Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1229–1234

Periodate Oxidation of Aromatic Amines: Kinetics and Mechanism of Oxidation of N-Ethylaniline in Acetone Water Medium

R.D. KAUSHIK,* R.K. ARYA and SANDEEP KUMAR
Department of Chemistry, Gurukula Kangri University
Hardwar-249 404, India

The kinetics of oxidation of N-ethylaniline by periodate in acetone-water medium has been studied. The order with respect to both periodate and N-ethylaniline has been found to be one in each. The rate increases marginally on increasing ionic strength while it decreases with a decrease in dielectric constant. The rate-pH profile shows a maxima at pH 5.5. An interpretation for it has been given. There is no effect of free radical scavengers on rate of reaction. The thermodynamic parameters are also reported and discussed. The main product of oxidation characterized by UV-VIS and IR spectra and melting point studies was *p*-benzoquinone. A suitable mechanism has been proposed and the rate law derived.

INTRODUCTION

The oxidation of aromatic amines with different oxidising agents provides interesting possibilities, such as a number of complex products are formed, out of which some are important from physiological and industrial point of view. The periodate oxidation is of special significance from this point of view.

The kinetic studies on non-malapradian oxidation of aromatic amines by periodate are rather few[1–4] and reported results are contradictory. The earlier investigations, made by us as well as by other workers[5] on periodate oxidation of some anilines show that these complex reactions require more studies for understanding their complex behaviour. The present paper deals with the results of periodate oxidation of N-ethylaniline (NEA) in acetone-water medium.

EXPERIMENTAL

N-Ethylaniline and sodium metaperiodate of E. Merck AR grade were used after redistillation/recrystallization respectively. All other chemicals used were of AR grade. Doubly distilled water was used for the preparation of solutions and reaction mixtures. Thiel, Schultz and Coch buffer[6] was used for maintaining the pH of solutions.

The reaction being quite fast at ordinary temperatures, was studied in 10% (v/v) acetone-water medium and in the absence of any catalyst. The pH of the reaction mixture was kept constant at 7.0 during the course of reaction.

The progress of reaction was followed spectrophotometrically on a Shimadzu double beam spectrophotometer, UV-150-02. However, stoichiometry was determined iodometrically. The reaction between NEA and periodate ion in acetone-water medium produced violet colour which showed maximum absorbance at 480 nm. The λ_{max} did not change during the period for which the kinetic studies were made.

RESULTS AND DISCUSSION

The reaction was studied at different concentrations of periodate and NEA, respectively, keeping the other constant. Initial rates in terms of $(dA/dt)_i$ at different [NEA] and [periodate] (Table-1), showed that the reaction follows second order kinetics, being first order each in NEA and periodate, The second order kinetics can also be proved by the fact that the rate was linearly related to the concentration of the reactant which varied in each case.

TABLE-1
EFFECT OF REACTANT CONCENTRATION ON RATE AT 35 ± 0.1°C

λ_{max} = 480 nm, Acetone = 10.0% (v/v)

[NEA] $\times 10^3$	[$NaIO_4$] $\times 10^3$	$(dA/dt)_i$ $\times 10^3$
10.0	1.0	2.7
10.0	2.0	5.5
10.0	3.0	8.0
10.0	4.0	11.0
10.0	5.0	13.5
10.0	6.0	16.0
1.0	10.0	2.2
2.0	10.0	4.5
3.0	10.0	6.0
4.0	10.0	8.5
5.0	10.0	11.5
6.0	10.0	13.5

Under pseudo first order conditions, the plot of $1/k_1$ vs 1/[S] (where S is the reactant taken in excess) was linear with a negligible intercept indicating that the intermediate formed in slow step got consumed in a subsequent fast step[7]. The stoichiometry of the reaction determined by estimating the unreacted $NaIO_4$ iodometrically, was found to be 2 : 1 (oxidant-substrate)

Initially the reaction mixture was violet in colour. On standing overnight, it changed to reddish brown colour followed by precipitation. This reaction mixture was extracted with petroleum ether. On evaporation of the solvent, a yellow compound with m.p. 116°C (lit. value 115–117°C)[8] was obtained. This compound was found to be TLC single and responded positively for quinone[9].

In UV-VIS spectrum, the λ_{max} obtained for this compound in C_2H_5OH solvent were 246 nm and 320 nm which suggests the presence of quinonoid structure in the compound.[10].

The IR spectrum in KBr showed the presence of bands at 3254 cm^{-1} (s) (due to ring C—H stretch), 2013 cm^{-1} (w) and 1858 cm^{-1} (w) (due to overtones and combination bands), 1632 cm^{-1} (s) (indicating the presence of quinonoid structure[11]) 1514 cm^{-1} (s) and 1469 cm^{-1} (s) (due to C=C ring stretch). The bands were also obtained at 1097 cm^{-1} (m) to 1354 cm^{-1} (m) (may be due to the in-plane C—H bending in the ring) and 689 cm^{-1} (m), 760 cm^{-1} (s) and 825 cm^{-1} (m) (due to out-of-plane C=C bending and C—H bending modes and substitution pattern in the ring).

On the basis of the melting point and spectral studies[8–12], this compound was characterized as *p*-benzoquinone.

Kinetic studies were carried out in the range of pH 4.0 to 7.0 using Thiel, Schultz and Coch buffer[6]. The data is presented in Table-2. The rate increases sharply up to pH 5.5 which may be due to the decrease in protonation of NEA. The concentration of periodate monoanion is maximum around pH 5.0 and decreases beyond this pH value[13], which may probably be the reason for the decrease in rate beyond pH 5.5. A simlar behaviour has been observed by previous workers[5] in case of periodate oxidation of other anilines

TABLE-2
EFFECT OF pH ON REACTION RATE

[NEA] = 0.001 M, $[NaIO_4]$ = 0.01 M, λ_{max} = 480 nm,
Acetone = 10.0% (v/v), Temp. = 35 ± 0.1°C

pH	4.0	4.5	5.0	5.5	6.0	6.5	7.0
$\left(\frac{dA}{dt}\right)_i \times 10^3$	2.0	4.0	5.5	6.5	4.8	3.5	2.2

To get further information about the participating reactants, different kinetic runs under pseudo first order conditions were carried out in presence of different amounts of acetone ranging from 2.5 to 15.0% (v/v). On decreasing dielectric constant the rate was found decreasing (Table-3). A plot between log $(dA/dt)_i$ *vs.* $\frac{I}{D}$ was found to be linear with negative slope indicating that the reaction may be of ion-dipole type with the possibility that the reacting ion is anion[14], which is periodate monoanion in the present study.

TABLE-3
EFFECT OF DIELECTRIC CONSTANT

[NEA] = 0.001 M, $[NaIO_4]$ = 0.01 M, λ_{max} = 480 nm,
Temp. = 35 ± 0.1°C

D	73.9	72.4	70.0	66.8
$\left(\frac{dA}{dt}\right)_i \times 10^3$	3.20	2.75	2.20	1.50

To study the effect of varying ionic strength (μ) on the specific rate, the reaction was carried out under pseudo-first order conditions and in the presence of different concentrations of a neutral salt NaCl (Table-4). The rate of reaction increased with an increase in ionic strength. The plot between $(dA/dt)_i$ *vs.* μ was of primary linear type, which indicates that the ion-dipole reaction is the rate determining step.

TABLE-4
EFFECT OF IONIC STRENGTH

[NEA] = 0.001 M, $[NaIO_4]$ = 0.01 M, λ_{max} = 480 nm,
Acetone = 10.0% (v/v), Temp. = 35 ± 0.1°C

$[NaCl] \times 10^3$ M	$\mu \times 10^2$	$\left(\frac{dA}{dt}\right)_i \times 10^3$
1.0	1.1	2.213
2.0	1.2	2.225
5.0	1.5	2.263
10.0	2.0	3.250
12.0	2.2	3.500
15.0	2.5	4.125

The kinetic studies were made under pseudo first order conditions (taking periodate in excess) at four different temperatures ranging from 30 to 45°C. Guggenheim method was used for evaluating the first order rate constant and the second order rate constant was calculated by dividing the first order rate constant by the concentration of periodate. The linear Arrhenius plot (log k_2 *vs.* $\frac{I}{T}$) was used for calculating the thermodynamic parameters. The mean values of various activation parameters are: E_a = 10.393 kcal/mol; A = 11.75×10^5 lit mol^{-1} sec^{-1}; $\Delta S^{\#}$ = –32.84 E.U.; $\Delta F^{\#}$ = 19.97 kcal/mol and $\Delta H^{\#}$ = 9.78 kcal/mol.

From these data, it is clear that the reaction is characterized by a low value of energy of activation and a large negative value of entropy of activation. The former is the characteristic of a bimolecular reaction in solution and the latter is mainly observed in polar solvents and also suggests the formation of a charged and rigid transition state which is expected to be strongly solvated in the polar solvent employed. The above assumption is also supported by the fact that the rate decreases with decreasing dielectric constant. The value of frequency factor of the order of 10^5 suggests the involvement of reactive species which are larger in size.

Before proposing a mechanism for this reaction, it is also to be noted that free radical scavengers have no effect on the rate of reaction. On the basis of the kinetic studies, insensitiveness towards free radical scavengers, product identified, thermodynamic parameters evaluated and the chances of the formation of benzoquinoneimine derivatives during such reactions as reported earlier[1-4], the proposed mechanism is given in Chart-I.

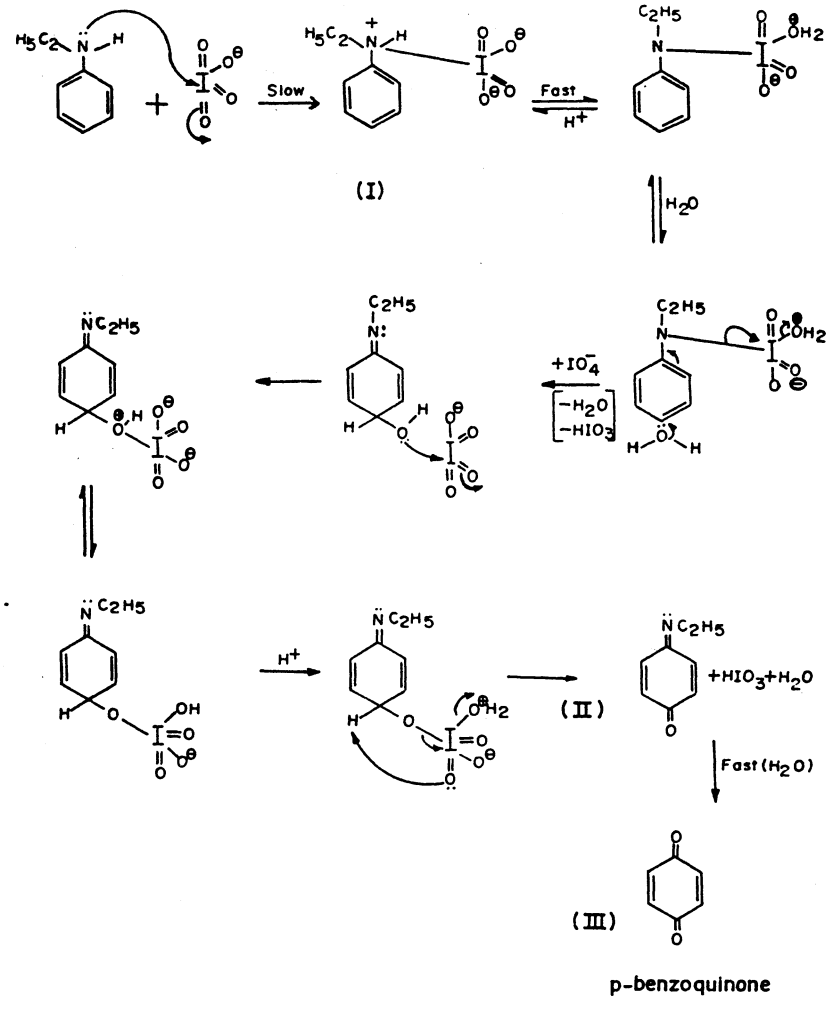

Chart-I

The value of $\Delta S^{\#}$ and effect of dielectric constant suggests the formation of a charged intermediate (I) as shown in the mechanism. This intermediate (I) reacts with another molecule of periodate to form quinoneimine (II). The last step seems to be the fast hydrolysis of (II) to give (III) which was isolated and characterized by us as *p*-benzoquinone.

On the basis of the above mechanism, the rate of the reaction should be given by $dA/dt = k_2 [NEA][IO_4^-]$.

The mechanism proposed and the rate law derived are in accordance with various kinetic features observed and the product identified.

REFERENCES

1. G. Dryhurst, in: R. Bether and D.M.W. Anderson (Eds.), Periodate Oxidation of Diols and Other Functional Groups, Analytical Structural Applications, Pergamon Press, p. 24 (1970).
2. H. Tanabe, *J. Pharm. Soc. (Japan)*, **73**, 943 (1953).
3. ————, *Yokugaku Zasshi*, **77**, 161 (1957); *ibid.*, 867; **78**, 410 (1958).
4. ————, *Chem. Pharm. Bull.*, **6**, 645 (1958); **7**, 177 (1959); *ibid.*, 316.
5. R.D. Kaushik, Vipin Kumar, R.K. Arya and Dheer Singh, *Asian J. Chem.*, **12**, 1123 (2000).
6. H.T.S. Britton, Hydrogen Ions, D. Van Nostrand Company, p. 40 (1956).
7. E.T. Kaiser and S.W. Weidman, *J. Am. Chem. Soc.*, **86**, 4354 (1964).
8. J. Buckingham (Ed.), Dictionary of Organic Compounds, Chapmann & Hall, N.Y., Vol. IV, 5th Edn. (1982).
9. A.I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, London, p. 747 (1975).
10. H.E. Ungnade, Organic Electronic Spectral Data, Vol. II, Interscience Publishers, Inc., N.Y. (1953–1955).
11. R.M. Silverstein, C. Clayton Bassler and Terrence C. Morrill, Spectrometric Identification of Organic Compounds, 5th Edn., John Wiley & Sons, Inc., N.Y. (1991).
12. J.P. Phillips and F.C. Nachod (Eds.), Organic Electronic Spectral Data, Interscience Publishers, New York, Vol IV (1958).
13. V.K. Pavolva, Ya. S. Sevchenko and K.B. Yatsimiriskii, *Zh. Fiz. Khim.*, **44**, 658 (1970).
14. E.S. Amis. Solvent Effects on Reaction Rates and Mechanism, Academic Press, N.Y., p. 42 (1966).

(*Received:* 11 May 2000; *Accepted:* 17 July 2000) AJC-2080