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Periodate Oxidation of Aromatic Amines—Kinetics and Mechanism of Oxidation of *p*-Toluidine in Acetone-Water Medium

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The kinetics of the periodate oxidation of *p*-toluidine in acetone-water medium has been followed spectrophotometrically. The total order of reaction is two, being first order in each reactant. The rate-pH profile has been given and discussed. The rate decreased with a decrease in dielectric constant while no appreciable increase in rate with an increase in ionic strength has been observed. The reaction was found insensitive towards free radical scavengers. The activation parameters have been evaluated. The main product isolated and characterised was 4-methyl-*o*-benzoquinone. The stoichiometry of 2 mol of periodate: 1 mol of *p*-toluidine was observed. A suitable mechanism has been proposed and the rate law derived.

INTRODUCTION

The non-malaparadian oxidation of aromatic amines by periodate has received comparatively less attention so far[1-4]. Kinetic studies on oxidation of N-N-diethylaniline as made by Pavolva *et al.*[5], oxidation of some anilines and xylidines as made by Srivastava *et al.* [6-8] are already a part of the literature. The present paper describes the results of kinetic studies of periodate oxidation of *p*-toluidine in acetone-water medium.

EXPERIMENTAL

Sodium metaperiodate and *p*-toluidine of Loba G.R. grade were used after recrystallization. All other chemicals used were of A.R. grade. Doubly distilled water was used for the preparation of solutions and reaction mixtures. Thiel, Schultz and Coch Buffer[9] was used for maintaining the pH of solutions. The pH of the reaction mixture was kept constant at 6.0 during the course of reaction.

The progress of reaction was followed spectrophotometrically on Shimadzu double beam spectrophotometer. Stoichiometry was found iodometrically. The reaction mixture developed violet colour with λ_{max} at 470 nm.The λ_{max} did not change during the period for which the kinetic studies were made.

RESULTS AND DISCUSSION

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 for about 20 h, it changed to reddish-yellow colour. For product analysis, the reaction mixture was filtered after 20 h and the filtrate was extracted with petroleum ether. The extracted portion was found to contain two components on being separated by TLC. One of the compounds was red in colour with m.p. 69°C (lit.[10], m.p. 68°C). This compound was found to be TLC single and responded positively for a quinone; IR (KBr disc): 2924 cm^{-1} (C–H), 1632 cm^{-1} (C=O, 1,2-quinone), 1386 cm^{-1} ($C–CH_3$). On the basis of the above data the compound was characterised as 4-methyl-*o*-benzoquinone.

The reaction was studied at different concentrations of amine and periodate respectively, while keeping the other constant. Initial rates were evaluated in terms of change in absorbance with time [$(dA/dt)_i$]. The results are presented in Table- 1. These results and the linear variation of rate with the concentration of the reactant varied suggesting that the reaction follows second order kinetics, being first order in each reactant.

TABLE-1
EFFECT OF REACTANT CONCENTRATION ON RATE
Temp. = 35 ± 0.1°C, λ_{max} = 470 nm, Acetone = 10% (v/v)

[*p*-Tol.] × 10^3 M	[$NaIO_4$] × 10^3 M	$(dA/dt)_i \times 10^2$
1.0	10.0	0.6
2.0	10.0	0.8
3.0	10.0	1.6
4.0	10.0	2.0
5.0	10.0	2.2
6.0	10.0	3.0
10.0	1.0	0.3
10.0	2.0	0.6
10.0	3.0	0.8
10.0	4.0	1.2
10.0	5.0	1.3
10.0	6.0	1.6

Fig. 1. shows the plot between $rate^{-1}$ and $[s]^{-1}$ (where [s] is the concentration of substrate) under pseudo-first order conditions and at high substrate concentration [s]. The plot which is linear and passes through the origin suggests that the intermediate formed in the slow step got consumed in a subsequent fast step[11].

The rate-pH profile for this reaction is depicted in Fig. 2. This pH effect may be explained by the fact that the rate determining step in the proposed mechanism is a reaction between the unprotonated amine and periodate monoanion. The rapid

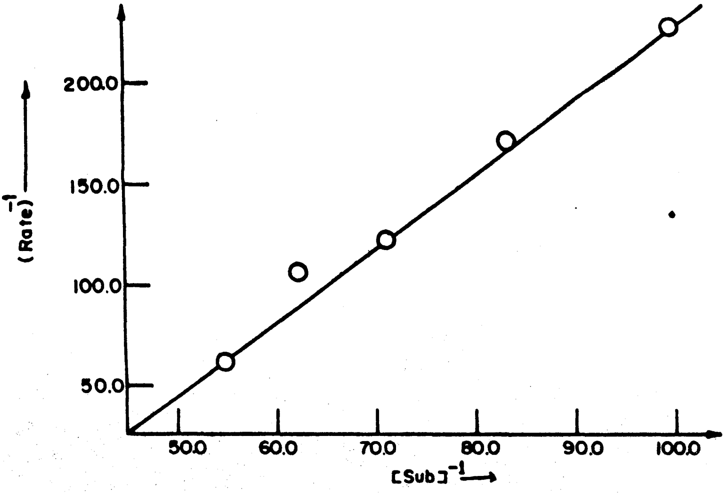

Fig. 1. Dependence of reciprocal rate on $[S]^{-1}$ under pseudo-first order conditions: $[NaIO_4] = 1.0 \times 10^{-3}$ M, Acetone = 20% (v/v), $\lambda_{max} = 470$ nm, Temp. = 30 ± 0.1°C

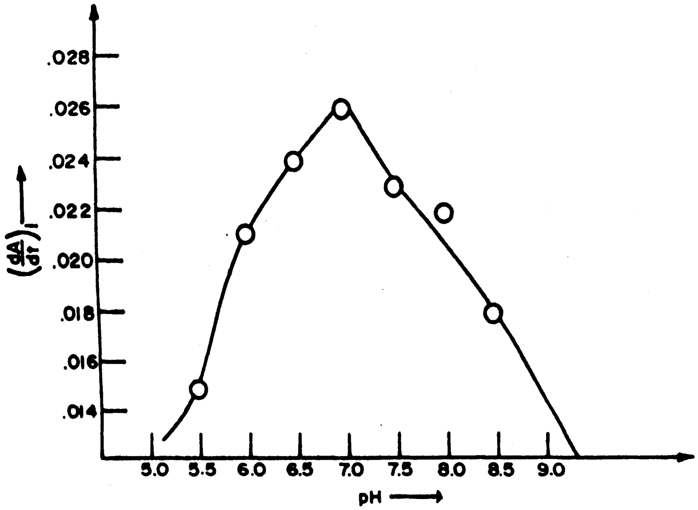

Fig. 2. Effect of pH on reaction rate : [*p*-Tol.] = 1.0×10^{-3} M, $[NaIO_4] = 1.0 \times 10^{-2}$ M, Acetone = 10% (v/v), $\lambda_{max} = 470$ nm, Temp. = 35 ± 0.1°C

increase in the rate between pH 5.5 to 7.0 may be due to decrease in protonation of *p*-toluidine. The concentration of periodate monoanion is maximum between the pH 5 to 7 and decreases beyond this pH value[5], which may probably be the reason for the decrease in rate beyond pH 7.0. After pH 7.0 the periodate dianion formation becomes predominant which is unreactive. It is worth mentioning that the rate-maxima corresponded to a pH value 5.0 in case of our studies on *m*-toluidine[11]. The shift in maxima in the present study appears to be due to a greater value of pK_a for *p*-toluidine. A similar behaviour has been observed by previous workers for the periodate oxidation of some aromatic amines[12–14].

Different kinetic runs, under pseudo-first order conditions, were carried out in the presence of different amounts of acetone ranging from 2.5% to 15.0% (v/v). the rate was found to decrease with decreasing dielectric constant (Table-2). A plot between log $(dA/dt)_i$ and 1/D (Amis plot) was found to be linear with negative slope suggesting thereby that the rate determining step was a reaction between a dipole and anion. This anion is periodate monoanion in the present study.

TABLE-2

EFFECT OF DIELECTRIC CONSTANT ON RATE

[*p*-Tol.] = 0.001 M, [$NaIO_4$] = 0.01 M, Temp. = 35 ± 0.1°C, λ_{max} = 470 nm

D (dielectric constant)	73.9	72.4	70.0	66.8
$(dA/dt)_i \times 10^3$	12.0	8.0	5.0	4.0

The reaction was studied at different ionic strengths maintained by using NaCl as neutral salt (Table-3). These data indicate that the rate increased with an increase in the ionic strength (μ) although it is not an appreciable increase. Further the plot between $(dA/dt)_i$ *vs.* μ was linear suggesting that the positive salt effect was primary linear type, again indicating that the rate determining step should be a reaction between an ion and dipole.

TABLE-3

EFFECT OF IONIC STRENGTH ON RATE

[*p*-Tol.] = 0.001 M, [$NaIO_4$ = 0.001 M, Acetone = 12% (v/v), Temp.= 35 ± 0.1°C, λ_{max}= 470 nm

$\mu \times 10^3$	0.60	1.10	1.60	2.10	2.60
$(dA/dt)_i \times 10^3$	2.50	2.60	2.70	2.90	3.00

The reaction was studied at four different temperatures between 30° to 45°C under pseudo-first order conditions by taking periodate in excess and evaluating the pseudo-first order rate constant by the Guggenheim method. These pseudo-first order rate constants were divided by the concentration of periodate (taken in excess) to get the second order rate constant K_2. Activation parameters were evaluated from the linear Arrhenius plot obtained by us. The main values of energy of activation E_a, frequency factor (A), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta F^{\#}$), as evaluated at these temperatures, are given in Table-4.

TABLE-4

ACTIVATION PARAMETERS

[*p*-Tol.] = 0.001 M, [$NaIO_4$] = 0.01 M, Acetone = 10% (v/v), λ_{max} = 470 nm

E_a (kcal/mole)	A ($dm^3\ mol^{-1}\ sec^{-1}$	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (E.U.)	$\Delta F^{\#}$ (kcal/mole)
8.64	1.49×10^5	8.03	–36.94	19.49

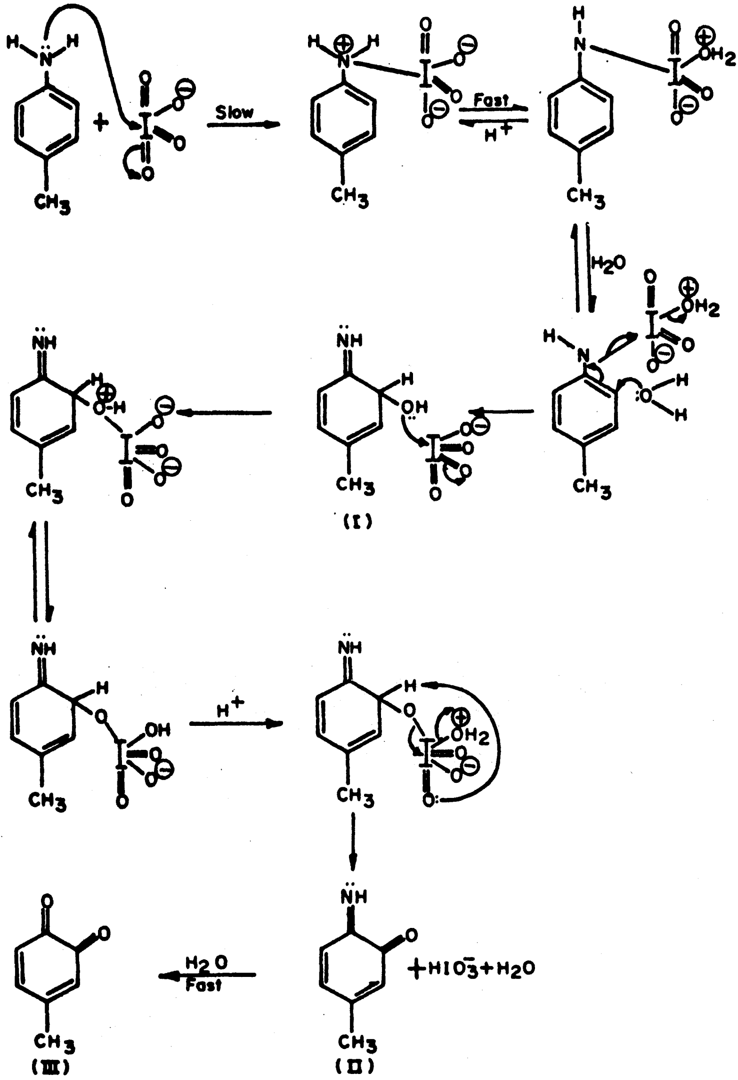

Chart- 1

A large negative value of entropy of activation observed by us is suggestive of the formation of a charged and rigid transition state which is expected to be strongly solvated in polar solvent employed and is in accordance with the first step in the proposed mechanism. A low value of activation energy is characteristic of a bimolecular reaction in solutions. The effect of dielectric constant on the rate also supports the above assumption. Further, a value of frequency factor A of the order of 10^5 indicates the involvement of a reactive species which is larger in size.

It is important to mention that the observed value of $\Delta S^{\#}$ is much lesser than that obtained in case of the periodate oxidation of *m*-toluidine[11]. It is due to the fact that *m*-toluidine is more polar[15] and so gets solvated to a greater extent.

Before proposing a mechanism for the reaction, it is worth while to point out that there was no effect of free radical scavengers on the rate of reaction. On the basis of the kinetics and product studies the mechanism (Chart-1) is proposed.

High negative value of entropy of activation and the effect of dielectric constant on rate indicate that the activated complex should be strongly solvated and thus supports the formation of a charged intermediate as concluded above. The formation of a charged intermediate visualised as (I) is shown in the mechanism. It is very likely that (I) reacts with another molecule of periodate to form quinoneimine (II). The last step seems to be the fast hydrolysis of (II) to give 4-methyl-*o*-benzoquinone (III).

On the basis of the above mechanism, the rate of the reaction should be given by

$$dA/dt = K_2\,[p\text{-toluidine}][IO_4^-]$$

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

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