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Periodate Oxidation of *p*-Bromoaniline in Acetone-water medium: A Kinetic Mechanistic Study

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Results of kinetic study on the periodate oxidation of *p*-bromoaniline (PBA) in acetone-water medium have been presented and discussed. Rate law has been derived and mechanism suggested on the basis of various results like first order in each reactant, stoichiometry, thermodynamic parameters, main product identified as 4-bromo-1,2-benzoquinone and various factors influencing the reaction rate such as the effect of pH, dielectric constant, ionic strength and free radical scavengers.

Key Words: Kinetics, Periodate oxidation, *p*-Bromoaniline, 4-Bromo-1,2-benzoquinone.

INTRODUCTION

In continuation with our earlier reports on non-malapradian oxidation of aromatic amines[1–4], here we report our results of the kinetic-mechanistic studies on the periodate oxidation of *p*-bromoaniline (PBA) in acetone-water medium.

EXPERIMENTAL

Chemicals of E. Merck/CDH AR grade were used after distillation/recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer was used for maintaining the pH of the reaction mixtures. The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV-150-02), at 490 nm, *i.e.*, the λ_{max} of the light violet coloured reaction mixture during the period in which the λ_{max} did not change keeping the pH at 5.0 in all kinetic runs except the sets in which pH variation was done. 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. The initial rates were used in place of pseudo first order rate constants for the purpose of interpretation of results in cases of failure of Guggenheim's method. High precision thermostatically controlled water bath with an accuracy of ±0.1°C was employed for maintaining the desired temperature.

RESULTS AND DISCUSSION

Reaction mixture containing oxidant in excess was processed by our earlier reported method[3] to get a red-brown coloured compound which, on recrystallization in ethanol, tested positive for a quinone and was characterized as 4-bromo-1,2-benzoquinone on the basis of m.p. 75°C (Lit.[5], 74–75°C), λ_{max} in $CHCl_3$ at 260 nm, 475 nm and 490 nm (the two longer wavelength bands being characteristic of *o*-benzoquinones[6]), characteristic C—Br stretching vibration band[7] at 525 cm^{-1} (s) besides all other expected bands[2] in IR spectrum in KBr, and the ^{1}H-NMR spectrum (in $CDCl_3$) which showed the signals at δ = 7.10 , S, (1H) and at δ = 6.60, D, (2H) for the three protons of the ring[3].

Stoichiometry of the reaction found iodometrically was 1 mol PBA : 2 mole periodate. The data (Table-1) were used to establish the second order for reaction, being first order in each reactant. Linear relation between concentration of the reactants and rate supported the second order kinetics. Under pseudo first order conditions (Table-2), the $[(dA/dt)]^{-1}$ *vs.* $[S]^{-1}$ plots were linear with almost negligible intercept. It suggests Michaelis-Menten type kinetics being followed with respect to both reactants. Rate-pH profile indicates a maxima at pH = 4.5 (Table-3). A linear relation between log $(dA/dt)_i$ and 1/D (where D is the dielectric constant of the medium) with negative slope and a primary linear type plot between log $(dA/dt)_i$ *vs.* ionic strength (μ) expected from the data in Table-4, indicates an ion-dipole interaction in this reaction. 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°C to 50 ± 0.1°C and taking [PBA] = 0.001 M, $[NaIO_4]$ = 0.01 M and acetone = 10.0% (v/v) are: E_a = 6.72 kcal mol^{-1}; A = 7.47 × 10^3 lit mol^{-1} sec^{-1} ; $\Delta S^{\neq}$ = –42.92 e.u. $\Delta F^{\neq}$ = 19.63 kcal mol^{-1} and $\Delta H^{\neq}$ = 6.09 kcal mol^{-1}.

In addition to the effect of D and μ the 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. Low value of energy of activation is characteristic of a bimolecular reaction in the solution while a high frequency factor is expected when the reacting species are larger in size.

TABLE-1
DETERMINATION OF ORDER WITH RESPECT TO REACTANTS

[PBA] × 10^3 M	10.0	10.0	10.0	10.0	10.0	10.0	1.0	2.0	3.0	4.0	5.0	6.0
$[NaIO_4]$ × 10^3 M	1.0	1.0	1.0	1.0	1.0	1.0	10.0	10.0	10.0	10.0	10.0	10.0
$(dA/dt)_i$ × 10^3 (min^{-1})	3.5	6.0	9.0	11.0	13.0	17.0	3.0	7.0	9.0	12.0	14.0	18.0

λ_{max} = 490 nm; pH = 5.0; Acetone = 10.0% v/v; Temp. = 35 ±0.1°C

TABLE-2

$[PBA] \times 10^3$ M	10.0*	12.0*	14.0*	16.0*	18.0*	20.0*	1.5#	1.5#	1.5#	1.5#	1.5#	1.5#
$[NaIO_4] \times 10^3$ M	1.00	1.00	1.00	1.00	1.00	1.00	10.0	12.0	14.0	16.0	18.0	20.0
$(dA/dt)_i \times 10^4$ (min^{-1})	5.00	6.00	7.00	8.00	9.00	10.0	20.0	24.0	27.0	30.0	34.0	38.0
$(dA/dt)_i \times 10^4$ (min^{-1}) (Calculated from eqns. (9) and (14)	4.93	5.89	6.86	7.81	8.76	9.71	19.2	23.7	27.6	30.1	33.6	37.0
K_m	66.67×10^{-2}						25.0×10^{-2}					

λ_{max} = 490 nm; pH= 5.0; *Acetone = 20.0% (v/v); #Acetone = 10.0 % (v/v); Temp. = 35.0 ± 0.1°C.

TABLE-3
RATE-pH PROFILE

pH	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5
$(dA/dt)_i \times 10^4$ (min^{-1})	12.0	12.5	13.0	14.5	12.0	11.0	6.0	5.0	5.0	5.0

$[PBA] = 1.0 \times 10^{-3}$ M; $[NaIO_4] = 1.0 \times 10^{-2}$ M; λ_{max} = 490 nm; Acetone = 2.5% (v/v); Temp. = 35.0 ± 0.1°C

TABLE-4
EFFECT OF D AND μ ON REACTION RATE

D	73.7	72.4	71.0	69.7	–	–	–	–
$*\mu \times 10^3$	–	–	–	–	30.0	40.0	50.0	60.0
$(dA/dt)_i \times 10^4$ (min^{-1})	13.0	8.0	5.2	3.0	1.0	1.4	2.0	3.0

$[PBA] = 1.5 \times 10^{-3}$ M; $[NaIO_4] = 1.5 \times 10^{-2}$ M; λ_{max} = 490 nm; pH = 5.0; Temp. = 3.5 ± 0.1°C
*Acetone = 10% (v/v)

Based on these studies, the mechanism proposed in chart shows the first step as a reversible bimolecular reaction between *p*-bromoaniline and periodate monoanion. The formation of a charged intermediate complex [IC] 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 are well supported by our earlier LFER studies on this type of reaction series[4]. 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 another intermediate [II] followed by its reaction with another IO_4^- to form quinoneimine [III] in a fast step are the expected steps of the mechanism involved. The overall reaction may be represented as follows:

$$PBA + [IO_4^-] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{First intermediate [IC]} \xrightarrow[\text{slow}]{k_3} \text{Second intermediate [II]} \longrightarrow \text{Product[III]}$$

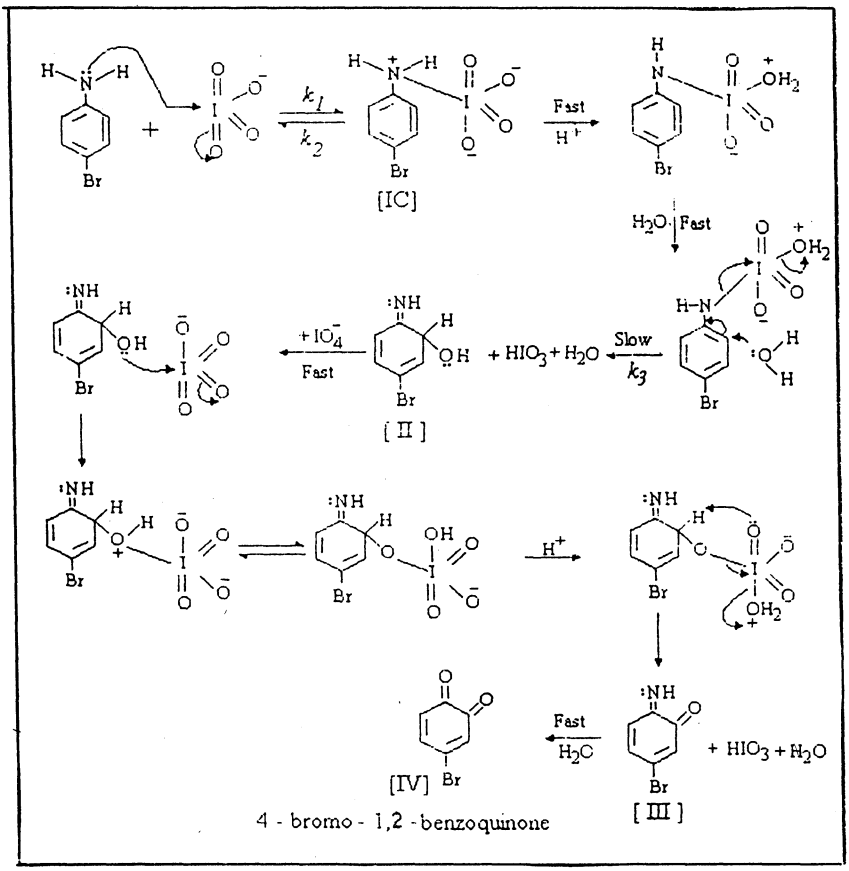

Fig. 1. Mechanism of oxidation of *p*-bromoaniline

It should be noted that the initial part of the reaction is significant in the present case and the second molecule of IO_4^- reacting later is not significant. Product [III] changes by fast hydrolysis into product [IV] (*i.e.*, the main product of reaction, 4-bromo-1,2-benzoquinone, that has been isolated, separated and characterized in the present case). The rate law derived on the basis of proposed mechanism and in accordance with the second order behaviour observed for this reaction, is as follows:

$$\text{Rate of reaction} = -\frac{d[IC]}{dt} \alpha[IC]$$

or

$$-\frac{d[IC]}{dt} = k_3 [IC] \quad (1)$$

Concentration of the complex [IC] can be calculated by applying the steady state concept.

Further, rate of formation of IC = $k_3[PBA]\,[IO_4^-]$ (2)

and rate of disappearance of IC = $k_2 [IC] + k_3 [IC]$ (3)

where [PBA] and $[IO_4^-]$ are the equilibrium concentrations.

In steady state situation,

$$k_1 [PBA][IO_4^-] = k_3[IC] + k_3[IC] \quad (4)$$

Further,

$$[IO_4^-] = [IO_4^-]_T - [IC] \quad (5)$$

where $[IO_4^-]_T$ is the total concentration of IO_4^-

From (4) and (5), $$[IC] = \frac{[PBA][IO_4^-]_T}{K_m + [PBA]} \quad (6)$$

where $$K_m = \frac{k_2 + k_3}{k_1}$$

From (1) and (6), $$\frac{d[IC]}{dt} = \frac{k_3 [PBA][IO_4^-]_T}{K_m + [PBA]}$$

or $$\frac{d[IC]}{dt} = k_{obs} [IO_4^-]_T \quad (7)$$

where k_{obs} is the observed pseudo first order rate constant (when [PBA] is in excess).

Here, $$k_{obs} = \frac{k_3 [PBA]}{K_m + [PBA]} \quad (8)$$

or $$\frac{1}{k_{obs}} = \frac{K_m}{k_3 [PBA]} + \frac{1}{k_3} \quad (9)$$

K_m can be calculated from slope/intercept of the plot, $[(dA/dt)_i]^{-1}$ *vs.* $[PBA]^{-1}$ (when PBA has been taken in excess). This indicates that the intermediate complex (IC) is formed between the substrate and the oxidant[8, 9]. The value of K_m as calculated by using initial rates in place of k_{obs}, in eqn. (9), is 66.66×10^{-2} (Table-2). Similarly, taking $[IO_4^-]$ in excess, the rate eqns. (8) and (9) can be written as follows:

$$k_{obs} = \frac{K_3[IO_4^-]}{K_m + [IO_4^-]} \quad (10)$$

or $$\frac{1}{k_{obs}} = \frac{K_m}{k_3[IO_4^-]} + \frac{1}{k_3} \quad (11)$$

K_m calculated in this case is 25.0×10^{-2}. The values of pseudo first order initial rate calculated by using equs. (9) and (11) were found to match with those observed experimentally verifying thereby the rate equations (Table-2). Based on the above discussion, the general rate law for this oxidation process can be given as follows:

$$\frac{dx}{dt} = k_3 [IC] = k_3 \cdot K[m\text{-}ANIS][IO_4^-] \quad (12)$$

where, $K = k_1/k_2$.

The effect of pH can be explained by using the equilibria of aromatic amines and different species of periodate ion. The first part of the rate-pH profile (Table-3) indicates the increase in the rate from pH 3.0 to 4.5 that may be due to the decrease in the protonation of PBA from pH 3.0 to 4.5 which makes greater concentrations of PBA available for the reaction. This leads to the assumption that unprotonated PBA is the reactive species in the reaction mechanism. Second part of this profile suggests that the periodate monoanion $[IO_4^-]$ is the reactive species of periodate whose concentration goes on decreasing with increase in pH beyond the value 4.5 which may be the reason[10] for the decrease in the rate of reaction beyond pH 4.5.

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