A Kinetic and Mechanistic Study of Periodate Oxidation of N,N-Dimethyl-*p*-Toluidine in Acetone-Water Medium

R.D. Kaushik*, Dheer Singh, P.K. Garg and Rajesh Joshi
Department of Chemistry
Gurukula Kangri University, Hardwar-249 404, India

The kinetics of oxidation of N,N-dimethyl-*p*-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 case. 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 confirmed by IR and NMR study was N-methyl, 4-methyl, *o*-benzoquinoneimine. 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-malaparadian oxidation of aromatic amines by periodate are rather few[1-4] and reported results are contradictory. The oxidation of N,N-dimethylaniline by periodate was studied by Pavlova *et al.*[5], while the kinetics of Ru(III) catalysed oxidation of benzidines, *o*-toluidine and *o*-dianisidine was studied by Kalinina[6]. 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 toluidines show that these complex reactions require more studies for understanding their complex behaviour. The present paper describes the results of periodate oxidation of N,N-dimethyl-*p*-toluidine (DMT) in acetone-water medium.

EXPERIMENTAL

N,N-dimethyl-*p*-toluidine and sodium metaperiodate of Loba GR grade are 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 15% (v/v) acetone-water medium and in the 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 DMT and periodate ion in acetone-water medium produced violet colour which showed maximum absorbance at 565 nm. The λ_{max} did not change during the period for which kinetic studies were made.

RESULTS AND DISCUSSION

The reaction was studied at different concentrations of periodate and N,N-dimethyl-*p*-toluidine, respectively, keeping the other constant. Initial rates in terms of (dA/dt)$_i$ at different [DMT] and [Periodate] (Table-1), showed that the reaction follows second order kinetics, being first order each in DMT 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 and varied in each case.

TABLE-1

EFFECT OF REACTANT CONCENTRATION OF RATE AT 35°C

λ_{max} = 565 nm, Acetone = 15.0% (v/v).

[Substrate] $\times 10^3$ M	[NaIO$_4$] $\times 10^3$ M	(dA/dt)$_i$ $\times 10^2$
5.0	0.5	1.10
5.0	1.0	2.20
5.0	1.5	2.95
5.0	2.0	3.25
5.0	2.5	4.40
5.0	3.0	5.30
1.0	10.0	1.32
2.0	10.0	2.80
3.0	10.0	4.50
4.0	10.0	5.50
5.0	10.0	6.00
6.0	10.0	6.60

At higher [substrate] the reaction followed pseudo first order kinetics. The plot of $1/k_1$ *vs.* $1/[S]$ was linear passing through the origin, 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).

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 brownish compound with m.p. 68°C was obtained. This compound was found to be TLC single and responded positively for quinone[11]: IR (KBr disc): 2926 cm^{-1} (C—H); 2854 cm^{-1} (Ar, C—H); 1632 cm^{-1} (C=O, 1,2-benzoquinone); 1516 cm^{-1} (imine group), 1386 cm^{-1} (C—CH$_3$); PMR (CDCl$_3$, TMS internal ref.): δ 6.5–7.5 (Ar, 3-H); δ 3.3 (Ar—NCH$_3$, 3-H) and δ 2.4 (Ar—CH$_3$, 3-H). On the basis of the above data the compound was characterised as N-methyl, 4-methyl-*o*-benzoquinoneimine.

Kinetic studies were carried out in the range of pH 4.0 to 7.0 using Thiel, Schultz and Coch buffer[12]. The rate-pH profile is depicted in Fig. 1. The rate increases sharply between pH 4.0 to 5.0 which may be due to the decrease in protonation of DMT. The concentration of periodate monoanion is maximum around pH 5.0 and decreases beyond this pH value[5], 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. A similar behaviour has been observed by previous workers[9, 13, 14].
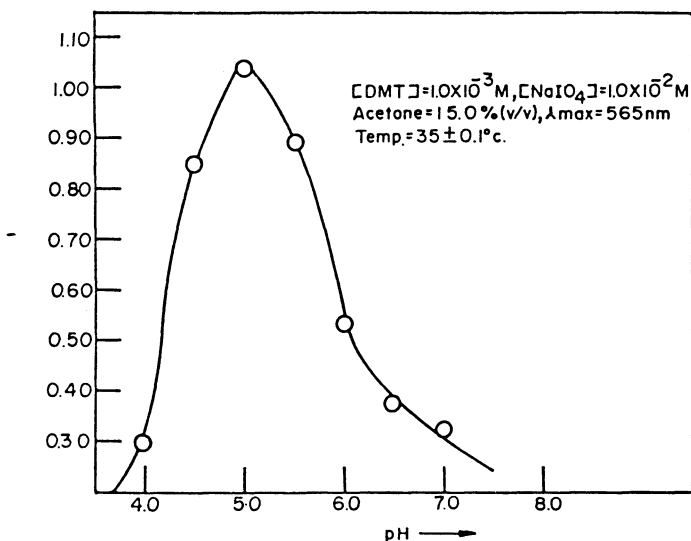

Fig. 1   Effect of pH on reaction rate

To get the 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. A plot between log (dA/dt)$_i$ *vs.* 1/D was found to be linear (Fig. 2) 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 an anion, which is a periodate monoanion in the present study.
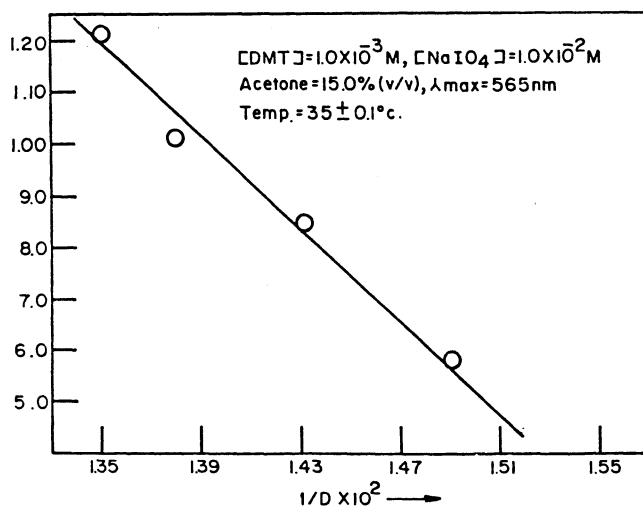
Fig. 2   Effect of dielectric constant on reaction rate

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-2). 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-2
EFFECT OF IONIC STRENGTH

[DMT] = 0.001 M, [NaIO$_4$] = 0.01 M, Acetone = 15.0% (v/v).
Temperature = 35 ± 0.1°C, λ_{max} = 565 nm.

[NaCl] $\times 10^3$ M	$\mu \times 10^2$	$(dA/dt)_i$ $\times 10^2$
1	1.1	4.4
2	1.2	4.6
5	1.5	4.8
10	2.0	5.4
12	2.2	5.6
15	2.5	5.8

The kinetic studies were made under pseudo-first order conditions (taking periodate in excess) at four different temperatures ranging between 30 to 45°C. Guggenhein 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.* 1/T) was

used for calculating the thermodynamic parameters. The mean values of various activation parameters are $E_a = 4.73$ kcal/mol; $A = 7.01 \times 10^2$ L mol^{-1} s^{-1}; $\Delta S^{\#} = -47.61$ E.U. $\Delta F^{\#} = 18.90$ kcal/mol and $\Delta H^{\#} = 4.11$ 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
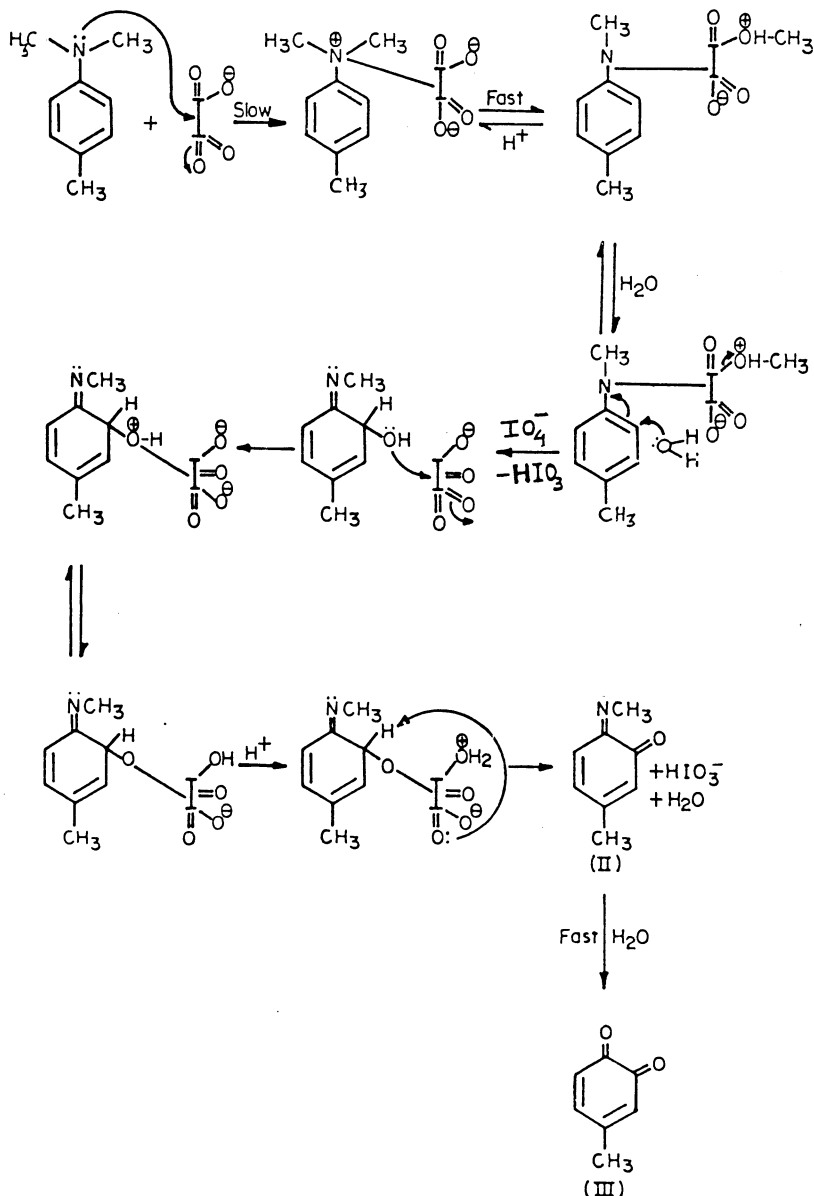

Chart-1

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 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-1.

The value of $\Delta S^{\#}$ 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 quinineimine (II) which was isolated and characterised by us as N-methyl, 4-methyl-*o*-benzoquinoneimine. The last step seems to be the fast hydrolysis of (II) to give (III).

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

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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