism (Scheme-I) of Mn^{II} catalyzed periodate oxidation of *m*-Toluidine.

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