Spectrophotometric Study of Kinetics and Mechanism of Oxidation of *o*-Ethoxyaniline by Periodate Ion

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The reaction between *o*-ethoxyaniline and periodate in acetone-water medium has been found to follow second order behaviour, being first order in each reactant. The rate of reaction decreases with decrease in dielectric constant of the medium. The reaction speeds up in presence of neutral salt. Free radical scavengers do not affect the reaction rate. The stoichiometry has been found to be 1 mol of *o*-ethoxyaniline: 2 mol of periodate. Thermodynamic parameters evaluated are: E_a = 18.2 kcal mol^{-1}, A = 1.54×10^{12} dm^3 mol^{-1} s^{-1}; $\Delta S^{\#}$ = - 4.9 cal mol^{-1}, $\Delta G^{\#}$ = 19.2 kcal mol^{-1} and $\Delta H^{\#}$ = 17.6 kcal mol^{-1}. The derived rate law is in agreement with the results of kinetic studies. The rate law (k_2) *versus* pH profile passes through the maximum. Main reaction product was characterized as ethoxy-1,4-benzoquinone. Molecular mechanism involving an ion-dipole interaction has been proposed on the basis of the kinetic studies and the reaction product isolated, separated and characterized.

Key Words: Kinetics, *o*-Ethoxyaniline, Periodate oxidation, Ethoxy-1,4-benzoquinone.

INTRODUCTION

In continuation to our earlier studies[1-7], the results of kinetic studies on the periodate oxidation of *o*-ethoxyaniline (OEA) in acetone-water medium aimed to study the mechanism of the reaction and rate law particularly for seeking an explanation for the unique rate-pH profile observed are being presented and discussed in the present communication. The already available reports[8-14] are contradictory in regard to the ionic or free radical mechanism being followed.

EXPERIMENTAL

Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[15], 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), *o*-ethoxyaniline (Sigma-Aldrich), acetone (E. Merck) and all other chemicals of analytical reagent/guaranteed reagent grade were used after redistillation/recrystallization. High precision thermostatically controlled water bath with an accuracy of ± 0.1 ºC was employed for maintaining the desired temperature. Systronics digital pH-meter-802 was used

for measuring the pH of reaction mixture. The reactions were initiated by adding temperature equilibrated NaIO$_4$ solution of known concentration to the reaction mixture containing the *o*-ethoxyaniline 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 (that was due to the intermediate, C) at different time on Shimadzu double beam spectrophotometer (UV Pharmaspec-1700), at 510 nm, *i.e.*, the λ$_{max}$ of the pink reaction mixture. λ$_{max}$ was found to remain unchanged during the period of study of the reaction as well as on changing the pH.

Product analysis: Reaction mixture containing oxidant in excess was left for 24 h to ensure completion of the reaction. Initially the solution turned pink, there-after brown 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. On separation of a droplet (due to moisture), solid residue was left on the watch glass. This brown coloured residue was dissolved in petroleum ether and was found to be TLC single spot (plate thickness = 0.5 mm, stationary phase = silica gel G, eluent = mixture of acetone and benzene in the volume ratio 20:80, elution time = 35 min). The remaining part of filtrate might be having other products that could not be separated and characterized. The brown coloured comp-ound was recrystallized in petroleum ether subjected to characterization studies. It responded positive for quinone[16] with m.p. 92 ºC. Its UV-Vis spectrum in ethanol showed absorption maxima at 245, 278 and 440 nm, suggesting the presence of quinonoid structure in this compound[17]. The IR spectrum of compound (in KBr) showed the presence of bands at 2760 cm^{-1} (s) (due to ring C-H stretch), 1650 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 ethoxy group[18]), 3280 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 1395 cm^{-1} (s), 1510 cm^{-1} (s) may be due to C=C ring stretch. The bands at 1240 cm^{-1} (m) and 1036 cm^{-1} (m) may be due to asymmetric and symmetric C-O-C strech. Bands at 744 cm^{-1} (m) and 831 cm^{-1} (m) were assigned to the out of plane C=C bending mode. The NMR spectrum of this compound in CDCl$_3$ showed the peaks at δ = 7.262, s, (1H); at δ = 6.988, d, (2H), at δ = 4.084, q, (2H) and δ = 1.257, t, (3H). A quartet at δ = 4.084 may be due to -OCH$_2$ group attached to the ring while the triplet at δ = 1.257 was due to three protons of -CH$_3$ of -OC$_2$H$_5$ group. The other signals in spectrum at δ = 7.262 and δ = 6.988 were due to the three protons of the ring. On the basis of these studies, this reaction product was characterized as ethoxy-1,4-benzoquinone.

RESULTS AND DISCUSSION

Preliminary observations: As described earlier, the development of various colours followed by precipitation during the reaction indicates the formation of more than one intermediate prior to the formation of final reaction product. The

rapid scan of the pink solution showed the λ_{max} of the intermediate 'C' to be 510 nm. The UV-visible spectra of IO_4^- and *o*-ethoxyaniline indicated these to show no absorption in visible region. Hence for following the kinetics the absorbance changes were recorded at 510 nm at which only the intermediate C absorbs. Plane mirror and Guggenheim's methods, respectively were used for evaluation of initial rates, (dA/dt) and pseudo first order rate constants, k_{obs}.

Stoichiometry: Stoichiometry of the reaction was determined by allowing a known excess of $NaIO_4$ 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 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 *o*-ethoxyaniline: 2 mol periodate as in eqn. 1.

$$C_2H_5OC_6H_4NH_2 + 2IO_4^- + 2H^+ \longrightarrow C_5H_5OC_6H_3O_2 + 2HIO_3 + NH_3 \quad (1)$$
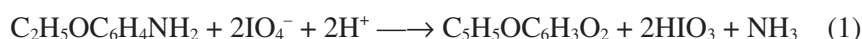
Rate law: The order in each reactant was found by using Van Hoff differential method (Table-1). Also, the kinetics was studied under pseudo order conditions, *viz.*, $[IO_4^-]_0 \gg [S]$ and $[S]_0 \gg [IO_4^-]$. Under both these conditions the reaction displayed first order. Under the condition, $[S]_0 \gg [IO_4^-]$, the results (Table-2) were defined by the eqn. 2 and pseudo first order rate constant, k_{obs}, was equal to $k_2 [S]_0$.

TABLE-1
DETERMINATION OF ORDER WITH RESPECT TO
o-ETHOXYANILINE AND PERIODATE; Temp. = 35 ± 0.1 ℃

[NaIO$_4$] (mol dm^{-3})	[OEA] (mol dm^{-3})	Acetone % (v/v)	pH	(dA/dt) × 10^3 (min^{-1})
0.0005	0.0005	5.0	6.5	1.5
0.0005	0.0010	5.0	6.5	3.0
0.0005	0.0015	5.0	6.5	4.5
0.0005	0.0020	5.0	6.5	6.0
0.0005	0.0025	5.0	6.5	7.5
0.0005	0.0030	5.0	6.5	8.5
0.0005	0.0035	5.0	6.5	10.5
0.0005	0.0040	5.0	6.5	12.0
0.0005	0.0045	5.0	6.5	13.0
0.0005	0.0005	5.0	6.5	1.5
0.0010	0.0005	5.0	6.5	2.8
0.0015	0.0005	5.0	6.5	4.5
0.0020	0.0005	5.0	6.5	6.3
0.0025	0.0005	5.0	6.5	7.3
0.0030	0.0005	5.0	6.5	9.0
0.0035	0.0005	5.0	6.5	10.8
0.0040	0.0005	5.0	6.5	11.8
0.0045	0.0005	5.0	6.5	13.5

TABLE-2
EFFECT OF VARIATION OF CONCENTRATION OF
REACTANTS AND pH ON THE REACTION RATE

$[NaIO_4]$ (mol dm^{-3})	$[OEA]$ (mol dm^{-3})	Acetone % (v/v)	Temp. ± 0.1 °C	pH	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^2$ (dm^3 mol^{-1} s^{-1})
0.0005	0.005	5.0	35	6.5	9.2	18.4
0.0005	0.006	5.0	35	6.5	10.7	17.9
0.0005	0.007	5.0	35	6.5	13.1	18.6
0.0005	0.008	5.0	35	6.5	14.6	18.2
0.0005	0.009	5.0	35	6.5	16.5	18.3
0.0005	0.010	5.0	35	6.5	18.4	18.4
0.0050	0.0005	5.0	35	6.5	13.4	26.9
0.0060	0.0005	5.0	35	6.5	15.7	26.2
0.0070	0.0005	5.0	35	6.5	19.2	27.4
0.0080	0.0005	5.0	35	6.5	21.5	26.9
0.0090	0.0005	5.0	35	6.5	23.8	26.4
0.0100	0.0005	5.0	35	6.5	26.9	26.9
0.0005	0.005	5.0	45	5.0	14.2	28.4
0.0005	0.005	5.0	45	5.5	16.5	33.1
0.0005	0.005	5.0	45	6.0	18.8	37.6
0.0005	0.005	5.0	45	6.5	22.6	45.3
0.0005	0.005	5.0	45	7.0	18.0	36.1
0.0005	0.005	5.0	45	7.5	15.0	29.9
0.0005	0.005	5.0	45	8.0	12.7	25.3

$$d[C]/dt = k_2 [IO_4^-] [S]_0 \qquad (2)$$

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

On the other hand under the condition $[IO_4^-]_0 \gg [S]$, the rate was defined by eqn. 3 and k_{obs} was equal to $k_2 [IO_4^-]_0$.

$$d[C]/dt = k_2 [IO_4^-]_0 [S] \qquad (3)$$

In eqns. 2 and 3 $[IO_4^-]_0$ 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 of periodate and *o*-ethoxyaniline.

Effect of ionic strength, dielectric constant of the medium, free radical scavengers, pH and temperature: On increasing the ionic strength by addition of sodium chloride, the rate was found to increase and a graphical plot between log k_2 and μ was straight line with excellent value of correlation coefficient of 0.9999 (Fig. 1). An increase in dielectric constant increased the rate of reaction as indicated by a linear plot between log k_2 *versus* 1/D (correlation coefficient = 0.995), where D is the dielectric constant of the medium (Fig. 2). Free radical scavengers like acrylamide, allyl alcohol and allyl acetate had no effect of on the reaction rate. These effects indicate an ion-dipole type interaction in the rate-determining step and that the reacting ion is possibly an anion.
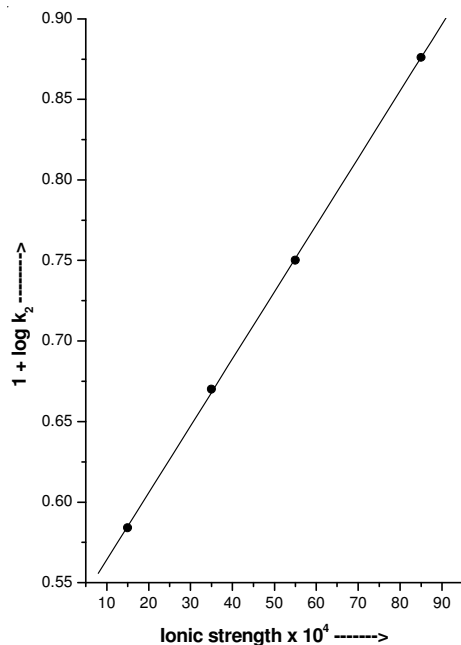
Fig. 1.   Effect of ionic strength on reaction rate at $[NaIO_4] = 0.0005$ mol dm^{-3}, $[OEA] = 0.005$ mol dm^{-3}, acetone = 5.0 % (v/v), Temp. = 35 ± 0.1 ℃, pH = 6.5
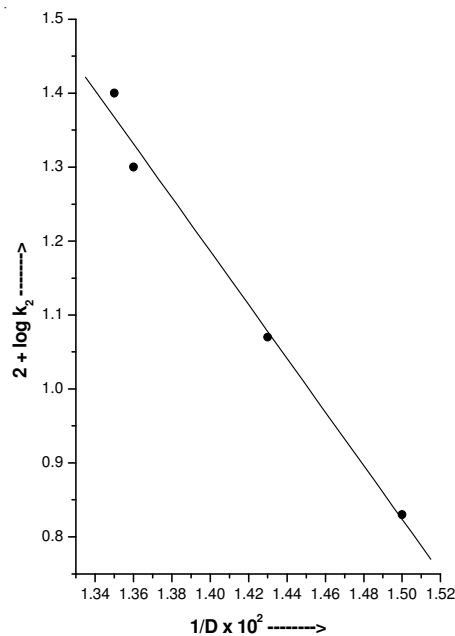
Fig. 2.   Effect of dielectric constant of the medium on reaction rate at $[NaIO_4] = 0.0005$ mol dm^{-3}, $[OEA] = 0.005$ mol dm^{-3}, Temp. = 35 ± 0.1 ℃, pH = 6.5

The effect of pH was examined in pH range 5.0-8.0. Rate-pH profile indicates a maximum at pH = 6.5 (Table-2, Fig. 3), which could be due to change in the nature of species and their relative reactivity when the pH is changed. The activation parameters evaluated by determining the rate constants at four different temperatures ranging from 35.0 to 50.0 ℃ are given in Table-3.

TABLE-3
ACTIVATION PARAMETERS FOR THE PERIODATE
OXIDATION OF *o*-ETHOXYANILINE IN ACETONE-WATER
$[OEA] \times 10^3 = 5.0$ mol dm^{-3}, $[NaIO_4]$ x $10^4 = 5.0$ mol dm^{-3}, Acetone = 5.0 % (v/v), pH = 6.5

Temp. ± 0.1 ℃	$k_{obs} \times 10^4$ s^{-1}	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}	Ea k cal mol^{-1}	$A \times 10^{-12}$ dm^3 mol^{-1} s^{-1}	$\Delta S^{\#}$ cal mol^{-1}	$\Delta G^{\#}$ kcal mol^{-1}	$\Delta H^{\#}$ kcal mol^{-1}
35	9.2	18.4	18.2	1.54	- 4.9	19.2	17.6
40	14.2	28.4	–	–	–	–	–
45	22.6	45.3	–	–	–	–	–
50	35.3	70.6	–	–	–	–	–

Initially, there is appearance of pink colour which continues to darken with increase in the concentration of the intermediate, C and finally the product settles on standing for long time. Obviously, the coloured intermediate is formed on a
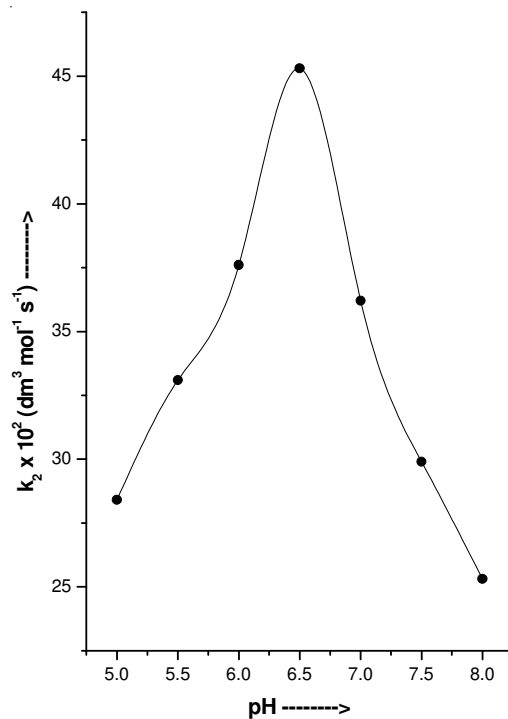
Fig. 3. Rate-pH profile at [NaIO$_4$] = 0.0005 mol dm^{-3}, [OEA] = 0.005 mol dm^{-3}, acetone = 5.0 % (v/v), Temp. = 45 ± 0.1 ºC

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 oxidation of *o*-ethoxyaniline into benzoquinone. Further, the kinetic order of one in periodate but requirement of the two periodate molecules for each *o*-ethoxyaniline 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 pink coloured intermediate is quite stable and its concentration is not in steady state. Thus, there should 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$_2$-pH profile indicates the presence of at least three differently reactive reactant species in the pH region chosen for study.

It is important to consider and discuss the speciation of *o*-ethoxyaniline and periodate species in aqueous solutions before proposing a mechanism for the reaction under consideration. In aqueous solutions, periodate exists in three forms represented by the equilibria:
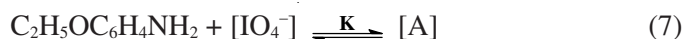
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, \qquad K_1 = 2.3 \times 10^{-2} \qquad (4)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \qquad K_2 = 4.35 \times 10^{-9} \tag{5}$$

The value of K_1 indicates that in the pH range 5-9 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 case of *o*-ethoxyaniline[19], in aqueous solution the following acid-base equilibrium with $K_b = 2.95 \times 10^{-10}$ operates.

$$C_2H_5OC_6H_4NH_2 + H_2O \rightleftharpoons C_2H_5OC_6H_4N^+H_3 + OH^- \tag{6}$$

In the studied pH-range, both $C_2H_5OC_6H_4NH_2$ and $C_2H_5OC_6H_4N^+H_3$ shall exist and both of these have been considered.

Assuming $C_2H_5OC_6H_4NH_2$ and $H_4IO_6^-$ as the reactive species and based on the observed kinetic rate laws (2-3) and pH-dependence, the following mechanism is proposed:

$$C_2H_5OC_6H_4NH_2 + [IO_4^-] \xrightleftharpoons{K} [A] \tag{7}$$

$$[A] \xrightleftharpoons{k} \text{Intermediate [B] (slow)} \tag{8}$$

$$[B] + IO_4^- \longrightarrow \text{Intermediate [C] (fast)} \tag{9}$$

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

$$\text{Intermediate [C]} \longrightarrow \text{Product} \tag{10}$$

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 (8-9) lead to the rate law:

$$d[C]/dt = k[A] \tag{11}$$

$$= kK[C_2H_5OC_6H_4NH_2][IO_4^-] \tag{12}$$

Since the observed kinetics shows first order in each of $[C_2H_5OC_6H_4NH_2]$ and $[IO_4^-]$, the value of K must be low.

At affixed pH, under the condition $[S]_0 \gg [IO_4^-]$, the rate of formation of intermediate, C, is given by eqn. 13.

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

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

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

Since the reaction shows first order in each of [S] and $[IO_4^-]$, the inequalities $K[S]_0 \ll 1$ and $K[IO_4^-]_0 \ll 1$ should operate in eqns. 13 and 14, respectively leading to the rate laws in eqns. 2 and 3.

On substituting the values of concentrations of the reactive species $[CH_3OC_6H_4NH_2]$ and $[IO_4^-]$ in terms of equilibria (4-5) and (6), respectively, in eqn. 12, the complete rate law including $[H^+]$-dependence becomes:

$$d[C]/dt = kK\{([S]_0[OH^-]/([OH^-] + K_b)\}\{([IO_4^-][H^+]/(K_2 + [H^+])\} \tag{15}$$

On replacing $[OH^-][H^+]$ by K_w and $[OH^-]$ by $K_w/[H^+]$ in denominator and on rearranging, we get,

$$d[C]/dt = kKK_w[S]_0[IO_4^-]\ [H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\}\ (16)$$

On comparing eqns. 2 and 16, we get

$$k_2 = kK\ K_w[H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\} \qquad (17)$$

Equation 17 on rearranging becomes eqn. 18.

$$1/k_2 = (K_2/kK[H^+]) + \{(K_w + K_bK_2)/kKK_w\} + K_b[H^+]/kKK_w \qquad (18)$$

Scheme-I
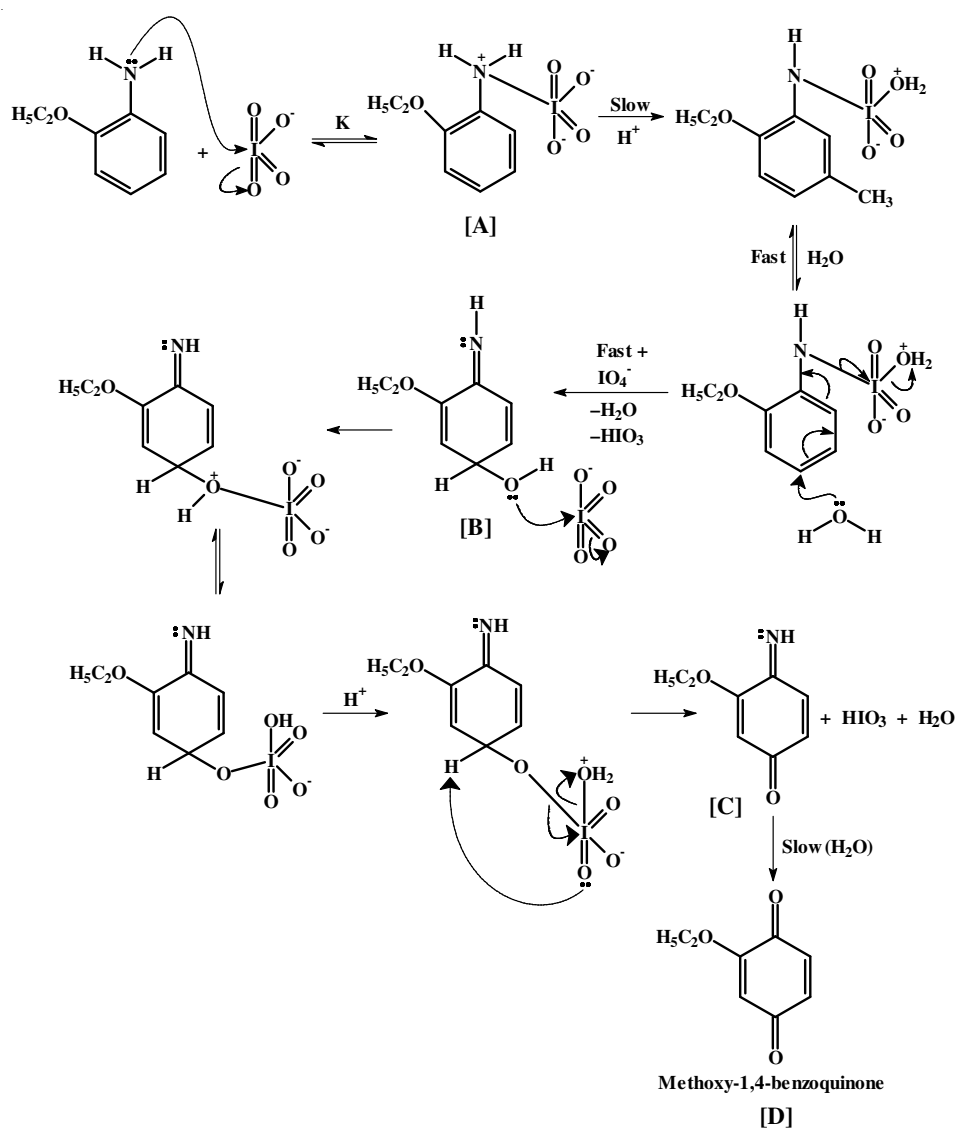
The nature of the rate law shows that a plot of $1/k_2$ *versus* $[H^+]$ shall pass through a minimum as discussed in detail in a review by Gupta and Gupta[20]. On differentiating $1/k_2$ with respect to $[H^+]$ in eqn. 18, we get the values of $d^2[1/k_2]/d[H^+]^2$. The value of second derivative is found to be positive showing the plot of $1/k_2$ *versus* $[H^+]$ to pass through a minimum. Thus, on setting $d[1/k_2]/d[H^+]$ equal to zero for obtaining hydrogen ion concentration at which the $1/k_2$ *vs.* $[H^+]$ profile will pass through minimum (or k_2 *vs.* pH profile will pass through a maxima), we obtain,

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

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

$$[H^+]_{min} = 3.84 \times 10^{-7} \text{ mol dm}^{-3}$$

In our observations, the rate-pH profile (Fig. 3) indicates a maxima at pH = 6.5 corresponding to $[H^+]_{min}$ of 3.16×10^{-7} mol dm^{-3}. This observed value is in excellent agreement with the calculated value of $[H^+]_{min}$ *i.e.* 3.84×10^{-7} mol dm^{-3}.

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 *o*-ethoxyaniline 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 LFER studies on this type of reaction series[21-23]. 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 ethoxy-1,4-benzoquinone (D), *i.e.*, the main product of the reaction that has been isolated, separated and characterized.

REFERENCES

1. S.P. Srivastava, M.C. Jain and R.D. Kaushik, *Nat. Acad. Sci. Lett.*, **2**, 63 (1979).
2. V.K. Gupta, R. Bhushan, R.D. Kaushik, M.C. Jain and S.P. Srivastava, *Oxid. Commun.*, **7**, 409 (1984).
3. R.D. Kaushik, R.P. Singh and Shashi, *Asian J. Chem.*, **15**, 1655 (2003).
4. R.D. Kaushik, Amrita, M. Dubey and R.P. Singh, *Asian J. Chem.*, **16**, 831 (2004).
5. R.D. Kaushik, M. Dubey and R.K. Arya, *J. Curr. Sci.*, **3**, 119 (2003).
6. R.D. Kaushik, A.K. Chaubey and P.K. Garg, *Asian J. Chem.*, **15**, 1655 (2003).
7. R.D. Kaushik, R.P. Singh and Amrita, *J. Curr. Sci.*, **5**, 7 (2004).
8. G. Dryhurst, Periodate Oxidation of Diols and Other Functional Groups, Analytical and Structural Applications, Pergamon Press (1970).
9. V.K. Kalinina, *Kinet. Katal.*, **12**, 100 (1971).
10. V.K. Pavolva, Ya. S. Sevchenko and K.B. Yatsmiriskii, *Zh. Fiz. Khim.*, **44**, 658 (1970).
11. M.P. Rao, B. Sethuram and T.N. Rao, *Indian J. Chem.*, **17A**, 52 (1979).
12. S.P. Srivastava, G. Bhattacharjee, V.K. Gupta and S. Pal, *React. Kinet. Catal. Lett.*, **13**, 231 (1980).
13. M.K. Beklemishev, E.N. Kiryushchenkov, E.K. Skosyrskaya and A.M. Petrenko, *J. Anal. Chem.*, **61**, 1067 (2006).

14. H.W. Sun, H.M. Shi, S.G. Shen and Z.F. Guo, *Chin. J. Chem.*, **26**, 615 (2008).
15. H.T.S. Britton, Hydrogen Ions, D. Von Nostrand Co., p. 354 (1956).
16. 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).
17. E.A. Braude, *J. Chem. Soc.*, 490 (1945).
18. P.S. Kalsi, Spectroscopy of Organic Compounds, New Age International Ltd., New Delhi, India, edn. 2 (1996).
19. J.A. Dean, Lange's Handbook of Chemistry, McGraw-Hill Book Company, New York, edn. 13, pp. 5-28 (1985).
20. K.S. Gupta and Y.K. Gupta, *J. Chem. Educ.*, **61**, 972 (1984).
21. S.P. Srivastava, V.K. Gupta, M.C. Jain, M.N. Ansari and R.D. Kaushik, *Thermochim. Acta*, **68**, 27 (1983).
22. R.D. Kaushik, D. Singh, R. Joshi and S. Kumar, *Asian J. Chem.*, **10**, 573 (1998).
23. R.D. Kaushik, R. Joshi and D. Singh, *Asian J. Chem.*, **10**, 567 (1998).