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Kinetics and Mechanism of Periodate Oxidation of *p*-Phenetidine

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Kinetics of periodate oxidation of *p*-phenetidine in acetone-water medium has been investigated spectrophotometrically. Reaction has been found to be first order in each of the reactants. 4-Ethoxy-1,2-benzoquinone has been separated and characterized as the main product. Rate law has been derived and suitable mechanism suggested based on the stoichiometry and thermodynamic parameters evaluated, the product identified and the effect of pH, dielectric constant, ionic strength and free radical scavengers on the reaction rate.

Key Words: Kinetics, Mechanism, Periodate oxidation, *p*-Phenetidine.

INTRODUCTION

In continuation with our earlier studies[1–5], the results of the kinetic-mechanistic studies on the periodate oxidation of *p*-phenetidine (PEA) in acetone-water medium are being reported and discussed in the present communication.

EXPERIMENTAL

All the chemicals were of E. Merck/CDH AR grade and used after Zn-dust distillation/recrystallization. Doubly distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[6] was used for maintaining the pH of the reaction mixtures. The progress of the reaction was followed by recording the absorbance of the light orange coloured reaction mixture on Shimadzu double beam spectrophotometer (UV-150-02), at the wavelength 445 nm, *i.e.*, the λ_{max} of the reaction mixture, keeping the pH at 7.0 (except for the kinetic runs in which the effect of pH was being studied) during the period in which the λ_{max} did not change. Plane mirror method and Guggenheim's method were used for evaluation of initial rates in terms of $(dA/dt)_i$ and pseudo first order rate constant k_1. The k_1 values were divided by [S], *i.e.*, the concentration of the reactant taken in excess, to find out the second order rate constant k_2.

RESULTS AND DISCUSSION

Reaction mixture containing oxidant in excess was kept for 24 h. It developed light orange colour changing into red followed by precipitation. It was filtered,

the filtrate extracted with petroleum ether and evaporated at room temperature. On separation of a droplet (due to water), a red coloured solid residue was left on the petri plate which was found to be TLC single using benzene + acetone in the ratio 80 : 20 c.c. This compound melted at 96°C and responded positively for a quinone[7]. The UV-Vis spectrum of this compound in $CHCl_3$ showed λ_{max} at 262 nm, 314 nm and 496 nm, suggesting a quinonid structure for it, the two longer wavelength bands being characteristic of *o*-benzoquinones[8]. IR spectrum (in KBr) showed bands at 2971 m, 1635 s, 1492 s, 1393), 1166 m, 1108 s, 831 m, 506 m, 1245 s and 1041 s (cm^{-1}), the last two being due to the characteristic asymmetric and symmetric C—O—C stretch.

^1H NMR spectrum in $CDCl_3$ showed peaks at $\delta = 4.07$, Q, (2H) (due to $—OCH_2$ of ethoxy group attached to the ring), $\delta = 1.254$, T, (3H) (due to the three protons of $—CH_3$ of ethoxy group), $\delta = 7.267$, S, (1H), at $\delta = 7.246$, D, (1H) and at $\delta = 6.946$, D, (1H) (due to the three protons of the ring). Based on these studies, this compound may be characterized as 4-ethoxy-1,2-benzoquinone[7-9].

Stoichiometry (1 mol PEA : 2 mol periodate) was determined iodometrically. Order of reaction is one in each reactant as evaluated by using Van't Hoff's differential equation, a linear variation of rate with concentration of each reactant and constant value of k_2 (Table-1). Under pseudo first order conditions, a linear correlation between $(dA/dt)^{-1}$ or $[k_1]^{-1}$ and $[S]^{-1}$ with almost negligible intercept, can be foreseen from the data in the same table, indicating the formation of an unstable intermediate in slow step which is consumed in a subsequent fast step[13].

TABLE-1

$[PEA] \times 10^3$ M	1.2*	1.5*	1.8*	2.0*	2.5*	3.0*	0.5#	0.5#	0.5#	0.5#	0.5#
$[NaIO_4] \times 10^3$ M	0.1	0.1	0.1	0.1	0.1	0.1	5.0	6.0	7.0	8.0	9.0
$(dA/dt)_i \times 10^3$ (min^{-1})	4.5	5.5	6.5	7.5	8.5	11.0	43.0	54.0	61.0	71.0	76.0
$k_1 \times 10^4$ (sec^{-1})	5.37	6.62	8.25	8.83	11.1	13.9	11.5	13.8	16.5	18.4	20.7
$k_2 \times 10^2$ (L mol^{-1} sec^{-1})	44.8	44.1	45.8	44.1	44.5	46.4	23.0	23.0	23.6	23.0	23.0

λ_{max} = 445 nm; pH = 7.0; *Acetone = 10.0% (v/v); Acetone = 15.0% (V/V);
Temp. = 25.0 ± 0.1°C

The first part of the rate-pH profile (Table-2) indicates an increase in the rate from pH 5.0 to 6.5 that may be due to the decrease in the protonation of PEA from pH 5.0 to 6.5 which makes greater concentrations of PEA available for the reaction. This leads to the assumption that unprotonated PEA is the reactive species in the reaction machanism. Second part of this profile suggests that the periodate monoanion $[IO_4^-]$ is the reactive species of periodate[1-5, 10, 11], whose concentration goes on decreasing with increase in pH beyond the value 6.5 which may be the reason for the decrease in the rate of reaction beyond pH 6.5.

TABLE-2

pH	5.0	5.5	6.0	6.5	7.0	7.5	8.0
$k_2 \times 10^2$ (L mol^{-1} sec^{-1})	22.1	33.6	49.9	75.8	42.2	34.5	28.8

$[PEA] = 1.0 \times 10^{-3}$ M; $[NaIO_4] = 1.0 \times 10^{-4}$ M; λ_{max} = 445 nm; Acetone = 7.5% (v/v),
Temp. = 35.0 ± 0.1°C

A linear relation exists between log k_2 and 1/D (where D is the dielectric constant of the medium) with negative slope (Table-3) indicating an ion-dipole interaction in this reaction[12], which is further supported by the data in Table-4 that fits a primary linear type plot between log k_2 *vs.* ionic strength (μ).

TABLE-3

Dielectric constant	73.9	72.4	70.0	66.8
$k_2 \times 10^2$ (L mol^{-1} sec^{-1})	58.5	47.9	35.5	24.9

[PEA] = 1.0×10^{-3} M; [$NaIO_4$] = 1.0×10^{-4} M; λ_{max} = 445 nm; pH = 7.0; Temp. = 35 ± 0.1°C

TABLE-4

$\mu \times 10^4$	11.0	31.0	51.0	81.0
$k_2 \times 10^2$ (L mol^{-1} sec^{-1})	46.1	50.9	55.7	65.3

[PEA] = 1.0×10^{-3} M; [$NaIO_4$] = 1.0×10^{-4} M; λ_{max} = 445 nm; pH = 7.0;
Acetone = 10.0% (v/v); Temp. = 35.0 ± 0.1°C

The values of different thermodynamic parameters evaluated from the linear Arrhenius plot obtained by using the results of the kinetic studies made at four temperatures ranging from 30 ± 0.1°C to 45 ± 0.1°C and taking [PEA] = 0.001 M, [$NaIO_4$] = 0.0001 M and acetone = 10.0% (v/v) are: E_a = 11.99 kcal mol^{-1}; $A = 11.37 \times 10^7$ L mol^{-1} sec^{-1}; $\Delta S^{\neq}$ = 23.73 e.u.; $\Delta F^{\neq}$ = 18.74 cal mol^{-1} and $\Delta H^{\neq}$ = 11.37 kcal mol^{-1}. In addition to the effect of D and μ discussed above, ion-dipole interaction is well supported by the high negative value of the entropy of activation and no effect of free radical scavengers on the reaction rate observed separately. Also, a large negative value of entropy of activation supports the formation of a charged and rigid transition state that is expected to be strongly solvated in the polar solvent employed. A low value of energy of activation is characteristic of a bimolecular reaction in the solution.

On the basis of these studies, a mechanism similar to our earlier reports on periodate oxidation of *o*-chloroaniline[2], 2,4-dimethylaniline[4], *o*-toluidine[5], *o*-ethylaniline[5] and N-ethylaniline[5] may be proposed and the rate law may be given as follows.

$$(dA/dt) = k_2[PEA][IO_4^-]$$

The first step in the proposed mechanism should be the bimolecular reaction between *p*-phenetidine and periodate monoanion. The formation of a charged intermediate complex taking place by the attack of periodate monoanion on the nitrogen of anilino group and stabilization of positive charge on the nitrogen of anilino group may be safely assumed in this reaction also, based on our earlier LFER studies on this type of reaction series[5]. The high negative value of entropy of activation and the effect of dielectric constant on the reaction rate support the involvement of solvation effects in this reaction. The slow formation of intermediate complex followed by its reaction with another IO_4^- to form quinoneimine in a fast step are expected to be the essential steps of the mechanism involved. Quinoneimine might undergo fast hydrolysis to give 4-ethoxy-1,2-benzoquinone,

i.e., the main product of the reaction that has been isolated, separated and characterized by us. The proposed mechanism is in good agreement with the various kinetic results and the main product of the reaction reported above.

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