International Journal of Progressive Research in Science and Engineering
Volume-1, Issue-5, August-2020
www.ijprse.com

Kinetic and Thermodynamic Aspects of Oxidation of 4-Hydroxy Phenyl acetic acid by N-Bromosuccinimide in Aqueous Medium

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Abstract: The kinetics of oxidation of 4-Hydroxy phenyl acetic acid by n-bromosuccinimide in aqueous medium has been studied at 303K. The reaction stoichiometry was determined and oxidation products were identified. A first order dependence on oxidant, fractional order on substrate and inverse fractional order on [H^+] of rate was observed. A slight negative effect by dielectric constant was observed. Involvement of nonionic species in rate determining step was indicated by unchanged rate with ionic strength. Thermodynamic parameters were computed by performing the kinetic runs at different temperature and a mechanism consistent with observed parameters is proposed and rate law is derived.

Key Words: - ***Kinetic Oxidation, N-Bromosuccinimide, stoichiometry, 4-Hydroxy phenyl acetic.***

I. INTRODUCTION

The use of N-bromosuccinimide as an allylic brominating reagent was reported from past several years since its first synthesis [1] in 1893. The use of N-bromoacetamide (NBA) as an allylic brominating reagent was reported. [2]. After more than two decades, a series of papers on the application of N-bromosuccinimide for allylic bromination [3] were published. N-bromosuccinimide and eight other N-bromoimides or amides, were prepared, but found them to be far less satisfactory than NBS for allylic bromination. An excellent review on the allylic bromination reaction under different conditions, this group of N-Halogen compounds reacts with alkenes to add bromine to the double bond or to act as a source of hypohalous acid in aqueous solution [4]. N-bromosuccinimide have, therefore, been used extensively as brominating and oxidizing agent. Other reviews [5-7] on N-haloimides which also includes studies on oxidation have since been published. NBS has been used as a bromination agent for a wide variety of organic compounds, and as an oxidizing agent for the conversion of primary and secondary aliphatic alcohols to the corresponding aldehydes and ketones [8-12]. In many cases its action is highly selective

4-Hydroxy phenyl acetic acid or p-Hydroxy phenyl acetic acid is produced in the degradation of some plant materials in animal intestinal tracts. It is a fermentation product of aromatic amino acids.

II. MATERIAL AND METHODS

Experimental: Aqueous solution of the oxidant NBS (E. Merck) was standardized by the iodometric method and preserved in brown bottle to prevent any further deterioration photo chemically. A solution of the substrate HPAC (Sigma-Aldrich) in water of required strength was freshly prepared each time. The other reagents used were of analytical grade. Double distilled water was used for the kinetic studies. Concentrated solution of sodium per chlorate was used to maintain ionic strength. Methanol was added to alter the dielectric constant. An excess of 4-HPAC over NBS was maintained to keep pseudo first-order conditions.

Kinetic measurements: A mixture of required amounts of solutions of 4-HPAC, and $NaClO_4$ along with requisite volume of water to keep the total volume constant for all runs is taken in a glass-stoppered Pyrex boiling tube and thermos stated at 303K. An equilibrated solution of NBS of required amount was added to the mixture and shaken appropriately. The reaction progress was studied iodometrically by the estimation of unreacted NBS in a measured aliquot **(**mL) of the reaction mixture with time up to about two half-lives. The pseudo first-order rate constants calculated from the plots of log [NBS] against time are reproducible within ±3%.

Stoichiometry and product analysis: The kinetic runs performed by keeping excess of HPAC over NBS at 303 K confirm the following stoichiometry that one mole of HPAC consumed two moles of NBS.

$$C_8H_8O_3 + C_4H_4O_2NBr + H_2O \longrightarrow$$

$$C_7H_6O_2 + CO_2 + C_4H_5O_2N + HBr \qquad (1)$$

The reaction products were extracted with ether. From the ether layer the oxidation product of substrate 4-Hydroxy phenyl acetic acid was tested. 4-hydroxyphenyl aldehyde is confirmed. The reduction product of NBS, succinamide was extracted with ethyl acetate and confirmed by TLC.

Test for free radicals: Addition of the reaction mixtures to aqueous acrylamide solution did not initiate polymerization indicating the absence of in situ formation of free radical's species in the reaction sequence.

Test for Aldehyde -Tollen's Reagent Test: It gives bright silver mirror with Tollen's reagent.

Test for amides: Substance is boiled strongly with 20%NaOH solution. Then cooled & acidified with dil.HCl :-ammonia gas is evolved.

III. RESULTS AND DISCUSSION

The reaction was carried out under pseudo first order conditions by keeping an excess of substrate over NBS. The kinetics of oxidation of 4-HPAC by NBS was investigated at several initial concentrations of the reactants at constant temperature (30^0C)

Effect of reactants on the rate of reaction: The rate was first order in [NBS], since plot of log [4-HPAC] versus time was linear (Table 3.1, fig 3.1) at fixed [4-HPAC], and temperature. The value of pseudo first order rate constant k' were constant for varying [NBS] (Table 3.2]. The k' values increased with increase in $[4\text{-HPAC}]_0$ (Table-3.3). The linear plot of log k' versus log $[4\text{-HPAC}]_0$ (Figure-3.2) with a slope of 0.275 indicate fractional-order dependence on $[4\text{-HPA}]_0$.

Effect of ionic strength on the rate of reaction: The ionic strength of the reaction mixture varied by using a saturated solution of $NaClO_4$(2.0×10^{-3} to 8.0×10^{-3} mol dm^{-3}). This indicates ionic strength had no effect on the rate (Table 2).

Table.1. Effect of oxidant, substrate and acid concentration on rate

10^4 [NBS] mol dm^{-3}	10^3 [HPAC] mol dm^{-3}	10^3 $[HClO_4]$ mol dm^{-3}	K^I $10^4 S^{-I}$
3	6	0	13.1606
6	6	0	13.1606
9	6	0	13.1606
12	6	0	13.4670
6	3	0	11.2121
6	6	0	13.5212
6	9	0	15.4831
6	12	0	16.4560
6	6	3	12.2231
6	6	6	12.1265
6	6	9	11.9828
6	6	12	11.8513

$[NBS] = 6 \times 10^{-4}$mol dm^{-3}, $[HPAC] = 6 \times 10^{-3}$mol dm^{-3}, $[H^+] = 6 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.5$ mol/dm^{-3}.

Effect of dielectric constant on the rate of reaction: Kinetic runs were performed by varying dielectric constant of the medium adding different proportions (5 - 30 %, v/v) of methanol. Increase in dielectric permittivity (D) of the medium increased the rate of reaction (Table-3.8). The plot of log k' versus 1/D is linear with a negative slope (Figure-3.4). Under the experimental conditions methanol was ionized to very slight extent (<1%) as confirmed by the blank experiments.

Effect of temperature on the rate of reaction: The reaction was studied by varying temperature from 298 K to 313 K and the values of k' were determined (Table3.9) from pseudo-first-order plots. The energy of activation (E_a) was calculated from the Arrhenius plot of logk' versus 1/T (Fig3.5). The other thermodynamic parameters, $\Delta H^{\neq}, \Delta G^{\neq}, and\ \Delta S^{\neq}$ were then calculated by making use of the value of E_a.(Table3).

Table.2.

% Methanol(v/v)	*$k^{I} \times 10^{-4}$ sec^{-1}*
0	9.2314
5	9.1303
10	9.0361
15	8.9161

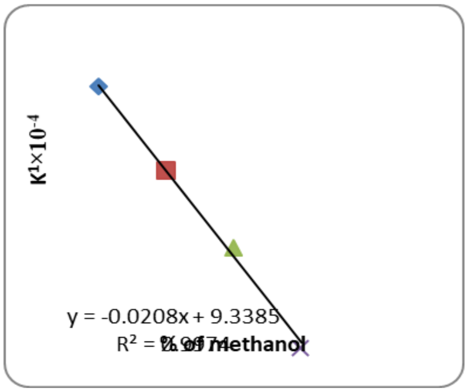


Fig.1. Plot of k'x 10^{-3} versus % Methanol

Table.3. Effect of temperature on rate of reaction

$1/T\times10^3$	**$4+\log(k')$**
3.4129	0.9961
3.3557	1.0992
3.3003	1.1719
3.2467	1.2231
3.1948	1.2802

Table.4.

Ea(KJ mol^{-1})	**19.14711**
$\Delta H^{\neq}$(kJ mol^{-1})	16.62801
$\Delta S^{\neq}$(k J mol^{-1})	-245.04548
$\Delta G^{\neq}$(k J mol^{-1})	90.83831

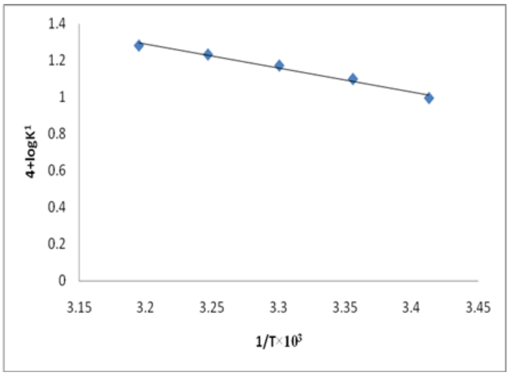


Fig.2. Plot of logk$'$ versus 1/T

Activation parameters for the oxidation of HPAC by NBS: In aqueous solution NBS behaves as a source of positive halogen and this reagent has been exploited as an oxidant for a variety of substrates in both acid and alkali solutions. It acts as mild oxidant with a two electron change to give reduced product succinamide [13-20]. In aqueous acidic solution it produces different ionic species with following equilibria.

$$-NBr + H_2O \rightleftharpoons NH + HOBr \qquad (2)$$

$$-NBr + H^+ \rightleftharpoons -N^+BrH \qquad (3)$$

$$-NBr + H^+ \rightleftharpoons -NH + Br^+ \qquad (4)$$

$$Br^+ + H_2O \rightleftharpoons (H_2OBr)^+ \qquad (5)$$

In the present studies the negative effect of [H$^+$] on the reaction rate observed allows us to assume effect of [H$^+$] on the reaction rate observed allows us to assume either protonated NBS i.e., or Br$^+$ or $(H_2OBr)^+$ as active oxidizing species, and negative effect of the initially added product, succinimide restricts us to take Br$^+$ as the oxidizing species. On the basis of the above discussions and observed kinetic data, a probable mechanism (Scheme I) is proposed for the oxidation.

Considering the experimental results of oxidation of HPAC by NBS the following scheme 1 is proposed. In scheme 2 the detailed plausible mechanism of reaction is picturized.

Let NBS represent the active oxidant, HPAC represent the substrate and X and X^I represent the intermediate complex species. The oxidation reaction is initiated by NBS through the attack of substrate to give an intermediate complex X. This complex eliminates a proton in the rate determining step to give the complex X^I which further reacts to give products.

$$NBS + H_2O \overset{k_1}{\rightleftharpoons} NH + HOBr \qquad \text{(i) fast}$$

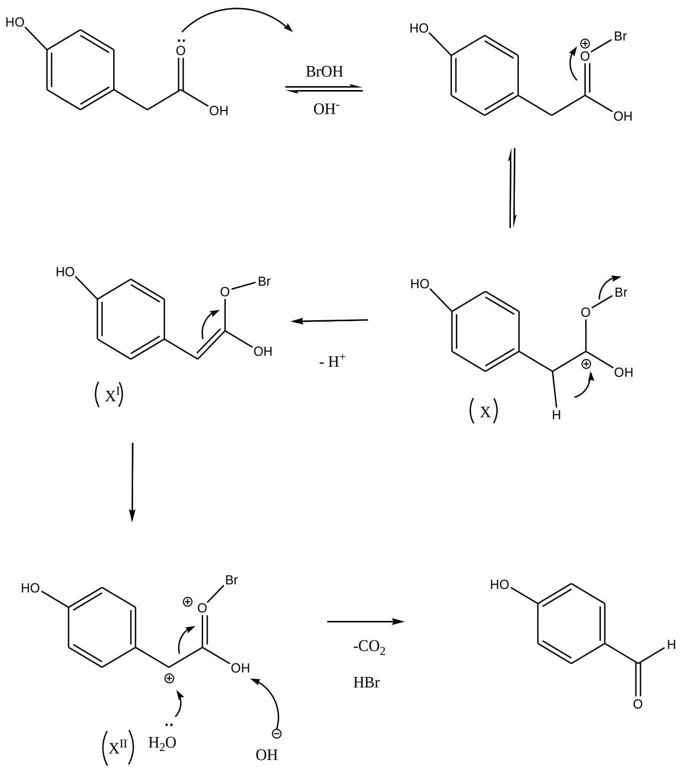
$$HOBr + S \overset{k_2}{\rightleftharpoons} X \qquad \text{(ii) fast}$$

$$X \overset{k_3}{\rightleftharpoons} X^I \qquad \text{(iii) slow \& rds}$$

$$X^I \overset{k_4}{\rightleftharpoons} \text{Produts} \qquad \text{(iv) fast}$$

Scheme.1.

$$C_4H_4O_2NBr + H_2O \rightleftharpoons C_4H_5O_2N + HOBr$$



Scheme 2

For slow and rate determining step of scheme-1 the differential rate equation is

$$\frac{d[NBS]}{dt} = k_3\,[X] \qquad \textbf{(6)}$$

Let $[NBS]_t$ be the effective total concentration of NBS, then

$$[NBS]t = [HOBr] + [H_2OBr^+] + [X] \qquad \textbf{(7)}$$

$$[NBS]t = ([HOBr][H^+])/k_1 + \frac{[X]}{k_2[HPAC]} + [X] \qquad \textbf{(8)}$$

On solving for X,

$$[X] = \frac{k_1\ k_2\,[NBS]\,[HPAC]}{[\ H^+]\,k_1(\,1 + k_2\ \ [HPAC]} \qquad (9)$$

$$\frac{d[CAT]}{dt} = \frac{k_1 k_2 k_3\,[NBS]_t\,[HPAC]}{[\ H^+] + k_1(\,1 + k_2)\,[HPAC]} \qquad (10)$$

The rate law derived agrees with the experimental results that a first, fractional and inverse fractional order dependence of reaction rate on $[NBS]_0$, $[HPAC]_0$ and $[H^+]$ respectively.

Since rate = $k^I\,[NBS]_0$, from equation (9) we have,

$$k^I = \frac{k_1\ k_2\ k_3\ [HPAC]}{[\ H^+] + k_1(\,1 + k_2)\,[HPAC]} \qquad (11)$$

$$\frac{1}{k^I} = \frac{1}{k_2\ k_3\ [HPAC]}\left\{\frac{[H^+]}{k_1} + 1\right\} + \frac{1}{k_3} \qquad (12)$$

From equations (11) and (12), plots of 1/k' versus 1/[HPAC] and 1/ k' versus $[H^+]$ were linear (Figure 2). The values of k_1, k_2 and k_3 were calculated from the slopes and intercepts.

experimental results. Formation of a properly ordered compact transition state complex with lesser degrees of freedom is supported by large negative value of entropy of activation and moderate positive values of free energy of activation and enthalpy of activation.

IV. CONCLUSION

The redox reaction between NBS-HPAC has been carried out in aqueous medium. The reaction stoichiometry of 1:1 (eq.1) involving the HPAC oxidation by NBS has been observed. 4-The dielectric constant of the medium was varied by adding methanol in different proportions (0 - 40 %, v/v). The dielectric effect is negligible. The reduction product succinamide when added fails to change the rate. This indicates its non-involvement in pre-equilibrium. The rate remains same on varying ionic strength of the medium indicating the involvement of non-ionic species in the rate determining step. Bromide ions have no significant effect on the rate of reaction Further the proposed mechanism is supported by the thermodynamic parameters computed from the hydroxyphenyl aldehyde and carbon dioxide are the products of oxidation. The effect of dielectric constant and halide ions on reaction rate was studied. From the Arrhenius plots the thermodynamic parameters, Ea, $\Delta H^{\neq}$, $\Delta G^{\neq}$, and $\Delta S^{\neq,}$ have been computed. For the observed parameters a consistent mechanism has been proposed and rate law was derived.

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