# PERIODATE OXIDATION OF o-CHLOROANILINE IN ACETONE-WATER MEDIUM : A KINETIC AND MECHANISTIC STUDY

## P.K. GARG[1*], A. AGARWAL[2] AND R.K. ARYA[2]

[1]Department of Chemistry, Institute of Engineering & Technology, ALWAR 301001 (Raj.) India
[2]Department of Chemistry, Chinmaya P.G. Degree College, HARDWAR (UA) 249403, India
e-mail:drprudeep73@rediffmail.com

## ABSTRACT

The kinetics of oxidation of o-chloroaniline by periodate in acetone-water medium has been studied. The order with respect to both oxidant and subtrate has been found to be one in each case. The rate increases on increasing ionic strength while it decreases with a decrease in dielectric constant. The rate of pH profile has been given and discussed. There is no effect of free radical scavengers on rate of reaction. The thermodynamics parameters are also presented and discussed. The main product of oxidation confirmed by IR and NMR study was chloro-1, 4-benzoquinone. A suitable mechanism has been proposed and the rate law dried.

**Key words:** o-Chloroaniline, Oxidation, Periodate ion, Benzoquinone, Kinetics and mechanism

## INTRODUCTION

The oxidation of aromatic amines with different oxidizing 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 made on the non-malapradian oxidation of aromatic amines by periodate ion are rather few[1-5]. Recently, we have communicated[6,7], the results on the basis of N, N-dimethyl-p-toluidine, 2, 4-dimethylaniline and p-ethylaniline by periodate under various conditions. The oxidation of o-chloroaniline has not been investigated with periodate and hence, the present work of oxidation of o-chloroaniline (OCA) with periodate has been taken up.

## EXPERIMENTAL

OCA and sodium metaperiodate (E. Merck A.R. grade) were used after Zn-dust distillation/recrystallization. Doubly distilled water and other chemicals of A.R. grade were used. Thiel, Schultz and Kotch buffer[8] was used for maintaining the pH of reaction mixtures.

---

*Address for Correspondence

The progress of the reaction was followed by recording the absorbance of the light red colored reaction mixture on Shimadzu double beam spectrophotometer, UV-150-02 at the $\lambda_{max}$ 460 nm keeping the pH at 5.0, during the period in which the $\lambda_{max}$ did not change. Initial rate in terms $(dA/dt)_i$ was evaluated by plane mirror method while the pseudo first order rate constant $k_1$, was calculated by using Guggenheim method. The second order rate constant $k_2$ was obtained by dividing the $k_1$ by [S] where S is the reactant taken in excess. The stoichiometry of the reaction was determined iodimetrically.

## RESULTS AND DISCUSSION

### Effect of oxidant and substrate

The reaction was studied at different concentrations of periodate and o-chloroaniline, respectively, keeping the other parameters constant. Initial rates in terms of $(dA/dt)_i$ at different [OCA] and [Periodate] (Table-1), showed that the reaction follows second order kinetics, being first order each in OCA and periodate, as found by the application of Vant-Hoff's differential method. The second order kinetics can also be proved by the fact that the rate was linearly related to the concentration of the reactant and varied in each case.

**Table 1**

| $\lambda_{max}$ = 460 nm | | | | Acetone = 20.0% (v/v) | | | | Temp. = $30 \pm 0.1$°C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| [OCA] x $10^3$ (M) | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| [NaIO$_4$] x $10^2$ (M) | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| $(dA/dt)_i$ x $10^3$ min$^{-1}$ | 3.3 | 3.8 | 4.8 | 6.0 | 7.0 | 7.0 | 8.5 | 9.5 | 10.0 | 12.5 |

At higher [substrate] the reaction followed pseudo first order kinetics. The plot of $k_1$-1 vs $[S]^{-1}$ was linear passing through the origin, indicating that the unstable intermediate formed in slow step, which got consumed in a subsequent fast step.

### Effect of pH, dielectric constant and ionic strength

Kinetics studies in the pH range 3.5 to 8.5 (Table-2) indicate the rate maxima at pH 5.0. The first part of this profile i.e. the increase in the rate from pH 3.5 to 5.0 may be due to the decrease in the protonation of OCA from 5.0 to 8.5, which makes greater concentrations of OCA available for reaction. This assumption is in the line with the fact that unprotonated OCA is the reactive species as shown in the mechanism. Further, the concentration of the periodate monoanion is maximum around pH 5.0 and it decreases beyond this pH value[1,2,9-11], which may be the reason for the decrease in the rate of reaction beyond pH 5.0. This behaviour also supports our assumption in the proposed mechanism that out of the various species of the periodate, the species taking part in the reaction in this case is the periodate monoanion [IO$^-$].

The data in Table-3 suggest, that the rate decreases with decrease in dielectric constant. The plot of log $(dA/dt)_i$ vs $1/D$ was found to be linear with a negative slope, indicating that the reaction may be ion-dipole type. The negative slope of this is in accordance with Amis view[12] that the slope will be negative if the reacting species is an anion, which is a periodate monoanion.

The effect of varying ionic strength ($\mu$) on the specific rate was observed under pseudo-first order condition in the presence of different concentrations of a neutral salt NaCl (Table-4). The rate of reaction increased with an increase in ionic strength. A plot between log $(dA/dt)_i$ vs $\mu$ was primary linear type, which indicates that the ion-dipole reaction is the rate-determining step.

The effect of temperature was also studied and the values of different thermodynamics parameters were evaluated from the linear Arrhenius plot (obtained from the results of kinetic studies at four temperatures ranging from 30 to 45°C). These are $E_2 = 10.95$ k.cal.mol$^{-1}$; $A = 1.691 \times 10^6$ lit. mol$^{-1}$. sec$^{-1}$; $\Delta S^{\#} = -32.10$ e.u.; $\Delta F^{\#} = 20.295$ k.cal. mol$^{-1}$ and $\Delta H^{\#} = 10.32$ k.cal.mol$^{-1}$.

**Table 2**

$\lambda_{max} = 460$ nm    Acetone = 5.0% (v/v)    Temp. = $35 \pm 0.1$°C
[OCA] = $3.0 \times 10^{-3}$ M    [NaIO$_4$] = $3.0 \times 10^{-2}$ M

| pH | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 |
|---|---|---|---|---|---|---|
| $(dA/dt)_i \times 10^4$ min$^{-1}$ | 20.0 | 25.0 | 30.0 | 40.0 | 30.0 | 25.0 |

**Table 3**

$\lambda_{max} = 460$ nm    Temp. = $30 \pm 0.1$°C
[OCA] = $3.0 \times 10^{-3}$ M    [NaIO$_4$] = $3.0 \times 10^{-3}$ M

| Dielectric constant (D) | 72.4 | 71.0 | 69.5 | 68.4 |
|---|---|---|---|---|
| $1/D \times 10^4$ | 138.1 | 140.8 | 143.5 | 146.2 |
| $(dA/dt)_i \times 10^3$ min$^{-1}$ | 3.75 | 2.40 | 1.60 | 1.00 |

**Table 4**

$\lambda_{max} = 460$ nm    Acetone = 5.0% (v/v)    Temp. = $35 \pm 0.1$°C
[OCA] = $3.0 \times 10^{-3}$ M    [NaIO$_4$] = $3.0 \times 10^{-2}$ M

| $\mu \times 10^2$ (M) | 4.0 | 5.0 | 6.0 | 7.0 |
|---|---|---|---|---|
| $(dA/dt)_i \times 10^3$ min$^{-1}$ | 3.5 | 4.0 | 4.5 | 5.25 |

## Stoichiometry and product analysis

The stoichiometry of the reaction was also determined. It was found that 1 mole of o-chloroaniline consume 2 moles of periodate.

For the product analysis, reaction mixture (OCA: NaIO$_4$ = 1:10) was filtered after 30 hours, filtrate was extracted with petroleum ether and an orange colored component was separated from this extract by preparative T.L.C. Its melting point was found to be 59°C. This compound responded positively for a quinone[13-14]. $\lambda_{max}$ for this compound in CHCl$_3$ were found to be 270, 370 and 520 nm, which are in good agreement for the values reported in literature[15] for chloro-1, 4-benzoquinone.

The IR spectrum (in KBr) of this compound showed the presence of bands at 2713 cm$^{-1}$ (s) (due to ring C-H strech), 1632 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, 3255 cm$^{-1}$ (w) (may be due to overtone of C=O strech). Further bands at 1514 cm (s) and 1469 cm$^{-1}$ (s) may be due to C=C ring stretch, the band at 1114 cm$^{-1}$ may be due to in plane C-H bending in the ring. The bands were also obtained at 744 cm$^{-1}$ (m) and 825 cm$^{-1}$ (m), which were due to the out of plane C=C and C-H bending modes. A band at 761 cm$^{-1}$ (s) is characteristics of C-Cl stretching. On the basis of these data, this compound may be characterised as chloro-1,4-benzoquinone.

## MECHANISM

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 bimolecular reaction in solution and the latter (mainly in polar solvents) also suggests the formation of a charged and rigid transition state, which is expected to be strongly solvated in polar solvent employed. The above assumption is also supported by the above fact that the rate decreases with decreasing dielectric constant. The value of frequency factor of the order of 10$^6$ is suggestive of the fact that the reactive species are large 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 kinetics studies, insensitiveness towards free radical scavengers, product characterized and the chance of the formation of benzoquinoneimine derivatives during such reactions[16-18], a mechanism has been proposed.

The value $\Delta S^\#$ and the effect of dielectric constant suggest 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) and subsequent fast hydrolysis of (II) will give chloro-1, 4-benzoquinone (III). On the basis of above mechanism, the rate of the reaction should be given by rate expression

$$(dA/dt) = k_2[OCA][IO_4-]$$
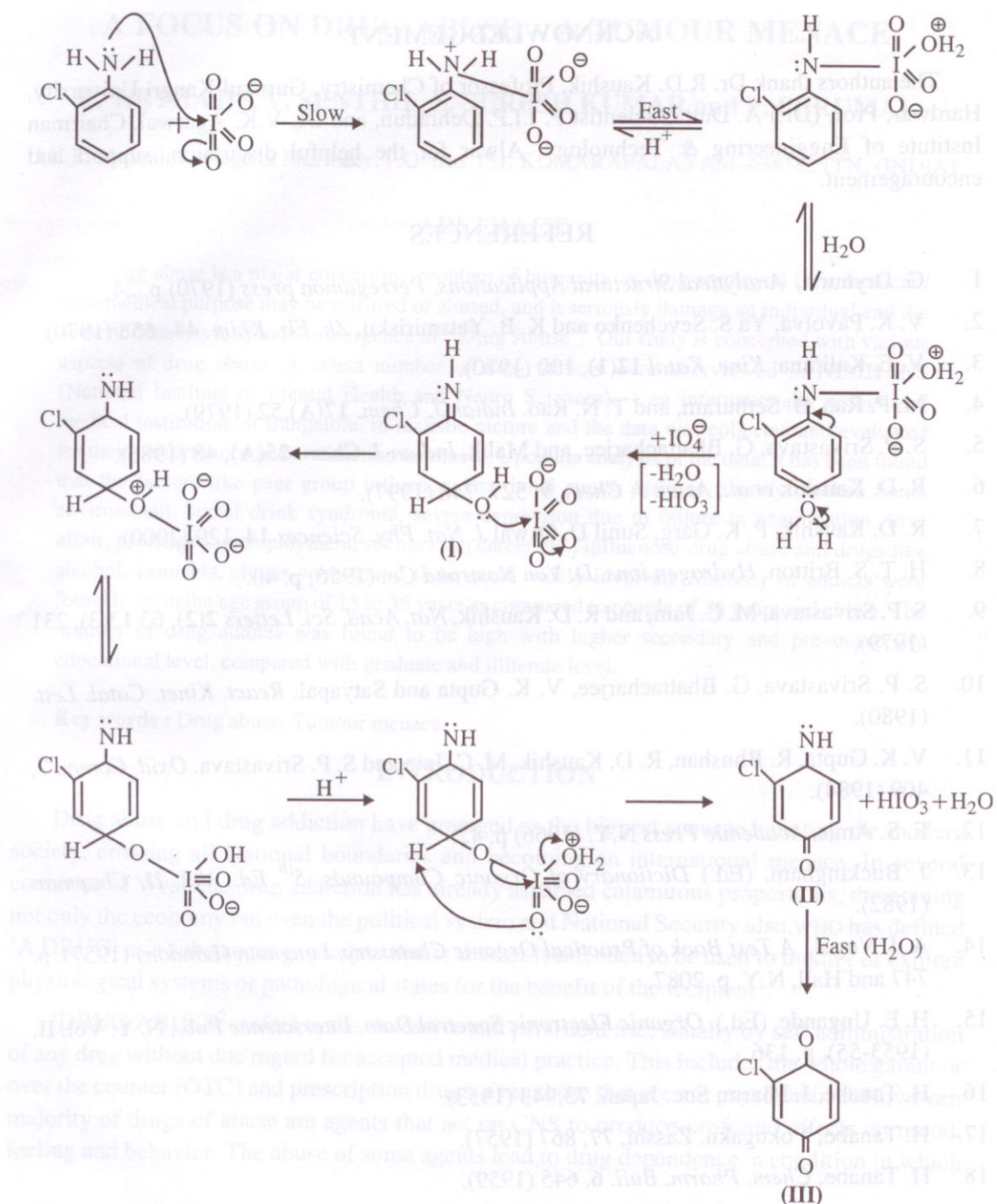
Oxidation of o-chloroaniline

## ACKNOWLEDGEMENT

## REFERENCES

1.   G. Dryhurst, *Analytical Structural Applications, Perregamon press* (1970) p. 24

2.   V. K. Pavolva, Ya S. Sevchenko and K. B. Yatsmiriskii, *Zh. Fiz. Khim.* **44** : 658 (1970).

3.   V. E. Kalinina, *Kine. Katal* **12(1)**, 100 (1970).

4.   M. P. Rao, B. Sethuram, and T. N. Rao. *Indian J. Chem.* **17(A)**,52 (1979).

5.   S. P. Srivastava, G. Bhattacharjee, and Malik. *Indian J. Chem.* **25(A)**, 48 (1986).

6.   R. D. Kaushik *et al.*, *Asian J. Chem.* **9**, 527, 746 (1997).

7.   R. D. Kaushik, P. K. Garg, Sunil D. Oswal *J. Nat. Phy. Sciences* **14,** 129 (2000).

8.   H. T. S. Britton. *Hydrogen ions, D. Von Nostrand Co.* (1956) p. 40.

9.   S. P. Srivastava, M. C. Jain, and R. D. Kaushik, *Nat. Acad. Sci. Letters* **2(2)**, 63 **13**(3), 231 (1979).

10.  S. P. Srivastava, G. Bhattacharjee, V. K. Gupta and Satyapal. *React. Kinet. Catal. Lett.* (1980).

11.  V. K. Gupta, R. Bhushan, R. D. Kaushik, M. C. Jain and S. P. Srivastava. *Oxid. Comm.* **7,** 409 (1984).

12.  E. S. Amis, *Academic Press* N.Y. (1966) p. 42.

13.  J. Buckingham, (Ed.) *Dictionary of Organic Compounds, 5th Ed., Vol. II, Chapman* (1982).

14.  A. I. Vogel, *A Text Book of Practical Organic Chemistry, Longman (London)* (1957). p. 747 and Hall, N.Y. p. 2087.

15.  H. E. Ungande, (Ed.). *Organic Electronic Spectral Data, Interscience Pub.*, N. Y. Vol. II, (1953-55), p. 136.

16.  H. Tanabe, J. Pharm. Soc. Japan, **73**,943 (1953).

17.  H. Tanabe, Yokugaku. Zasshi, **77**, 867 (1957).

18.  H. Tanabe, *Chem. Pharm. Bull.* **6**, 645 (1959).