Asian Journal of Chemistry Vol. 22, No. 3 (2010), 2136-2146

Kinetic-Spectrophotometric Studies on Periodate Oxidation of 2-Amino-*p*-Xylene in Acetone-Water Medium

R.D. KAUSHIK*, PURNIMA SUNDRIYAL, TARUN KUMAR† and PRABHA SINGH†
Department of Chemistry, Gurukul Kangri University, Haridwar-249 404, India
E-mail: rduttkaushik@yahoo.co.in

The results of kinetic-mechanistic study on the periodate oxidation of 2-amino-*p*-xylene (XYL) have been presented and discussed. The reaction has been followed by monitoring the increase in the absorbance of reaction mixture spectrophotometrically. The reaction followed second order behaviour, being first order in each reactant. The rate of reaction decreases with decrease in dielectric constant of the medium. Free radical scavengers do not affect the reaction rate. A positive effect of ionic strength on rate is observed. The stoichiometry has been found to be 1 mol XYL: 2 mol of periodate. Thermodynamic parameters evaluated are: $E_a = 7.3$ kcal mol^{-1}, A = 9001 dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -43.7$ cal mol^{-1}, $\Delta G^{\#} = 20.4$ kcal mol^{-1} and $\Delta H^{\#} = 6.6$ kcal mol^{-1}. The rate law, under pseudo first order conditions, $[IO_4^-] >> [XYL]$, is given by, $d[C]/dt = kK [IO_4^-]_0[S] / (1+K[IO_4^-]_0)$. Likewise, under the conditions, $[XYL] >> [IO_4^-]$, it is: $d[C]/dt = kK [IO_4^-] [S]_0 / (1+K[S]_0)$. The complete rate law including the $[H^+]$ dependence under the conditions, $[IO_4^-] >> [XYL]$, is given by: $d[C]/dt = kKK_w [S] [IO_4^-]_0 [H^+]/\{K_2 K_w + (K_w + K_b K_2) [H^+] + K_b [H^+]^2\}$where kK is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$, K_b is base dissociation constant of XYL. [S] is the concentration of XYL and $[IO_4^-]_0$ represents the concentration of periodate that has been taken in excess. The value of $[H^+]$ at which minima is obtained in the $1/k_2$ - $[H^+]$ profile, is in excellent agreement with that calculated from the derived rate law. Main reaction product isolated and characterized is 2,5-dimethyl-1,4-benzoquinone.

Key Words: Kinetics and mechanism, 2-Amino-*p*-xylene, Periodate oxidation, 2,5-Dimethyl-1,4-benzoquinone.

INTRODUCTION

In the light of contrary reports already available in literature[1-6] and in continuation to our earlier studies[7-11], the results of kinetic studies on the periodate oxidation of 2-amino-*p*-xylene (XYL) in acetone-water medium are being presented in the present communication. Our results are contradictory in many respects with those reported earlier[12] in case of oxidation of 2,5-dimethylaniline and 2,3-dimethylaniline in acetic acid medium. Further, it is the first report on this reaction that tests the derived rate law with the observed $[H^+]$ dependence of reaction rate.

---

†Department of Chemistry, D.A.V. (P.G.) College, Muzaffarnagar-251 001, India.

EXPERIMENTAL

Thiel, Schultz and Koch buffer[13], 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. Sodium meta periodate (E. Merck), 2-amino-*p*-xylene (Sigma-Aldrich), acetone (E. Merck) 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. Systronics digital pH-meter-802 was used for measuring the pH of reaction mixture. High precision thermostatically controlled water bath with an accuracy of ± 0.1 ºC was employed for maintaining the desired temperature. The reactions were initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing the 2-amino-*p*-xylene and buffer and maintained at the desired temperature (± 0.1 ºC). The kinetics of the oxidation was followed by monitoring the increase in the absorbance of reaction mixture (due to the intermediate C) at different time on Shimadzu double beam spectrophotometer (UV Pharmaspec-1700), at 540 nm, *i.e.*, the λ_{max} of the light orange coloured reaction mixture. λ_{max} was found to remain unchanged during the period of study of the reaction as well as on changing the pH. pH of reaction mixtures was kept constant by using the buffer at 5.5 except the case where the effect of pH was studied.

Product analysis: Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially the solution turned light orange, thereafter dark orange and finally the product was precipitated on standing. It was filtered and the filtrate was extracted with petroleum ether (40-60 ºC). The extract was evaporated at room temperature to get a yellow coloured solid that was characterized by single spot in TLC. It was recrystallized in ethyl alcohol and characterized as 2,5-dimethyl-1,4-benzoquinone on the basis of positive test for quinone[14], m.p. 126 ºC (literature value 125 ºC for 2,5-dimethyl-1,4-benzoquinone), UV spectrum (in ethanol giving absorption maxima at 252, 315, 420 and 450 nm, (literature values 255, 310, 425 and 444 nm for 2,5-dimethyl-1, 4-benzoquinone[15]).

The IR spectrum of compound (in KBr) showed the presence of bands at 2700 cm^{-1} (s) (due to ring C-H stretch), 1640 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), 3275 cm^{-1} (s) (may be due to overtones of C=O stretch as the frequency is about twice that of C=O stretch). Further, the bands at 1400 cm^{-1} (s), 1500 cm^{-1} (s) may be due to C=C ring stretch. The bands at 1110 cm^{-1} (m) to 1165 cm^{-1} (m) may be due to in plane C-H bending and at 820 cm^{-1} (m) (due to out of plane C=C bending mode). The melting point, UV-Vis spectrum and IR spectrum are in good agreement with those reported/expected for 2,5-dimethyl-1,4-benzoquinone.

RESULTS AND DISCUSSION

Preliminary observations: On mixing the reactants, the solution becomes light orange which later darkens and 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 yellow solution showed the λ_{max} of the intermediate C to be 540 nm. The UV-visible spectra of IO_4^- and 2-amino-*p*-xylene indicated no absorption in visible region. Hence for following the kinetics the absorbance changes were recorded at 540 nm at which only the intermediate C absorbs. Plane mirror and Guggenheim's methods, respectively were used for evaluation of initial rates, (dC/dt) and pseudo first order rate constants, k_{obs}.

Stoichiometry: A known excess of $NaIO_4$ was added to react with substrate. At suitable intervals of time, the reaction mixture was pipetted out and the product, either in turbid or in precipitated form was extracted with chloroform. Now the reaction mixture was estimated for the unconsumed $NaIO_4$ iodimetrically. The graphical plot (Fig. 1) obtained in this way, followed the pseudo first order behaviour upto a point after which inflexion was obtained in the curve. It was taken as the point corresponding to the completion of the first stage of the reaction for which the kinetic studies were made. The results indicate the stoichiometry to be 1 mol of 2-amino-*p*-xylene: 2 moles of periodate as in eq. (1).

$$CH_3CH_3C_6H_3NH_2 + 2IO_4^- + 2H^+ \longrightarrow CH_3CH_3C_6H_2O_2 + 2HIO_3 + NH_3 \quad (1)$$

Order of reaction: The kinetics was studied under pseudo order conditions, *viz.*, $[IO_4^-]_0 >> [S]$ and $[S]_0 >> [IO_4^-]$. Under both these conditions the reaction displayed first order reaction. Under the condition, $[S]_0 >> [IO_4^-]$, the results (Table-1) were defined by following equation and pseudo first order rate constant, k_{obs}, was equal to $k_2[S]_0$.

$$d[C]/dt = k_2\,[IO_4^-]\,[S]_0$$

where k_2 is a pH-dependent second order rate constant.

On the other hand under the condition $[IO_4^-]_0 >> [S]$, the rate was defined by following equation and k_{obs} was equal to $k_2\,[IO_4^-]_0$.

$$d[C]/dt = k_2\,[IO_4^-]_0\,[S]$$

In these equations $[IO_4^-]_0$ and $[S]_0$ represent the initial concentrations of reactants in excess. The values of k_2 determined from k_{obs} values clearly indicate first order in each reactant *i.e.*, periodate and 2-amino-*p*-xylene.

Effect of pH, ionic strength, dielectric constant of the medium, free radical scavengers and temperature: A positive salt effect was indicated by a graphical plot between log k_2 and μ (ionic strength) that was straight line. An increase in dielectric constant increased the rate of reaction as indicated by a linear plot between log k_2 *versus* 1/D, where D is the dielectric constant of the medium. Free radical scavengers like acrylamide, allyl alcohol and allyl acetate had no effect on the reaction rate. These effects (Table-1) indicate an ion-dipole type interaction in the rate-determining step and that the reacting ion is possibly an anion.

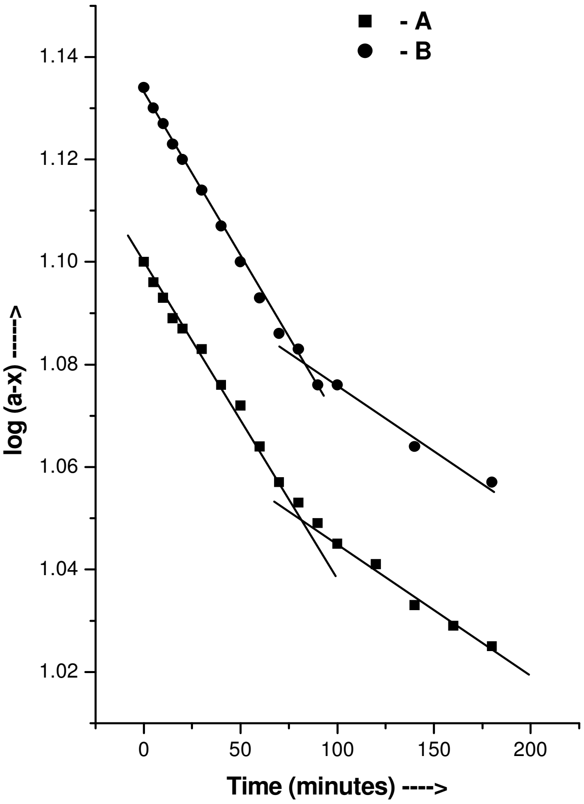


Fig. 1. Determination of stoichiometry of periodate oxidation of 2-amino-*p*-xylene in acetone -water medium at [XYL] × 10^3 = 1.0 mol dm^{-3}, acetone = 5.0 % (v/v), pH = 5.5, Temp. = 35 ± 0.1 ºC and [$NaIO_4$] = 0.01 mol dm^{-3} for curve A and 0.015 mol dm^{-3} for curve B

The effect of pH was examined in the range 4.0-8.5. $1/k_2$ - [H^+] profile indicated a minima at pH = 6.5 (Table-1, Fig. 1), which could be due to change in the nature of species and their relative reactivity when the pH is changed.

The thermodynamic parameters evaluated by determining the rate constants at four different temperatures ranging from 35 to 50 ºC are: E_a = 7.3 kcal mol^{-1}, A = 9001 dm^3 mol^{-1} s^{-1}; $\Delta S^{\#}$ = -43.7 cal mol^{-1}, $\Delta G^{\#}$ = 20.4 kcal mol^{-1} and $\Delta H^{\#}$ = 6.6 kcal mol^{-1}, at [XYL] = 0.002 mol dm^{-3}, [$NaIO_4$] = 0.02 mol dm^{-3}, acetone = 5.0 % (v/v) and pH = 5.5.

Initially, there is appearance of light orange colour which continues to darken with increase in the concentration of the intermediate, C and finally the product settles on standing for long time. We can say that the coloured intermediate C is formed on a time scale of minutes and the final product on a time scale of hours. It appears that the overall reaction involves several steps and possibly several transient intermediates, in addition to comparatively stable one C, are formed during the

TABLE-1
EFFECT OF VARIATION OF CONCENTRATION OF REACTANTS, IONIC STRENGTH, DIELECTRIC CONSTANT AND pH ON THE REACTION RATE; Temp = 35 ± 0.1 ºC

$[NaIO_4]$ (mol dm^{-3})	[XYL] (mol dm^{-3})	Acetone % (v/v)	[NaCl] (mol dm^{-3})	pH	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^2$ (dm^3 mol^{-1} s^{-1})
0.002	0.020	5.0	-	5.5	5.80	2.90
0.002	0.022	5.0	-	5.5	6.10	2.80
0.002	0.024	5.0	-	5.5	6.90	2.90
0.002	0.026	5.0	-	5.5	7.30	2.80
0.002	0.028	5.0	-	5.5	8.10	2.90
0.002	0.030	5.0	-	5.5	8.40	2.80
0.002	0.040	5.0	-	5.5	10.9	2.80
0.020	0.002	5.0	-	5.5	2.30	1.15
0.022	0.002	5.0	-	5.5	2.50	1.12
0.024	0.002	5.0	-	5.5	2.80	1.15
0.026	0.002	5.0	-	5.5	2.90	1.12
0.028	0.002	5.0	-	5.5	3.20	1.15
0.030	0.002	5.0	-	5.5	3.40	1.13
0.040	0.002	5.0	-	5.5	4.50	1.13
0.02	0.002	5.0	-	4.0	0.60	0.30
0.02	0.002	5.0	-	4.5	0.84	0.42
0.02	0.002	5.0	-	5.0	1.20	0.60
0.02	0.002	5.0	-	5.5	2.30	1.15
0.02	0.002	5.0	-	6.0	3.00	1.50
0.02	0.002	5.0	-	6.5	5.00	2.50
0.02	0.002	5.0	-	7.0	2.20	1.10
0.02	0.002	5.0	-	7.5	2.00	1.00
0.02	0.002	5.0	-	8.0	1.60	0.80
0.02	0.002	5.0	-	8.5	1.55	0.78
0.02	0.002	2.5	-	5.5	2.46	1.23
0.02	0.002	5.0	-	5.5	2.30	1.15
0.02	0.002	7.5	-	5.5	2.15	1.07
0.02	0.002	10.0	-	5.5	2.03	1.02
0.02	0.002	5.0	0.001	5.5	2.35	1.18
0.02	0.002	5.0	0.004	5.5	2.46	1.23
0.02	0.002	5.0	0.008	5.5	2.76	1.38
0.02	0.002	5.0	0.120	5.5	3.00	1.50

oxidation of 2-amino-*p*-xylene into benzoquinone. Further, the kinetic order of one in periodate but requirement of the two periodate molecules for each 2-amino-*p*-xylene molecule as per stoichiometry indicates the involvement of only one periodate in the rate determining step and second IO_4^- ion is consumed in a fast step in the formation of the intermediate, C. It also indicates the orange coloured intermediate is quite stable and its concentration is not in steady state. Thus, there should have been no change in its concentration with time. On the contrary, concentration of C increases continuously with time and reaches a limiting value - the happening that was used in following the kinetics of this reaction. Moreover, k_2-$[H^+]$ profile indicates the presence of at least three differently reactive reactant species in the pH region chosen for study.

Rate law: The stoichiometry is given by eqn. 1 as given earlier. Assuming $CH_3CH_3C_6H_3NH_2$ and $H_4IO_6^-$ as the reactive species and based on the observed kinetic data and pH- dependence, the following mechanism can be proposed:

$$CH_3CH_3C_6H_3NH_2 + [IO_4^-] \xrightleftharpoons{K} [A] \qquad (2)$$

$$[A] \xrightleftharpoons{k} \text{Intermediate [B] (slow)} \qquad (3)$$

$$[B] + IO_4^- \longrightarrow \text{Intermediate [C] (fast)} \qquad (4)$$

The intermediate, C, appear to undergo very slow reorganization/hydrolysis to yield the reaction product.

$$\text{Intermediate [C]} \longrightarrow \text{Product} \qquad (5)$$

In the mechanism for simplicity, $H_4IO_6^-$ has been written as IO_4^-. Since the elementary reactions in liquid phase are a rarity, the formation of a transient intermediate [C], which could be a collisional complex/reactant pair in a rapid step having a low value of equilibrium constant, K, is assumed in the proposed gross mechanism.

The mechanistic steps (2-3) lead to the rate law

$$d[C]/dt = k\,[A] \qquad (6)$$

$$= kK[CH_3CH_3C_6H_3NH_2]\,[IO_4^-] \qquad (7)$$

Since the observed kinetics shows first order in each of $[CH_3CH_3C_6H_3NH_2]$ and $[IO_4^-]$, the value of K must be low. This can be proved as follows.

If $[IO_4^-]_0$ and $[S]_0$ represent the initial concentrations of reactants in excess, at a fixed pH, under the condition $[IO_4^-]_0 >> [S]$, the rate formation of intermediate, C, is given by:

$$d[C]/dt = kK\,[IO_4^-]_{free}\,[S]_{free} \qquad (8)$$

where $[IO_4^-]_{free}$ $[S]_{free}$ are the free concentration of two reactants. As $[IO_4^-]$ is in excess initially, its free concentration and initial concentration can be taken as almost the same.

$$d[C]/dt = kK\,[IO_4^-]_0\,[S]_{free} \qquad (9)$$

If total concentration of substrate is represented by [S], then,

$$[S] = [S]_{free} + [S]_C \qquad (10)$$

where $[S]_C$ is the concentration used for formation of complex 'A'.

Further,

$$[S]_C = [A] = K\,[S]_{free}\,[IO_4^-]_0 \qquad (11)$$

From eqns. 10 and 11,

$$[S] = [S]_{free} + K\,[S]_{free}\,[IO_4^-]_0$$

$$\text{or} \quad [S] = [S]_{free}\,(1 + K\,[IO_4^-]_0)$$

$$\text{or} \quad [S]_{free} = [S]\,/\,(1+K[IO_4^-]_0) \qquad (12)$$

From eqns. 9 and 12,

$$d[C]/dt = kK\,[IO_4^-]_0[S]\,/\,(1 + K[IO_4^-]_0) \qquad (13)$$

Likewise, under the condition $[S]_0 >> [IO_4^-]$

$$d[C]/dt = kK\,[IO_4^-]\,[S]_0\,/\,(1 + K[S]_0) \qquad (14)$$

In eqns. 13 and 14, K must be very small to get $K[IO_4^-]_0$ or $K[S]_0$ negligible with respect to 1 and only than the order can be one in both reactants. As the order has been found experimentally one in each reactant, the value of K is very small.

Since the reaction shows first order in each of [S] and $[IO_4^-]$, the inequalities $K[S]_0 << 1$ and $K[IO_4^-]_0 << 1$ should operate in eqns. 13 and 14, leading to the rate laws in eqns. 15 and 16.

$$d[C]/dt = k_2\,[IO_4^-][S]_0 \qquad (15)$$

where k_2 is a pH-dependent second order rate constant and $k_{obs} = k_2[S]_0$.

On the other hand under the condition $[S]o >> [IO_4^-]$, the rate was defined by eqn. 16 and k_{obs} was equal to $k_2\,[IO_4^-]]_0$.

$$d[C]/dt = k_2\,[IO_4^-]_0[S] \qquad (16)$$

The values of k_2 determined from k_{obs} values (Table-1) indicate a clear in each reactant.

Complete rate law including [H$^+$] dependence: The speciation of periodate and 2-amino-*p*-xylene should be considered first.

Speciation of periodate ion:

$$H_5IO_6 \rightleftharpoons H_4IO_6^-, \qquad K_1 = 2.30 \times 10^{-2} \qquad (17)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-}, \qquad K_2 = 4.35 \times 10^{-9} \qquad (18)$$

Total concentration of periodate, $[IO_4^-]$ is sum of $[H_5IO_6]$, $[H_4IO_6^-]$ and $[H_3IO_6^{2-}]$, *i.e.*, $[IO_4^-] = [H_5IO_6] + [H_4IO_6^-] + [H_3IO_6^{2-}]$

From equilibria (17) and (18)

$$[IO_4^-] = \{[H_6IO_6^-]\,[H^+]/K_1\} + [H_4IO_6^-] + \{K_2\,[H_4IO_6^-]/[H^+]\} \qquad (19)$$

$$[IO_4^-] = [H_4IO_6^-]\,\{[H^+]/K_1 + 1 + K_2/[H^+]\} \qquad (20)$$

On substituting $[H^+] = 10^{-6}$ to 10^{-9} (pH = 6 to 9) and $K_1 = 2.30 \times 10^{-2}$ in eqn. 20, we get $[IO_4^-] = [H_4IO_6^-]\,[(4 \times 10^{-5}$ to $4 \times 10^{-8}) + 1 + (4.35 \times 10^{-3}$ to $4.35)]$.

So $[H^+]/K_1$ term is negligible in eqn. 20 as compared to two other terms. On neglecting $[H^+]/K_1$ in eqn. 20, we get

$$[IO_4^-] = [H_4IO_6^-]\,(1 + K_2/[H^+])$$

$$\text{or} \qquad [IO_4^-] = \{[H_4IO_6^-]([H^+] + K_2)\}/[H^+]$$

$$\text{or} \qquad [H_4IO_6^-] = [IO_4^-]\,[H^+]\,/\,([H^+] + K_2) \qquad (21)$$

Speciation of aniline:

$$CH_3CH_3C_6H_3NH_2 + H_2O \rightleftharpoons$$

$$CH_3CH_3C_6H_3NH_3^+ + OH^-;\ K_b = 3.39 \times 10^{-10} \qquad (22)$$

Similarly from equilibrium (6), the total concentration of the substrate, [S] is given by

$$[S] = [CH_3CH_3C_6H_3NH_2] + [CH_3CH_3C_6H_3NH_3^+]$$

$$[S] = [CH_3CH_3C_6H_3NH_2] + K_b[CH_3OC_6H_4NH_2]/[OH^-]$$

$$[S] = [CH_3CH_3C_6H_3NH_2](1 + K_b/[OH^-])$$

$$[S] = \{[CH_3CH_3C_6H_3NH_2]([OH^-] + K_b)\}/[OH^-]$$

Reactive free $[CH_3CH_3C_6H_3NH_2]$ is given by

$$[CH_3CH_3C_6H_3NH_2] = [S]\,[OH^-]/\{[OH^-] + K_b\} \qquad (23)$$

The rate is given by

$$\text{Rate} = kK[CH_3CH_3C_6H_3NH_2][H_4IO_6^-] \qquad (7)$$

where $[H_4IO_6^-] = [IO_4^-]$

Under the condition when oxidant is taken in excess and on substituting the values of $[CH_3OC_6H_4NH_2]$ and $[H_4IO_6^-]$ from eqns. 21 and 23 in to eqn. 7,

$$\text{Rate} = kK\big([S][OH^-]/\{[OH^-] + K_b\}\big)\big([IO_4^-]_0\ [H^-]/([H^+] + K_2)\big) \tag{24}$$

or $\text{Rate} = kK\{[S]\ [OH^-]/[OH^-] + K_b\}\{[IO_4^-]_0\ [H^+]/[H^+] + K_2\}$

or $$\text{Rate} = kK[S][OH^-][IO_4^-]_0\ [H^+]/\big(\{[OH^-] + K_b\}([H^+] + K_2)\big) \tag{25}$$

On putting, $K_w = [OH^-][H^+]$ in numerator in eqn. 25,

$$\text{Rate} = kKK_w[S][IO_4^-]_0/\big(([OH^-] + K_b)\ ([H^+] + K_2)\big) \tag{26}$$

or $\text{Rate} = k\ K\ K_w[S][IO_4^-]_0/\{[OH^-][H^+] + [OH^-]K_2 + K_b[H^+] + K_2K_b\}$

Putting $[OH^-] = K_w/[H^+]$ and $[H^+]\ [OH^-] = K_w$ in denominator,

$$\text{Rate} = kKK_w[S][IO_4^-]_0/\{K_w + (K_wK_2/[H^+]) + K_b[H^+] + K_2K_b\} \tag{27}$$

Multiplying by $[H^+]$ in numerator and denominator,

$$\text{Rate} = kKK_w[S][IO_4^-]_0[H^+]/\{K_w[H^+] + K_wK_2 + K_b[H^+]^2 + K_2K_b[H^+]\} \tag{28}$$

On rearranging eqn. 28,

$$\text{Rate} = kKK_w[S][IO_4^-]_0[H^+]/\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\} \tag{29}$$

where kK is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$, K_b is base dissociation constant of 2-amino-*p*-xylene.

Comparing eqn. 29 with eqn. 16, we get,

$k_2[IO_4^-]_0[S] = kKK_w[S][IO_4^-]_0[H^+]/\{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\}$

or $$k_2 = k\ K\ K_w\ [H^+]\ /\ \{K_w\ K_2 + [H^+]\ (K_w + K_2\ K_b) + K_b\ [H^+]^2\} \tag{30}$$

Equation 30 on rearranging becomes eqn. 31

$$1/k_2 = \{K_wK_2 + [H^+](K_w + K_2K_b) + K_b[H^+]^2\}/kKK_w[H^+] \tag{31}$$

or $1/k_2 = \{K_wK_2/kKK_w[H^+]\} + \{[H^+](K_w + K_2K_b)/kKK_w[H^+]\} + \{K_b[H^+]^2/kKK_w[H^+]\}$

or $$1/k_2 = \{K_2/kK[H^+]\} + \{K_w + K_2K_b)/kKK_w\} + \{K_b[H^+]/kKK_w\} \tag{32}$$

Putting $1/k_2 = L$, eqn. 32 reduces to the following form,

$L = \{K_2/kK[H^+]\} + \{K_w + K_2K_b)/kKK_w\} + \{K_b[H^+]/kKK_w\}$

Differentiating this eqn with respect to $[H^+]$,

$$dL/d[H^+] = -\ K_2/kK[H^+]^2 + 0 + K_b/kKK_w \tag{33}$$

For minimum or maximum value of L (*i.e.* $1/k_2$), $dL/d[H^+] = 0$

Therefore, from eqn. 33 we have,

$0 = -\ K_2/kK[H^+]^2 + K_b/kKK_w$

or $K_2/kK[H^+]^2 = K_b/kKK_w$

or $K_2/[H^+]^2 = K_b/K_w$

or $[H^+]^2 = K_2K_w/K_b$

or $$[H^+] = [K_2K_w/K_b]^{1/2} \tag{34}$$

This is the desired equation for predicting the minima or maxima in $1/k_2$ *vs.* $[H^+]$ plot. Now for finding out whether a minima or maxima will be obtained, the value of second derivative *i.e.*, $d^2[1/k_2]/d[H^+]^2$ should be obtained. If the value of second derivative is positive than the plot of $1/k_2$ *versus* $[H^+]$ shall pass through a minimum. The following treatment should be applied for getting the value of second derivative:

Differentiating the eqn. 33 again with respect to $[H^+]$,

$$d^2L/d[H^+]^2 = 2K_2/kK[H^+]^3$$

This value of $d^2L/d[H^+]^2$ is positive, so we will get minima at $[H^+] = [K_2K_w/K_b]^{1/2}$.

Or we can say that L *i.e.* $1/k_2$ is minimum when $[H^+] = [K_2K_w/K_b]^{1/2}$.

$$\text{Or} \qquad [H^+]_{min} = (K_2K_w/K_b)^{1/2} \tag{35}$$

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

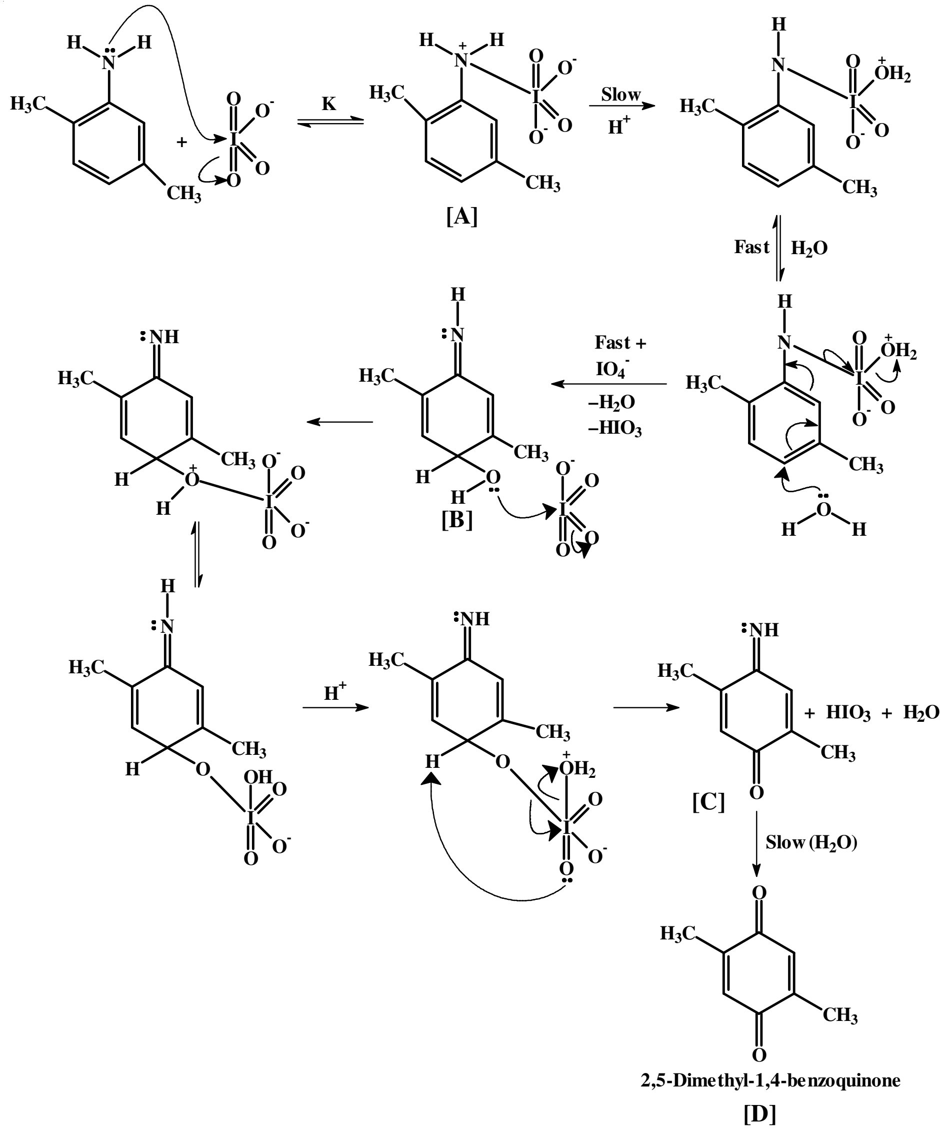
$$[H^+]_{min} = 3.58 \times 10^{-7} \text{ mol dm}^{-3}$$

In present observations, the rate-pH profile (Table-1) indicates a maxima at pH = 6.5 corresponding to $[H^+]_{min}$ of 3.16×10^{-7} mol dm^{-3}. Thus, it goes in support of present studies that the calculated value of $[H^+]_{min}$ is in excellent agreement with the experimental value of $[H^+]_{min}$ obtained from $1/k_2$ *versus* $[H^+]$ plot that can be made using the data given in Table-1. Alternatively, k_2 - pH profile will show a maxima at pH 6.5. Our results are also in accordance with the prediction made for similar cases in a review by Gupta and Gupta[16].

The pH effect may be explained by the fact that the rate determining step in the expected mechanisms is a reaction between unprotonated amine and periodate monoanion and thus the reaction rate will decrease when the concentration of either of these or both decreases. The concentration of periodate monoanion decreases with increasing pH after a pH of about 6.5 according to the equilibria involving different species of periodate ion. After this pH, dianion formation becomes predominant which is unreactive. In the equilibrium of 2-amino-*p*-xylene as discussed earlier, an increase in pH is expected to shift the equilibrium to right side and so the free [2-amino-*p*-xylene] is expected to increase which is probably the reason for an increase in the rate of reaction at comparatively lower pH values.

Molecular mechanism: It is necessary and interesting to discuss the possible molecular mechanism of the reaction. Mechanism proposed in **Scheme-I** shows the first step as a reversible bimolecular reaction between 2-amino-*p*-xylene and $[IO_4^-]$. The formation of a charged intermediate complex [A] taking place by the attack of $[IO_4^-]$ on the nitrogen of anilino group and stabilization of positive charge on this nitrogen are well supported by our earlier studies related to the effect of substituents on reaction rate and isokinetic relationship for this type of reaction series[9]. The high negative value of entropy of activation supports the involvement of solvation effects in this reaction. The formation of another intermediate [B] followed by its reaction with another IO_4^- to form quinoneimine [C] in a fast step are the expected steps of the mechanism involved. The last step (10) seems to be the slow hydrolysis and rearrangement of (C) to give 2,5-dimethyl-1,4-benzoquinone (D), *i.e.*, the main product of the reaction that has been isolated, separated and characterized by us.

It is important to mention that Srivastava *et al.*[13] reported the kinetics and mechanism of periodate oxidation of 2,3-dimethylaniline and 2,5-dimethylaniline in acetic acid-water medium and reported a sigmoid rate-pH profile (using the varied concentrations



Scheme-I

of acetic acid for maintaining the pH instead of using a buffer) in contrast to the maxima in rate-pH profile observed and explained by us. They were unable to apply Guggenheim's method for evaluation of k_{obs} and k_2 in most of the kinetic studies undertaken and therefore used initial rates in place of the rate constants for interpretation of the kinetic results in many cases. They did not work out a detailed mechanism as shown by us in the **Scheme-I**. In addition, they assumed the first step of mechanism as an irreversible process in contradiction to the reversible step established by us. They contradicted the work of Tanabe[17] on the periodate oxidation of aniline and assumed that the different type of the reaction products might have been formed due to the changed reactivity of dimethylanilines towards periodate caused by the presence of substituent methyl group at *o*- and *m*-position to amino group. Actually, they could not make use of the fact that Tanabe reported a free radical mechanism for the same. In contrast to the report of Srivastava *et al.*[9], we do expect, like Tanabe, that the oxidative process may continue further and finally the polymeric substances might separate out as the products of reaction reported by Tanabe. However, we reject the free radical nature of the mechanism as reported by Tanabe because free radical scavengers have no influence on the rate of this oxidation process. Further, they did not derive rate law equation and tested the same particularly from the view point of rate-pH profile, as done by us in the present report. The value of frequency factor of the order of 10^{10} to 10^{11} dm^3 mol^{-1} s^{-1}, as reported by them in contrast to the value of the order of 10^3 as evaluated by us, also suggests that they studied the later part of the reaction in which large size reactant particles of polymeric nature were involved. The initial part of any reaction is of main importance and therefore, our findings are more significant. The observations of Tanabe that different products are obtained in the periodate oxidation of aniline at different pH might be the reason for the different results reported by Srivastava *et al.*[9] as they made kinetic studies in acetic acid-water medium that would have affected the pH of medium leading to different course of reaction.

REFERENCES

1. G. Dryhurst, Periodate Oxidation of Diols and Other Functional Groups, Analytical and Structural Applications, Pergamon Press (1970).
2. V.K. Kalinina, *Kinet. Katal.*, **12**, 100 (1971).
3. M.P. Rao, B. Sethuram and T.N. Rao, *Indian J. Chem.*, **17A**, 52 (1979).
4. S.P. Srivastava, G. Bhattacharjee, V.K. Gupta and S. Pal, *React. Kinet. Catal. Lett.*, **13**, 231 (1980).
5. M.K. Beklemishev, E.N. Kiryushchenkov, E.K. Skosyrskaya and A.M. Petrenko, *J. Anal. Chem.*, **61**, 1067 (2006).
6. H.W. Sun, H.M. Shi, S.G. Shen and Z.F. Guo, *Chin. J. Chem.*, **26**, 615 (2008).
7. R.D. Kaushik, R.P. Singh and Shashi, *Asian J. Chem.*, **15**, 1655 (2003).
8. R.D. Kaushik, Amrita, M. Dubey and R.P. Singh, *Asian J. Chem.*, **16**, 831 (2004).
9. S.P. Srivastava, V.K. Gupta, M.C. Jain, M.N. Ansari and R.D. Kaushik, *Thermochim. Acta*, **68**, 27 (1983).
10. R.D. Kaushik, A.K. Chaubey and P.K. Garg, *Asian J. Chem.*, **15**, 1655 (2003).
11. R.D. Kaushik, R.P. Singh and Amrita, *J. Curr. Sci.*, **5**, 7 (2004).
12. S.P. Srivastava, G. Bhattacharjee and P. Malik, *Indian J. Chem.*, **25A**, 48 (1986).
13. H.T.S. Britton, Hydrogen Ions, D. Von Nostrand Co., p. 354 (1956).
14. B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, Vogel's Text Book of Practical Organic Chemistry, Addison-Wesley Longman Ltd., edn. 5, p. 1221 (1998).
15. J.P. Phillips and F.C. Nachod, Organic Electronic Spectral Data, Vol. 4, p. 163 (1958-1959).
16. K.S. Gupta and Y.K. Gupta, *J. Chem. Educ.*, **61**, 972 (1984).
17. H. Tanabe, *Chem. Pharm. Bull. (Tokyo)*, **6**, 645 (1958); **7**, 177, 316 (1959).

(*Received*: 3 June 2009; *Accepted*: 27 November 2009) AJC-8103