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Periodate Oxidation of *o*-Toluidine in Acetone-Water Medium: A Kinetic and Mechanistic Study

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The kinetics of oxidation of *o*-toluidine by periodate in acetone-water medium has been studied. The order with respect to both oxidant and substrate has been found to be one in each. The rate increases on increasing ionic strength while it decreases with a decrease in dielectric constant. The rate-pH profile has been given and discussed. There is no effect of free radical scavengers on rate of reaction. The thermodynamic parameters are also presented and discussed. The main product of oxidation is methyl-1,4-benzoquinone, which is confirmed by spectroscopic studies and melting point. A suitable mechanism has been proposed and the rate law derived.

INTRODUCTION

The kinetic studies on non-malapradian oxidation of aromatic amines by periodate are rather few[1–4] and reported results are contradictory. The oxidation of N,N-diethylaniline by periodate was studied by Pavolva *et al.*[5], while the kinetics of Ru(III) catalysed oxidation of benzidine, *o*-toluidine and *o*-dianisidine by IO_4^- in HCl containing $K_2RuCl_4 . H_2O$ or $K_4Ru_2OCl_{10}$ was studied by Kalinina[6]. The mechanism of the catalytic effect of Ru compounds involved alternate oxidation-reduction of Ru(III) and Ru(IV). However the detailed kinetic studies and isolation and characterization of reaction products was not undertaken and hence a clear picture regarding the mechanism could not be worked out. Rao *et al.*[7] proposed an ionic mechanism for the oxidation of aniline by periodate while Tanabe[2, 3] suggested a free radical mechanism for this complex reaction. Oxidation of 2,5-dimethylaniline in aqueous-acid medium has been reported by Srivastava *et al.*[8] Some investigations, made by us[9] on periodate oxidation of some anilines show that these complex reactions require more studies for understanding their complex behaviour. The present paper describes the results of periodate oxidation of *o*-toluidine (TOL) in acetone-water medium.

EXPERIMENTAL

o-Toluidine (TOL) and sodium metaperiodate of 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[12] was used for maintaining the pH of solutions.

The reaction being quite fast at ordinary temperatures, was studied in 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 TOL and periodate ion in acetone-water medium produced violet colour which showed maximum absorbance at 525 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 *o*-toluidine respectively, keeping the other constant. Initial rates in terms of $(dA/dt)_i$ at different [TOL] and [Periodate], showed that the reaction follows second order kinetics, being first order each in TOL 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 varied in each case.

Under pseudo first order conditions, the plot of rate^{-1} *vs.* $[S]^{-1}$ (where S is the reactant taken in excess) was linear with very small intercept (Table-1), indicating that the intermediate formed in slow step got consumed in a subsequent fast step[10]. The stoichiometry of the reaction determined by estimating the unreacted $NaIO_4$ iodometrically, was found to be 2 : 1 (oxidant-substrate).

TABLE-1

EFFECT OF REACTANT CONCENTRATION ON RATE AT 25 ± 0.1°C

λ_{max} = 525 nm, Acetone = 10.0% (v/v)

$[TOL] \times 10^3$	$[NaIO_4] \times 10^3$	$(dA/dt)_i \times 10^3$
1.0	10.0	3.50
1.0	12.0	4.25
1.0	14.0	4.75
1.0	16.0	5.50
1.0	18.0	6.25
10.0	1.0	3.00
13.0	1.0	4.12
15.0	1.0	4.75
18.0	1.0	5.75

Initially the reaction mixture was violet in colour. On standing overnight, it changed to reddish brown colour. This reaction mixture was extracted with petroleum ether. On evaporation of the solvent, the yellow compound with m.p. 68°C (lit. 67–70°C)[16] was obtained. This compound was found to be TLC single and responded positively for quinone[11].

IN UV-VIS spectrum, the λ_{max} obtained for this compound in C_2H_5OH solvent were 240 nm and 310 nm which suggests the presence of quinonoid structure in the compound. Further it is in agreement with the reported values for methyl-1,4-benzoquinone[18].

The IR spectrum in KBr of this compound showed the presence of bands at 3054 cm^{-1} (s) (due to ring C—H stretch), 2925 cm^{-1} (s) and 2854 cm^{-1} (s) (due to C—H stretching vibrations in $—CH_3$), 1709 cm^{-1} (w) and 1744 cm^{-1} (w) (due to overtones and combination bands), 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 alkyl group[19, 20]), and 3330 cm^{-1} (w) (may be due to overtone of C═O stretch). Further the bands at 1514 cm^{-1} (s) and 1457 cm^{-1} (s) may be due to C═C ring stretch, the bands at 1135 cm^{-1} (m) to 1330 cm^{-1} (m) may be due to the in-plane C—H bending in the ring. The bands were also obtained at 751 cm^{-1} (s) and 664 cm^{-1} (s) which were due to the out-of-plane C═C bending and ═C—H bending modes and substitution pattern in ring.

The NMR spectrum of this compound in $CDCl_3$ showed the peaks at $\delta = 7.091$, D, 2H; at $\delta = 6.658$, S, 1H; and at $\delta = 2.156$, S, 3H. A singlet at $\delta = 2.156$ may be due to $—CH_3$ group attached to the ring. The other signals in spectrum at $\delta = 6.658$ and $\delta = 7.091$, were due to 3 protons of the ring.

On the basis of the melting point[16] and spectral studies[18–21], this compound may be methyl-1,4-benzoquinone.

Kinetic studies were carried out in the range of pH 3.6 to 6.7 using Thiel, Schultz and Coch Buffer[12]. The rate increased sharply up to pH 5.2 (Table-2) which may be due to the decrease in protonation of TOL. The concentration of periodate monoanion is maximum around pH 5.0 to 7.0 and decreases beyond this pH value[5], which may probably be the reason for the decrease in rate beyond pH 5.2. After pH 5.0, the periodate dianion formation becomes predominant which is unreactive, a behaviour similar to one observed by previous workers in case of other anilines[9, 13, 14, 17].

TABLE-2

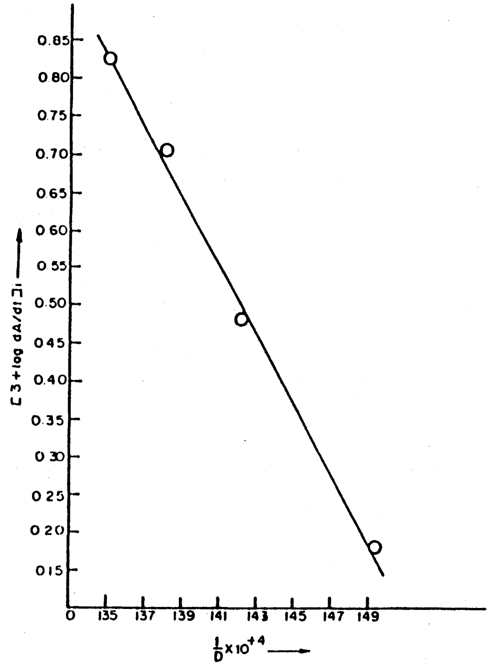
EFFECT OF pH ON REACTION RATE

[TOL] = 0.01 M, $[NaIO_4] = 0.001$ M, Temp. = 25 ± 0.1°C

$\lambda_{max} = 525$ nm, Acetone = 10.0% (v/v)

pH	3.6	3.9	4.2	5.2	5.7	6.2	6.7
$\left(\frac{dA}{dt}\right)_i \times 10^3$	2.75	4.5	7.0	10.0	8.0	3.5	1.5

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) (Fig. 1). On decreasing dielectric constant the rate was found decreasing. A plot between log $(dA/dt)_i$ vs I/D was found to be linear with negative slope indicating the reaction may be of ion-dipole type. The negative slope of this plot is in accordance with Amis' view[15] that the slope will be negative if the reacting ion is anion, which is periodate monoanion in the present study.



[O-TOL]=0.01M, [NaIO$_4$]=0.001M
λMax=525nm, Temp.=25 ±0.1°C

Fig. 1.

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. 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.

The kinetic studies were made under pseudo first order conditions (taking substrate in excess) at four different temperatures ranging between 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 substrate.

The linear Arrhenius plot (log k_2 vs I/T) was used for calculating the thermodynamic parameters. The mean values of various activation parameters are: $E_a = 5.18$ kcal/mol; $A = 1.540 \times 10^2$ lit $mol^{-1} sec^{-1}$; $\Delta S^{\#} = -50.55$ E.U.; $\Delta F^{\#} = 20.04$ kcal/mol $\Delta H^{\#} = 4.56$ 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 10^2 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 the kinetic studies, insensitiveness towards free radical scavengers, product identified 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.

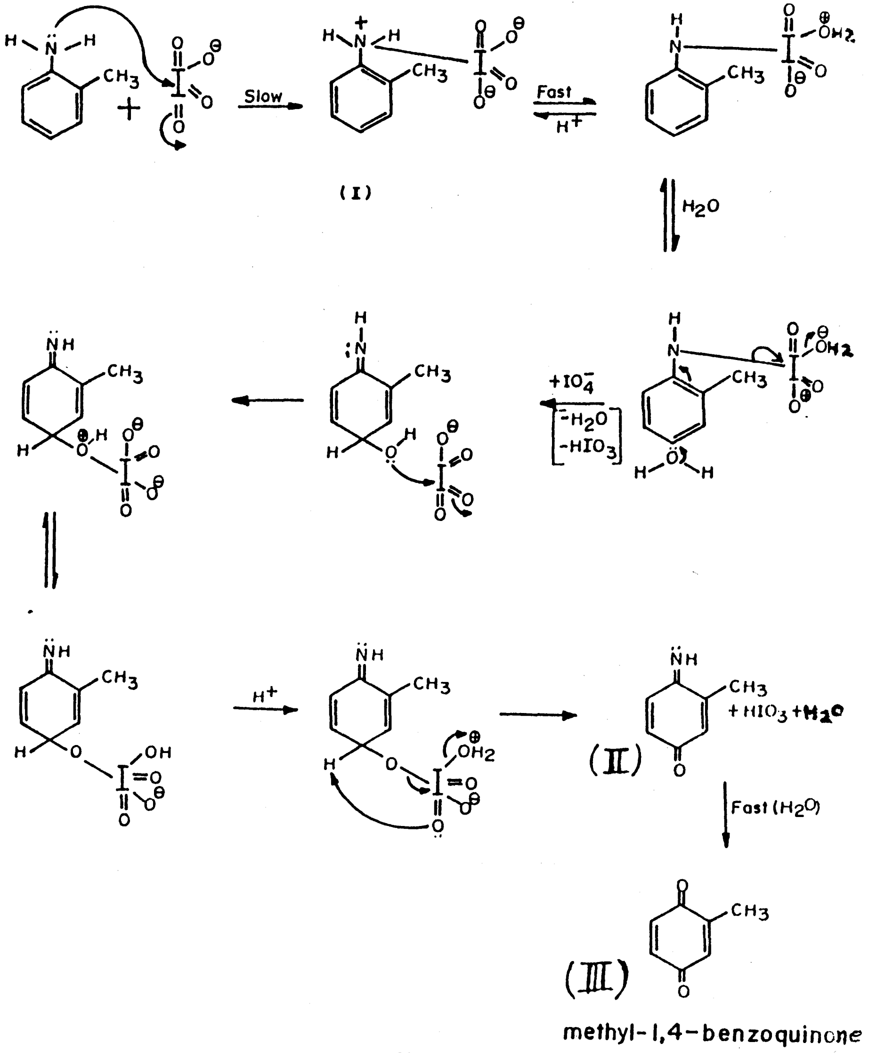


Chart-I

The value of $\Delta S^{\#}$ and effect of dielectric constant suggest the involvement of solvation effects. The plot of $[S]^{-1}$ *vs.* $[\text{rate}]^{-1}$ suggests the formation of a short lived charged intermediate (I) as shown in the mechanism. This intermediate (I) reacts with another molecule of periodate to form methyl quinoneimine (II). The last step seems to be the fast hydrolysis of (II) to give (III) which was characterized by us as methyl *p*-benzoquinone.

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

The mechanism proposed and the rate law derived is in accordance with various kinetic features observed, namely the second order kinetics, effect of pH, effect of dielectric constant, effect of ionic strength on rate and the product identified.

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