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Kinetics and Mechanism of Periodate Oxidation of *m*-Toluidine in Acetone-Water Medium

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The kinetics of the periodate oxidation of *m*-toluidine in acetone-water medium has been followed spectrophotometrically. This reaction followed second order kinetic behaviour, 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 it increased with an increase in ionic strength. The reaction was found insensitive towards free radical scavengers. The activation parameters have been evaluated. The main product of oxidation was 3-methyl-*p*-benzoquinone. The stoichiometry of 2 mol of periodate : 1 mol of *m*-toluidine was observed. A suitable mechanism has been proposed and the rate law derived.

INTRODUCTION

An attempt has been made by us to decide the nature of mechanism being followed in the periodate oxidation of aromatic amines. The results for the oxidation of *m*-toluidine are presented and discussed in this paper.

Out of the various oxidants employed for the oxidation of aromatic amines, periodate is of special interest from synthetic point of view. Oxidation of aniline from this point of view was studied by Tanabe[1]. However, kinetic studies of these non-malaparadian oxidations available in literature are rather few[2] and the reported results are contradictory for these studies. The kinetics of uncatalysed periodate oxidation of N,N′-diethylaniline was studied by Pavlova *et al.*[3], while the kinetics of Ru(III) catalysed oxidation of benzidine, *o*-toluidine and *o*-dianisidine was studied by Kalinina[4]. Tanabe suggested a free radical mechanism for the oxidation of aniline by periodate on the basis of non-kinetic evidences while Rao *et al.*[5] proposed an ionic mechanism for this complex reaction. Recently oxidation of 2,5-dimethylaniline in aqueous acetic acid medium has been reported[6]. Our earlier investigations on periodate oxidation of some aromatic amines[7–9] suggested the need for the study of periodate oxidation of more aromatic amines. The present paper describes the results of kinetic studies of periodate oxidation of *m*-toluidine in acetone-water medium.

EXPERIMENTAL

Sodium metaperiodate and *m*-toluidine of Loba GR grade were used after recrystallization or redistillation 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 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 absence of any catalyst. 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 a Shimadzu double beam spectrophotometer, UV-150–02. However, stoichiometry was determined iodometrically. The reaction between *m*-toluidine and periodate ion in acetone water medium produced reddish-violet colour which showed maximum absorbance at 540 nm. The λ_{max} did not change during the period for which the kinetic studies were made.

RESULT AND DISCUSSION

The stoichiometry of the reaction, determined by estimating unreacted $NaIO_4$ iodometrically, was found to be 2 : 1 (oxidant-substrate).

Initially the reaction mixture was reddish-violet in colour. On standing for about 24 h, it changed to a brown-red colour. For product analysis, the reaction mixture was filtered after 24 h and the filtrate was extracted with petroleum ether and a yellowish-brown compound m.p. 67°C (lit.[10] m.p. 67°–70°C) was obtained on evaporation of the solvent. This compound was found to be TLC single and responded positively for a quinone[11]; IR (KBr disc): 2816 cm^{-1} ν(C—H), 1590 cm^{-1} ν(C═O; 1,4 quinone), 1384 cm^{-1}ν (C—CH_3). On the basis of the above data the compound was characterised as 3-methyl-*p*-benzoquinone.

TABLE-1
EFFECT OF REACTANT CONCENTRATION ON RATE AT 35°C
λ_{max} = 540 nm, Acetone = 10% (v/v)

Substrate × 10^3 M	[$NaIO_4$] × 10^3 M	$(dA/dt)_i \times 10^2$
1.0	1.0	0.475
1.0	2.0	0.975
1.0	3.0	1.500
1.0	4.0	2.300
1.0	5.0	3.100
1.0	6.0	3.600
1.0	10.0	0.400
2.0	10.0	0.800
3.0	10.0	1.300
4.0	10.0	1.800
5.0	10.0	2.300
6.0	10.0	2.600

The reaction was studied at different concentrations of amine and periodate respectively, while keeping the other constant. Initial rates were evaluated in terms of $(dA/dt)_i$. The results as recorded in Table 1 showed that the reaction follows second order kinetics, being first order in each reactant. It is important to mention here that the rate was linearly related to the concentration of the reactant varied in each case, again giving first order with respect to each reactant with the overall order being two.

Further, 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], was found to be linear passing through the origin, suggesting that the intermediate formed in the slow step got consumed in a subsequent fast step[12].

The rate-pH profile for this reaction is depicted in Fig. 1. 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 increase in the rate between pH 4.1 to 5.0 may be due to decrease in protonation of *m*-toluidine. The concentration of periodate monoanion is maximum around pH 5.0 and decreases beyond this pH value, which may probably be the reason for the decrease in rate beyond pH 5.0. After pH 5.0 the periodate dianion formation becomes predominant which is unreactive[3–7]. A similar behaviour has been observed by previous workers[9, 13, 14]

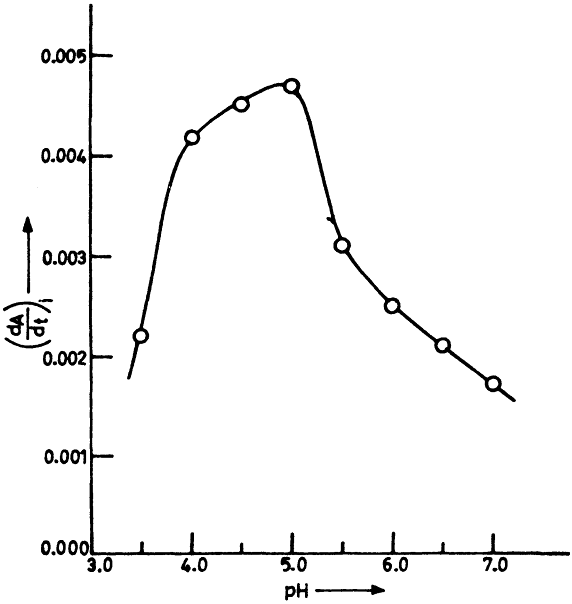

Fig. 1. Effect of pH on reaction rate [*m*-Toluidine] = 0.001 M, [$NaIO_4$] = 0.01 M, Acetone = 10% (v/v) Temp. = 35 ± 0.1°C, λ_{max} = 540 nm

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%. The rate was found to decrease with decreasing dielectric constant. A plot between log $(dA/dt)_i$ and 1/D (Amis plot) was found to be linear (Fig. 2) with negative slope suggesting thereby that the rate determining step was a reaction between an ion and dipole. 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.

The reaction was studied at different ionic strength maintained by using NaCl as neutral salt (Table-2). The data of this table clearly indicates that the rate increased with ionic strength (μ). 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.

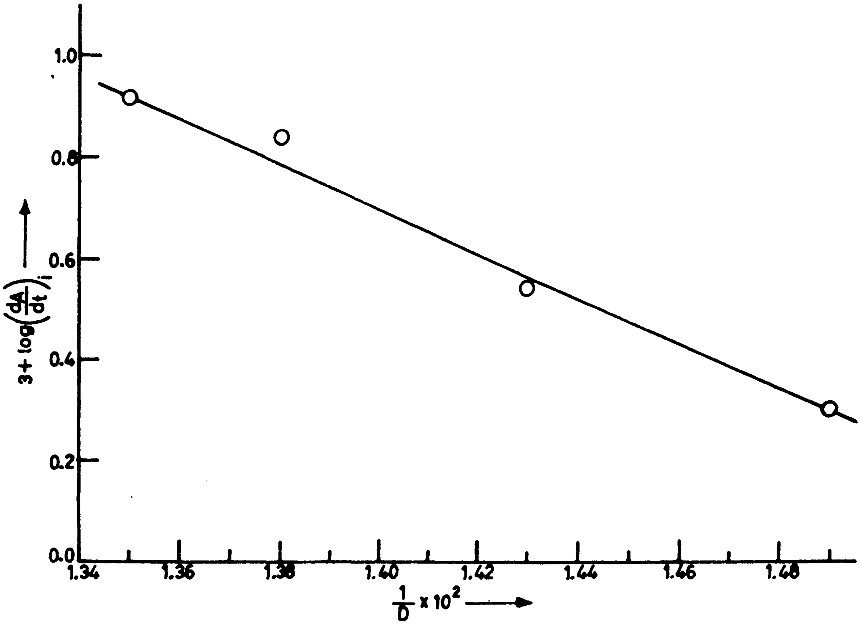

Fig. 2. Effect of dielectric constant on reaction rate
[*m*-Toluidine] = 0.001 M, [$NaIO_4$] = 0.01 M,
Acetone = 10% (v/v) Temp. = 35 ± 0.1°C, λ_{max} = 540 nm

TABLE-2
EFFECT OF IONIC STRENGTH [*m*-Touidine]= 0.01 M, [$NaIO_4$] = 0.001 M,
Acetone = 10% (v/v), λ_{max} = 540 nm, Temp. = 35± 0.1°C

[NaCl]	$\mu \times 10^2$	$(da/dt)_i \times 10^3$
0.010	1.1	5.0
0.015	1.6	5.4
0.020	2.1	5.6
0.025	2.6	6.0
0.030	3.1	6.6

The reaction was studied at four different temperatures under pseudo-first order conditions by taking periodate in excess and evaluating pseudo-first order rate constant by the Guggenheim method[16]. 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 (log k_2 vs 1/T) by carrying out the reaction at four different temperatures in the range 30° to 45°C. The mean values of various activation parameters are E_a = 8.46 kcal/mol; A = 2.38 × 10^3 $dm^2 mol^{-1} sec^{-1}$; $\Delta S^{\neq} = -52.30$ EU, $\Delta F^{\neq}$ = 20.45 kcal/mol and $\Delta H^{\neq}$ = 7.86 kcal/mol.

A perusal of data shows that the reaction is characterised by a large negative

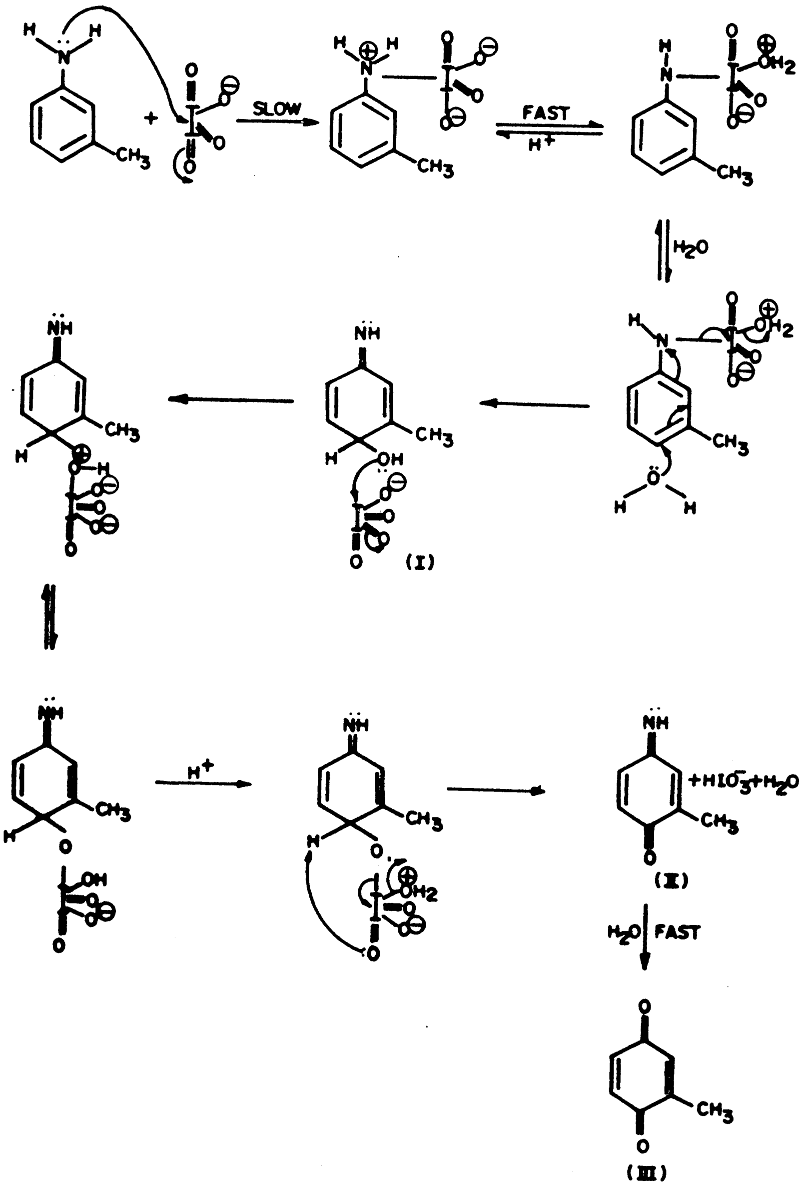

Chart-I

value of entropy of activation and a low value of energy of activation. The latter is characteristic of a bimolecular reaction in solution, the former 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 and is in accordance with the first step in the proposed mechanism. The decrease in the rate with decrease in dielectric constant observed also supports the above assumption. Further, a value of frequency factor A of the order of 10^4 is suggestive of the fact that the reactive species are large in size.

Before proposing a mechanism for the reaction, it is worthwhile to point out that there was no effect of free radical scavengers on the rate of reaction. On the basis of kinetic behaviour, the product identified and the insensitiveness of this reaction towards free radical scavengers and the chances of formation of benzoquinoneimine derivatives during such reactions as reported earlier[1–3, 7], the following mechanism 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 (Chart-I). 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 3-methyl-*p*-benzoquinone (III).

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

$$\frac{dA}{dt} = k_2[m\text{-toluidine}][IO_4^-]$$

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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