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Kinetic-mechanistic Study of Periodate Oxidation of *p*-Chloroaniline

R.D. KAUSHIK*, RAGHVENDRA P. SINGH and SHASHI

Department of Chemistry, Gurukul Kangri University, Hardwar-249 404, India

The kinetic-mechanistic studies related to the periodate oxidation of *p*-chloroaniline in acetone-water medium have been reported. The studies were made by employing the spectrophotometric technique. The order with respect to both oxidant and substrate has been found to be one in each. The rate increases on increasing the ionic strength and decreases with decrease in dielectric constant. The rate-pH profile has been discussed. The effect of free radical scavengers rejects the possibility of a free radical mechanism. The thermodynamic parameters have been evaluated and discussed. The main product of oxidation characterized by melting point and UV-VIS and IR and NMR spectrum was 4-chloro-1,2-benzoquinone. A suitable mechanism has been proposed and the rate law derived. 1 mol of the substrate was found to react with 2 moles of the oxidant.

Key Words: Kinetic, Mechanistic, Periodate, Oxidation, *p*-Chloroaniline.

INTRODUCTION

The kinetic studies made on the non-malapradian oxidation of aromatic amines by periodate ion are rather few[1–5]. In continuation of our earlier studies[6–9], the results of the periodate oxidation of *p*-chloroaniline (PCA) are being reported and discussed in the present communication.

EXPERIMENTAL

p-Chloroaniline and sodium metaperiodate of E. Merck AR grade were used after Zn-dust distillation/recrystallization. Doubly distilled water and other chemicals of CDH AR grade were used. Thiel, Schultz and Koch buffer[10] was used for maintaining the pH of the reaction mixtures.

The progress of the reaction was followed by recording the absorbances of the light orange coloured reaction mixture on Shimadzu double beam spectrophotometer, UV-150-02 at the wavelength 475 nm, *i.e.*, the λ_{max} of the reaction mixture, keeping the pH at 5.0 (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. Initial rates in terms of $(dA/dt)_i$ were evaluated by plane mirror method[11], while the pseudo first order rate constant k_1 was calculated by using Guggenheim's method. The second order rate constants k_2 were obtained by dividing the k_1 by [S] where S is the reactant taken in excess. The pH of solutions was measured by using Systronics digital pH-meter model-335. A high precision thermostatically controlled water bath with an accuracy of ±0.1°C was employed for maintaining the constant temperature during the kinetic runs. The stoichiometry of the reaction was determined iodometrically.

RESULTS AND DISCUSSION

Reaction mixture containing 0.001 M [PCA] + 0.02 M [$NaIO_4$] + 2.5% (v/v) acetone was prepared and kept for 24 h. It developed violet colour changing into orange followed by precipitation. It was filtered after 24 h, filtrate extracted with petroleum ether and evaporated at room temperature. On separation of a droplet (due to water), a solid residue was left on the petri-dish. This solid residue was dissolved in petroleum ether (40–60°C) and a little amount of silica gel was added to it and mixed with a clean spatula so as to adsorb the complete residue on silica gel. This silica gel was then applied on the top of a silica gel-H packed, 31 cm long column with 0.6 cm diameter. Gradient elution was employed using petroleum ether and chloroform in decreasing ratio. Three components (violet, red and orange) were separated. Orange coloured major component was collected, checked for purity by using TLC and crystallized in ethyl alcohol. Other components, being minor, could not be collected in sufficient amounts and, therefore, could not be identified. The melting point of orange coloured component was found to be 79°C. This compound responded positively for a quinone[12]. The UV-Vis spectrum of this compound was obtained and the λ_{max} for this compound in $CHCl_3$ were found to be 255 nm, 415 nm and 550 nm, which suggested the presence of quinonoid structure in the compound. The two longer wavelength bands are particularly characteristic of *o*-benzoquinones[13].

The IR spectrum of this compound in KBr showed bands at 1629 cm^{-1} (s) (due to 1,4-benzoquinone pattern); 3230 cm^{-1} (s) (due to the overtone of C=O stretch); 2738 cm^{-1} (w) (due to isolated C—H streching); 1514 cm^{-1} (s), 1469 cm^{-1} (s) and 1313 cm^{-1} (s) (due to C=C ring strech); 1212 cm^{-1} (s) and 1091 cm^{-1} (due to in-plane C—H bending); 828 cm^{-1} (m) (due to out-of-plane C—H bending in case of two adjacent H-atoms); 757 cm^{-1} (s) (a characteristic strong band due to C—Cl streching) and at 677 cm^{-1} (m) and 526 cm^{-1} (m) (both due to C—H bending mode).

The melting point[14] and the UV-Vis spectrum[13] obtained are in good agreement with the data reported in literature for 4-chloro-1,2-benzoquinone. The IR spectral studies support the same structure. This main product was finally characterized as chloro-1,4-benzoquinone on the basis of its NMR spectrum in $CDCl_3$ which showed the peaks at $\delta = 7.091$, S, (1H) and at $\delta = 6.658$, D, (2H) which are due to three protons of the ring[15].

Stoichiometry of reaction was found to be 1 mol PCA : 2 mol periodate. The data presented in the Table-1 were subjected to calculations by using the Van't Hoff's differential equation and it was established that the reaction is second order, being first order in each reactant. The second order kinetics was also 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 values of $(dA/dt)^{-1}$ *vs.* $[S]^{-1}$ (Table-2) were also used to get a linear plot with almost negligible intercept, indicating that the intermediate formed in the slow step should be unstable and it should have got consumed in a subsequent fast step.

TABLE-1

λ_{max} = 475 nm; pH = 5.0; Acetone = 15.0% (v/v); Temp. = 35 ± 0.1°C

$[PCA] \times 10^3$ M	20.0	20.0	20.0	20.0	20.0	20.0	1.0	2.0	3.0	4.0	5.0	6.0
$[NaIO_4] \times 10^3$ M	2.0	3.0	4.0	5.0	7.0	7.0	10.0	10.0	10.0	10.0	10.0	10.0
$(dA/dt)_i \times 10^3$ (min^{-1})	3.8	5.8	7.9	9.8	12.0	14.0	1.3	2.75	4.0	5.5	6.5	8.0

TABLE-2

λ_{max} = 475 nm; pH = 5.0; *Acetone = 15.0% (v/v); #Acetone = 10.0% (V/V);
Temp. = 35.0 ± 0.1°C

$PCA \times 10^2$ M	2.0*	2.2*	2.4*	2.6*	2.8*	3.0*	0.1#	0.1#	0.1#	0.1#	0.1#	0.1#
$[NaIO_4] \times 10^2$ M	0.2	0.2	0.2	0.2	0.2	0.2	1.0	1.2	1.4	1.6	1.8	2.0
$(dA/dt)_i \times 10^3$ (min^{-1})	4.25	4.5	5.0	5.5	6.0	6.5	3.0	3.5	4.25	4.75	5.5	6.0

Kinetic studies were also made in the pH range 3.5 to 7.5 (Table-3) indicating that the rate was maximum at pH 5.5. The first part of the profile, *i.e.*, the increase in the rate from pH 3.5 to 5.5 may be due to the decrease in the protonation of PCA from pH 3.5 to 5.5 which makes greater concentrations of PCA available for the reaction. This assumption is in line with the fact that unprotonated PCA is the reactive species as shown in the proposed mechanism (Chart-1). Further, out of the various species of periodate, the concentration of the periodate monoanion is maximum around pH 5.5 and decreases beyond this pH value as worked out by earlier workers[1, 3, 5–7]. This may be the reason for the decrease in the rate of reaction beyond pH 5.5. This behaviour also supports our assumption in the proposed mechanism that out of the various species of the periodate, the species taking part in the reaction in the present case is the periodate monoanion, *i.e.*, $[IO_4^-]$.

TABLE-3

EFFECT OF pH ON THE REACTION RATE

[PCA] = 2.0×10^{-2} M, $[NaIO_4] = 2.0 \times 10^{-3}$, M, λ_{max} = 475 nm; Acetone = 5.0% (v/v),
Temp. = 35.0 ± 0.1°C

pH	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5
$(dA/dt)_i \times 10^2$ (min^{-1})	0.96	1.46	2.10	2.55	2.85	2.10	1.60	1.22	0.95

The data in Table-4 suggest a linear relation between log $(dA/dt)_i$ and 1/D (where D is the dielectric constant of the medium) with negative slope indicating an ion-dipole interaction in this reaction[16]. This point is well supported by the high negative value of the entropy of activation and our observation that the free radical scavengers like acryl-amide and allyl alcohol exerted no effect on the reaction rate. A primary linear type plot between log $(dA/dt)_i$ *vs.* ionic strength

(μ) was obtained by us by using the data given in Table-5, which also supports the ion-dipole interaction assumed by us in the mechanism proposed.

TABLE-4

EFFECT OF DIELECTRIC CONSTANT OF THE MEDIUM ON THE REACTION RATE

[PCA] = 2.0×10^{-3} M, [$NaIO_4$] = 2.0×10^{-2} M, λ_{max} = 475 nm, pH = 5.0, Temp. = 35 ± 0.1°C

Dielectric constant	73.90	72.40	70.00	66.80
$(dA/dt)_i \times 10^2$ (min^{-1})	2.40	1.70	1.35	0.60

TABLE-5

EFFECT OF IONIC STRENGTH (μ) ON REACTION RATE

[PCA] = 2.0×10^{-2} M; [$NaIO_4$] = 2.0×10^{-3} M; λ_{max} = 475 nm; pH = 5.0; Acetone = 10.0% (v/v); Temp = 35.0 ± 0.1°C

$\mu \times 10^2$	1.00	1.20	2.20	3.20	4.20
$(dA/dt)_i \times 10^2$ (min^{-1})	1.41	1.45	1.50	1.55	1.60

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 35 ± 0.1 to 50 ± 0.1°C and taking [PCA] = 0.02 M, [$NaIO_4$] = 0.002 M and acetone = 10.0% (v/v) are E_a = 16.74 kcal mol^{-1}; A = 5.346×10^{10} lit mol^{-1} sec^{-1}; $\Delta S^{\neq} = -11.59$ e.u.; $\Delta F^{\neq}$ = 19.75 kcal mol^{-1} and $\Delta H^{\neq}$ = 16.10 kcal mol^{-1} where E_a is the energy of activation, A is the Arrhenius frequency factor, $\Delta S^{\neq}$ is the entropy of activation, $\Delta F^{\neq}$ is the free energy of activation and $\Delta H^{\neq}$ is the enthalpy of activation.

A large negative value of entropy of activation 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 and third steps in the mechanism proposed. The decrease in rate with the decrease in dielectric constant (Table-4) also supports this assumption. A low value of energy of activation is characteristic of a bimolecular reaction in the solution.

On the basis of these studies, the mechanism presented in Chart-1 may be proposed and the rate law may be given as follows:

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

The first step in the proposed mechanism is the bimolecular reaction between *p*-chloroaniline and periodate monoanion which is supported by the solvent effect and the salt effect observed by us as well as the order of the reaction established. The involvement of the IO_4^- as the reactive species is supported by the earlier reports[1, 3, 5–7], in which it has been established that periodate monoanion is the main species of periodate existing in the pH range in which the present studies have been made. The formation of charged intermediate complex (I) should take place by the attack of periodate monoanion on the nitrogen of anilino group and the development of positive charge on nitrogen in accordance with the studies reported by us earlier in reference to the linear free energy relationships for this type of reaction series[17]. 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 intermediate (I) is unstable and undergoes the oxidation in a fast process which is supported by the observation that $[S]^{-1}$ *vs.* $[rate]^{-1}$ plot has been found to be a straight line with a negligible intercept[18, 19]. Intermediate (I) is likely to be attacked by another molecule of periodate to form quinoneimine (II). The last step seems to be the fat hydrolysis of (II) to give 4-chloro-1,2-benzoquinone, *i.e.*, the main product of the reaction that has been isolated, separated and characterised by us. Thus, the proposed mechanism is in good agreement with the reaction product characterized and the different kinetic results reported and discussed above, *viz.*, the order of reaction in each reactant, stoichiometry observed and the studies related to the effect of solvent, ionic strength, pH, and free radical scavengers on the reaction rate as well as the thermodynamic parameters evaluated.

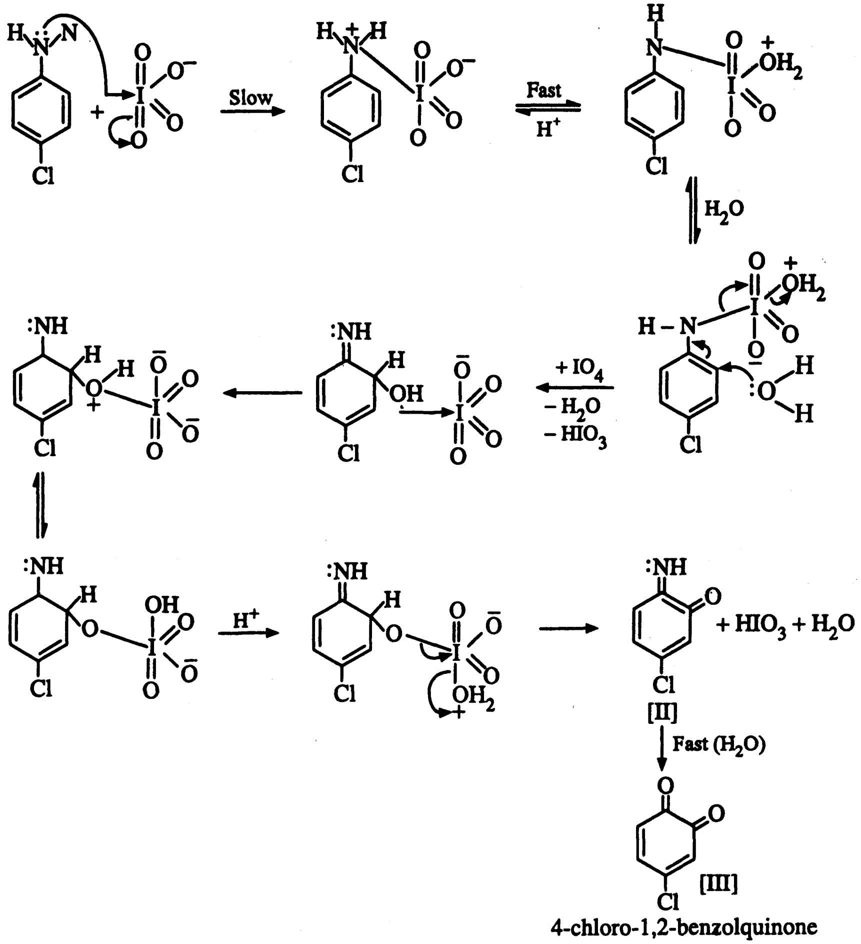

Chart-1

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