RUTHENIUM (III) - CATALYZED OXIDATIVE CLEAVAGE OF PHENYLPROPANOLAMINE HYDROCHLORIDE WITH SODIUM *N*-CHOROBEZENESULFONAMIDE IN ACID MEDIUM: A KINETIC AND MECHANISTIC STUDY

KIKKERI N. MOHANA*, NINGEGOWDA PRASAD

Department of Studies in Chemistry, University of Mysore Manasagangotri Mysore-570 006, India

(Received: January 2, 2008 - Accepted: July 19, 2008)

ABSTRACT

Phenylpropanolamine hydrochloride (2-amino-1-phenylpropanol hydrochloride) is a sympathomimetic drug used for nasal congestion associated with the common cold, allergies, high fever, or other respiratory illness. The kinetics of oxidation of phenylpropanolamine hydrochloride (PPA) with sodium *N*-chlorobenzenesulfonamide or chloramine-B (CAB) catalyzed by Ru (III) in hydrochloric acid medium has been studied at 308 K. The oxidation reaction follows the rate law, $-d[CAB]/dt = k[CAB]^x[H^+]^y[PPA]^z[Ru(III)]^2$, where x , y and z are less than unity. Addition of chloride ions, perchlorate ions and the reduction product of CAB, benzenesulfonamide (BSA), have no significant effect on the rate. Decrease of dielectric permittivity of the medium by increasing the CH_3CN content increased the rate. The reaction was studied at different temperatures and the activation parameters have been computed from the Arrhenius plot. The stoichiometry of the reaction was found to be 1:1 and the main oxidation products of PPA were found to be benzaldehyde and acetaldehyde. The rate constant decreases in D_2O medium and the normal isotope effect, $k'(H_2O)/k'(D_2O)$ is 2.39. Proton inventory studies have been made in H_2O - D_2O mixtures. Formation and decomposition constant of CAB-PPA complexes in the reaction scheme have been evaluated. The conjugate acid $C_6H_5SO_2NHCl$ has been assumed to be the reactive species. The observed results have been explained by plausible mechanisms and relative rate law has been deduced.

Keywords: Phenylpropanolamine hydrochloride, chloramine-B, oxidation Kinetics, Ru(III)-catalysis, acid medium.

INTRODUCTION

Considerable attention has centered on the chemistry of *N*-metallo-*N*-arylhalosulfonamides, generally known as organic haloamines, because of their versatility and their behavior both as bases and nucleophiles. The prominent member of this group is chloramine-T (CAT) and the mechanistic aspects of many of its reactions have been documented¹⁻³. The benzene analogue chloramine-B (CAB) is gaining importance as a mild oxidant⁴⁻⁶. Conductometric study of the interaction of CAB with some metal ion solutions⁷ and photolysis of aqueous solution of CAB has been reported⁸.

Phenylpropanolamine hydrochloride (PPA) is a sympathomimetic drug, differing from amphetamine by only a hydroxyl group on the β -carbon atom. PPA is used for nasal congestion associated with the common cold, allergies, high fever or other respiratory illness. It has been used as a non prescription diet-aid for weight loss⁹. Survey of literature reveals that, there was no information available on the oxidation kinetics of phenylpropanolamine with any oxidant. There was a need for understanding the oxidation mechanism of this drug, so that the study could through some light on the fate of the drug in the biological system.

In view of these facts, there is a considerable scope in the study of redox behavior of CAB towards PPA and understand its redox chemistry in solutions. In the light of the available information and our continued interest on mechanistic studies on haloaminometric reactions in general and bioactive compounds in particular, the present investigation was undertaken. The reaction of PPA with CAB in HCl medium without a catalyst was found to be sluggish, but the reaction was found to be facile in the presence of Ru(III) catalyst. The present paper reports the kinetics of Ru(III)-catalyzed oxidation of PPA with CAB in HCl medium at 308 K in order to (i) elucidate the reaction mechanism of metabolic conversions of the substrate in biological system, (ii) Put forward appropriate rate law, (iii) Ascertain the reactive species and (iv) identify the products of reaction.

EXPERIMENTAL

1. Materials

Chloramine-B was prepared and purified by the method reported earlier¹⁰. An aqueous solution of the compound was standardized iodometrically and preserved in brown bottles to prevent its photochemical deterioration. Pharmaceutical grade PPA (supplied by Cipla India Ltd., Mumbai, India) was used as received. Aqueous solution of the compound was prepared freshly each time. All other chemicals used were of analytical grade. Ionic strength of the reaction mixture was kept constant with a concentrated solution of $NaClO_4$

(Merck). Doubly distilled water was used for the preparation of aqueous solutions.

2. Kinetic measurements

The kinetic runs were performed under pseudo-first-order conditions. Required amounts of solutions of the PPA, HCl, $NaClO_4$, were charged into a stoppered Pyrex glass tubes whose outer surfaces were coated black to eliminate photochemical effects. In each case, a required amount of water was added to maintain a constant total volume. The tube was thermostated in water both set at a given temperature (308 ± 0.1 K). To this solution, a measured amount of pre-equilibrated CAB solution was added to give a known concentration. The progress of the reaction was monitored iodometrically for two half-lives by withdrawing aliquots of the reaction mixture at regular time intervals. The rate constants, k' were reproducible within ± 3 %. Regression analysis of the experimental data to obtain regression coefficient, r , was made using MS-excel program.

RESULTS

1. Stoichiometry and product analysis

Reaction mixtures containing different compositions of PPA and CAB were equilibrated in presence of HCl (0.1 mol dm^{-3}) and $RuCl_3$ ($1 \times 10^{-4} \text{ mol dm}^{-3}$) for 48 hrs at 308 K. Determination of unreacted oxidant in the reaction mixture showed that one mole of PPA was consumed per mole of oxidant, confirming the following stoichiometry:

where $R = C_6H_5SO_2$.

The products in the reaction mixture were extracted several times with diethyl ether. The combined ether extract was evaporated and subjected to column chromatography on silica gel using gradient elution (chloroform). The reduction product of CAB, benzenesulfonamide (BSA) was detected by paper chromatography¹¹. Benzyl alcohol saturated with water was used as the solvent with 0.5 % vanillin in 1% HCl solution in ethanol as spray reagent ($R_f = 0.88$). The oxidation products of PPA were found to be benzaldehyde, acetaldehyde and ammonia. Formation of ammonia was quantitatively estimated by micro-Kjeldahl procedure. Benzaldehyde and acetaldehyde were detected by spot tests¹². Benzaldehyde was identified by preparing 2, 4-DNP derivative. Further the products were confirmed by IR absorption bands. BSA: 3347, 3258 cm^{-1} (N-H stretch); 1334 cm^{-1} (SO_2 asym. stretch); 1660 cm^{-1} (SO_2 sym. stretch)

and 994 cm^{-1} (S-N stretch). Benzaldehyde: 1704 cm^{-1} (C=O stretch) and 2848 cm^{-1} (aldehydic C-H stretch). IR spectra were recorded on JASCO FT-IR spectrometer using KBr pellets.

2. Effect of varying reactant concentrations on the rate

The reaction was performed in presence of Ru(III)-catalyst and HCl under pseudo-first-order conditions ($[\text{PPA}] \gg [\text{CAB}]$). Plots of $\log [\text{CAB}]$ versus time were linear ($r > 0.996$). The linearity of these plots together with the constancy of the slope for various $[\text{CAB}]_0$, indicates a first-order dependence of the reaction rate on $[\text{CAB}]$. The pseudo-first-order rate constants, k' obtained at 308 K are listed in Table 1. The reaction rate increased with increase in $[\text{PPA}]$ (Table 1), and a plot of $\log k'$ versus $\log [\text{PPA}]$ was linear ($r = 0.988$) with a slope of 0.4 indicating a fractional-order dependence on $[\text{PPA}]_0$.

3. Effect of varying concentration of HCl on the rate

At constant $[\text{CAB}]$, $[\text{PPA}]$, $[\text{Ru(III)}]$, ionic strength and temperature, the rate of reaction increased with increase in $[\text{HCl}]$ (Table 1). A plot of $\log k'$ versus $\log [\text{HCl}]$ was linear ($r = 0.995$; Fig. 1), with a slope of 0.74 indicating a fractional-order dependence on $[\text{HCl}]$.

Table 1. Effect of varying concentrations of reactants and acid on the reaction rate constant at 308 K $[\text{RuCl}_3] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ and $\mu = 0.2 \text{ mol dm}^{-3}$

$10^4[\text{CAB}]$ (mol dm^{-3})	$10^3[\text{PPA}]$ (mol dm^{-3})	$10^2[\text{HCl}]$ (mol dm^{-3})	$10^4k'$ (s^{-1})
3.0	8.0	10.0	4.39
5.0	8.0	10.0	4.37
7.0	8.0	10.0	4.35
9.0	8.0	10.0	4.42
11.0	8.0	10.0	4.40
5.0	4.0	10.0	3.55
5.0	6.0	10.0	4.02
5.0	10.0	10.0	4.70
5.0	12.0	10.0	5.31
5.0	8.0	8.0	3.76
5.0	8.0	12.0	5.08
5.0	8.0	14.0	5.71
5.0	8.0	16.0	6.21
* 5.0	8.0	10.0	4.35
** 5.0	8.0	10.0	4.41

* In presence of benzenesulfonamide.

** At ionic strength 0.5 mol dm^{-3} .

Fig. 1

Fig. 1: Plot of $4 + \log k'$ vs. $2 + \log [\text{HCl}]$.

4. Effect of added $[\text{Cl}^-]$ on the rate

The addition of $[\text{Cl}^-]$ in the form of NaCl, keeping $[\text{H}^+]$ constant did not affect the rate of reaction (Table 2). Hence, the dependence of the rate on $[\text{HCl}]$ reflected the effect of $[\text{H}^+]$ only on the reaction.

5. Effect of varying $[\text{Ru(III)}]$ on the rate

The reaction rate increased with increase in $[\text{Ru(III)}]$ (Table 2), and a plot of $\log k'$ versus $\log [\text{Ru(III)}]$ was linear (Fig. 2; $r = 0.999$) with a slope of 0.24 indicating a fractional-order dependence on $[\text{Ru(III)}]$.

Table 2. Effect of varying Cl^- and RuCl_3 concentrations on the reaction rate constant $[\text{CAB}]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{PPA}] = 8 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 10 \times 10^{-2} \text{ mol dm}^{-3}$, $\mu = 0.2 \text{ mol dm}^{-3}$ and $T = 308 \text{ K}$

$10^2[\text{Cl}^-]$ (mol dm^{-3})	$10^4[\text{RuCl}_3]$ (mol dm^{-3})	$10^4k'$ (s^{-1})
12.0	1.0	4.41
14.0	1.0	4.38
17.0	1.0	4.35
20.0	1.0	4.33
25.0	1.0	4.36
10.0	0.5	3.71
10.0	0.8	4.16
10.0	1.0	4.37
10.0	2.0	5.25
10.0	3.0	5.85

Fig. 2

Fig. 2: Plot of $4 + \log k'$ vs. $5 + \log [\text{Ru(III)}]$.

6. Effect of varying benzenesulfonamide and ionic strength on the rate

Addition of the reduced product, benzenesulfonamide (2×10^{-4} to $8 \times 10^{-4} \text{ mol dm}^{-3}$) and variation of ionic strength of the medium using NaClO_4 to the reaction mixture had no significant effect on the rate.

7. Effect of relative permittivity of the medium on the reaction rate

The effect of relative permittivity (D) of the medium on the rate has been studied by using the $\text{CH}_3\text{CN} - \text{H}_2\text{O}$ content in the reaction mixture with all other conditions kept constant. The values of relative permittivity were computed from the values of the pure liquids¹³. The rate constant, k' increases with decreasing relative permittivity of the medium (Table 3). Plot of $\log k'$ versus $1/D$ gave a straight line ($r = 0.998$) with a positive slope. Blank experiments

performed showed that CAB did not oxidize CH_3CN under the experimental conditions employed.

Table 3. Effect of solvent composition and temperature on the reaction rate constant $[\text{CAB}]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{PPA}]_0 = 8 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HCl}] = 10 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{RuCl}_3] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ and $\mu = 0.2 \text{ mol dm}^{-3}$

Temperature (K)	CH_3CN (%, v/v)	$10^4 k'$ (s^{-1})
308	0	4.37
308	5	4.46
308	10	4.76
308	15	4.95
308	20	5.15
303.4	-	2.57
308	-	4.37
313	-	8.02
318	-	13.32
321	-	18.47

8. Effect of solvent isotope on the rate

As the rate is dependent on $[\text{H}^+]$, solvent isotope study in D_2O medium was made. The value of k' (H_2O) is $4.37 \times 10^{-4} \text{ s}^{-1}$ and that of k' (D_2O) is $1.83 \times 10^{-4} \text{ s}^{-1}$ leading to solvent isotope effect, $k'(\text{H}_2\text{O}) / k'(\text{D}_2\text{O}) = 2.39$. Proton inventory studies were made in H_2O - D_2O mixtures, and the results are shown in Table 4. The corresponding proton inventory plot for the rate constant k'_n in a solvent mixture containing deuterium atom fraction (n) is given in Fig. 3.

Fig. 3

Fig. 3: Plot of k' vs. n .

Table 4. Proton inventory studies for the oxidation of PPA in H_2O - D_2O mixture at 308 K $[\text{CAB}]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{PPA}]_0 = 8 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HCl}] = 10 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{RuCl}_3] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ and $\mu = 0.2 \text{ mol dm}^{-3}$

Atom fraction of D_2O (n)	$10^4 k'$ (s^{-1})
0.00	4.38
0.25	4.20
0.50	3.92
0.75	3.30
0.85	2.51

9. Effect of temperature on the rate

The reaction was studied at different temperatures (303.4–321 K) keeping other experimental conditions constant (Table 3). From the Arrhenius plot

of $\log k'$ versus $1/T$ ($r = 0.998$), activation energy and other thermodynamic parameters were found to be $E_a = 86.29 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 83.70 \text{ kJ mol}^{-1}$, $\Delta G^\ddagger = 71.99 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -37.46 \text{ JK}^{-1} \text{ mol}^{-1}$.

10. Test for free radicals

The addition of the reaction mixture to an aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of *in situ* formation of free radical species in the reaction sequence.

DISCUSSION AND MECHANISM

Bishop and Jennings¹⁴, Morris *et al.*¹⁵ and Higuchi and co-workers¹⁶ have shown the existence of similar equilibria in acid and alkaline solutions of metal salts of *N*-haloarenesulfonamides. Chloramine-B an analogue to chloramine-T behaves as a strong electrolyte in aqueous solutions and furnishes different types of reactive species in acidic solutions. To confirm this hypothesis, conductometric and pH-titrations between aqueous solutions of CAB and HCl were performed. The conductometric behavior of CAB is identical with that of CAT^{17,18}, while the pH titration curves observed are similar to those noted by Morris *et al.*¹⁵. The possible equilibria in acidified CAB solutions are,

where R is $\text{C}_6\text{H}_5\text{SO}_2$.

The possible oxidizing species in acidified CAB solutions are dichloramine-B (RNCl_2), the conjugate acid (RNHCl), HOCl and $\text{H}_2\text{O}^+\text{Cl}$. If RNCl_2 were to be the reactive species, then the rate law predicts the second-order dependence on $[\text{CAB}]_0$, and negative effect of BSA according to Eq. (5), which is not in agreement with the experimental observation. If HOCl acts as a reactive oxidant species a first-order retardation of rate on added BSA (RNH_2) was expected. However, there was no such effect is seen. Hardy and Johnston¹⁹, who studied the pH dependent relative concentrations of the species present in acidified bromamine-B solutions of comparable molarities, have shown that RNHBr is the likely oxidizing species in acid medium. Narayanan and Rao²⁰ and Subhashini *et al.*²¹ have reported that monohaloamines can be further protonated at pH 2 as shown in the following equations (7) and (8) for monochloramine-T ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl}$) and monochloramine-B ($\text{C}_6\text{H}_5\text{SO}_2\text{NHCl}$), respectively.

The second protonation constants for chloramine-T and chloramine-B are 102 M^{-1} and $61 \pm 5 \text{ M}^{-1}$ respectively at 25°C .

Cady and Connick²² and Connick and Fine²³ based on the ion exchange properties and UV-spectral studies have shown that octahedral complexes such as $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$, $[\text{RuCl}_3(\text{H}_2\text{O})_3]$, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ and $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ may not exist in aqueous solution of RuCl_3 . However other studies²⁴⁻²⁶ have shown that the following ligand substitution equilibrium in acidic solution,

Singh *et al.*^{27,28} have used the above equilibrium in Ru(III)-catalyzed

oxidation of primary alcohols by bromamine-T and ethylene glycols by *N*-bromoacetamide in HClO_4 medium. In the present study however, the absence of chloride ion effect on the rate indicates that, equilibrium (9) does not play a role in the reaction and hence the complex ion, $[\text{RuCl}_3(\text{H}_2\text{O})]^{2+}$ is assumed to be the reactive catalyzing species. Similar results were observed in the Ru(III)-catalyzed oxidations of chloroacetic acid²⁹, ethanol³⁰ by bromamine-T and *N*-heterocycles by chloramine-T³¹.

Ultraviolet spectral measurements showed that a sharp absorption band was noticed at 214 nm for RuCl_3 , 226.5 nm for CAB and around 216 nm for PPA in presence of 0.1 mol dm^{-3} HCl. A mixture of CAB and RuCl_3 solutions in the presence of HCl showed an absorption band at 268 nm, while for a mixture of PPA and Ru(III) solutions an absorption band was noticed at 212 nm. The spectral evidence showed that complex formation takes place only between Ru(III) and CAB.

Based on the preceding discussion, a detailed mechanistic interpretation (Scheme 1) for the Ru(III)-catalyzed CAB-PPA reaction in acid medium has been proposed to substantiate the observed kinetics.

Scheme 1

Step (iv) of Scheme 1 determines over all rate law,

$$\text{rate} = -d[\text{CAB}]/dt = k_4[\text{X}'] \quad (10)$$

If $[\text{CAB}]_t$ represents total [CAB] in solution, then

$$[\text{CAB}]_t = [\text{RNCl}^-] + [\text{RNHCl}] + [\text{X}] + [\text{X}'] \quad (11)$$

From, steps (i), (ii) and (iii) of Scheme 1

$$[\text{RNCl}^-] = \frac{[\text{RNHCl}]}{K_1[\text{H}^+]}$$

$$[\text{RNHCl}] = \frac{[\text{X}]}{K_1[\text{Ru(III)}]}$$

$$\text{and} \quad [\text{X}] = \frac{[\text{X}']}{K_2[\text{S}]}$$

Substituting these in equation (11) and solving for $[\text{X}']$ one obtains,

$$[\text{X}'] = \frac{K_1 K_2 K_3 [\text{CAB}]_t [\text{PPA}] [\text{Ru(III)}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{Ru(III)}] [1 + K_3 [\text{PPA}]]} \quad (12)$$

By substituting for $[\text{X}']$ from equation (12) in equation (10), the following rate law (13) is obtained,

$$\text{rate} = \frac{K_1 K_2 K_3 k_4 [\text{CAB}]_t [\text{PPA}] [\text{Ru(III)}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{Ru(III)}] [1 + K_3 [\text{PPA}]]} \quad (13)$$

The rate law (13) is in good agreement with all experimental results. Since

rate = $k' [\text{CAB}]_t$, rate law (13) can be transformed into equations (14) to (16).

$$k' = \frac{K_1 K_2 K_3 k_4 [\text{PPA}] [\text{Ru(III)}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{Ru(III)}] [1 + K_3 [\text{PPA}]]} \quad (14)$$

$$\frac{1}{k'} = \frac{1}{K_1 K_2 K_3 k_4 [\text{PPA}] [\text{Ru(III)}] [\text{H}^+]} + \frac{1}{K_2 K_3 k_4 [\text{PPA}] [\text{Ru(III)}]} + \frac{1}{K_3 k_4 [\text{PPA}]} + \frac{1}{k_4} \quad (15)$$

$$\frac{1}{k'} = \frac{1}{K_3 k_4 [\text{PPA}]} \left\{ \frac{1}{K_1 K_2 [\text{Ru(III)}] [\text{H}^+]} + \frac{1}{K_2 [\text{Ru(III)}]} + 1 \right\} + \frac{1}{k_4} \quad (16)$$

Based on equation (16), plot of $1/k'$ versus $1/[\text{PPA}]$ (Fig. 4) at constant $[\text{Ru(III)}]$, $[\text{H}^+]$ and temperature has been found to be linear ($r = 0.988$). The decomposition constant k_4 was calculated ($k_4 = 6.06 \times 10^{-3} \text{ s}^{-1}$) from the intercept of the plot.

Fig. 4: Plot of $1/k'$ vs. $1/[\text{PPA}]$.

In Scheme 1, S represents substrate, X and X' represent complex intermediate species whose structures are shown in Scheme 2, where a detailed mechanistic interpretation of Ru(III)-catalyzed PPA oxidation by CAB in HCl medium is proposed. PPA with one mole of CAB get oxidized to benzaldehyde, acetaldehyde and Ammonia. The oxygen atom of the oxidant is coordinated to the metal center of the active catalyst species, $[\text{RuCl}_3(\text{H}_2\text{O})]^{2+}$ to form a loosely bound metal complex X. [step (i) of Scheme 2]. Then the NH_2 group of the substrate readily reacts with the complex, X to give another intermediate complex, X', RNH_2 and releasing $[\text{RuCl}_3(\text{H}_2\text{O})]^{2+}$ [step (ii) of Scheme 2]. This intermediate X' undergo intermolecular rearrangements [steps (iii) and (iv)] forming benzaldehyde and acetaldehyde.

A change in solvent composition by varying the CH_3CN content in $\text{CH}_3\text{CN} - \text{H}_2\text{O}$ affects the reaction rate. The general equation relating to the effect of dielectric constant to the reaction rate in a bimolecular reaction has been derived by Landskroner and Laidler³². For the limiting case of zero angle of approach between two dipoles, Amis³³ has shown that,

$$\ln k'_D = \ln k'_{D=\infty} - \frac{2\mu_1\mu_2}{DkT r^3} \quad (17)$$

Where k'_D is a function of dielectric constant D, μ_1 and μ_2 are the dipole moments of reactions, r is the distance of approach for two dipoles, k is the Boltzmann constant and T is the absolute temperature. Equation (17) predicts a linear relation between $\log k'$ versus $1/D$. The slope of the line should be negative for a reaction between two dipole molecules and positive for ion-dipole reactions. In the present case, the plot of $\log k'$ versus $1/D$ is linear with a positive slope, thus supporting the participation of ion-dipole species in the rate determining step.

The observed solvent isotope effect supports the proposed mechanism and

the derived rate law. For a reaction involving a fast equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O medium, since D_2O^+ and OD^- are stronger acid and stronger base respectively than H_3O^+ and OH^- ions^{34,35}. In the present case, the observed solvent isotope effect of $k'(H_2O) / k'(D_2O) > 1$ is due to the protonation step followed by hydrolysis involving the OH bond scission. The retardation of rate in D_2O is due to the hydrolysis step which tends to make the normal kinetic isotope effect. The proton inventory studies made in H_2O – D_2O mixture could throw light on the nature of the transition state. The dependence of the rate constant, k'_n on the deuterium atom fraction 'n' in the solvent mixture is given by the following form of Gross-Butler equation^{36,37}.

$$\frac{k'_0}{k'_n} = \frac{\pi TS \{1 - n + n \phi_i\}}{\pi RS \{1 - n + n \phi_j\}} \quad (18)$$

Where ϕ_i and ϕ_j are isotope fractionation factor for isotopically exchangeable hydrogen sites in the transition state (TS) and in the ground/reactant state (RS), respectively. The Gross-Butler equation permits the evaluation of ϕ_i when the value of ϕ_j is known. However, the curvature of proton inventory plot could reflect the number of exchangeable proton in the reaction³⁶. Plot of k'_n versus n (Fig.4) is a curve in the present case, and this in comparison with the standard curves, indicate the involvement of a single proton or H-D exchange in the reaction sequence³⁸. This proton exchange is indicative of the participation of hydrogen ion in the formation of transition state.

The mechanism is further supported by the value of energy of activation and other thermodynamic parameters. The fairly high positive values of Gibb's free energy of activation and enthalpy of activation indicate that, the transition state is highly solvated, while the negative entropy of activation suggests the formation of the compact activated complex with fewer degrees of freedom. The reduction product (RNH_2) did not influence the rate, showing that it is not involved in pre-equilibrium. Addition of Cl^- ion has no effect on the rate indicating that no free chlorine is formed in the reaction. All these observations also confirm the proposed mechanism and derived rate law.

CONCLUSIONS

Oxidation of PPA with CAB in hydrochloric acid medium is sluggish, but the reaction is facile in presence of $RuCl_3$ catalyst. The conjugate acid, $C_6H_5SO_2NHCl$ was found to be reactive oxidizing species. The stoichiometry of the reaction was found to be 1:1 and the oxidation products of PPA in HCl medium were identified as benzaldehyde and acetaldehyde. The observed results have been explained by plausible mechanisms, and related rate law has been deduced.

ACKNOWLEDGEMENT

The authors are thankful to University of Mysore, Mysore, for financial support.

REFERENCES

1. M. M. Campbell, G. Johnson, *Chem. Rev.* **78**, 65 (1978).
2. K. K. Banerji, B. Jayaram, D. S. Mahadevappa, *J. Sci. Ind. Res.* **46**, 65 (1987).
3. D.H. Bremner, *Synthetic Reagents* **6**, 9 (1986).
4. D.S. Mahadevappa, M. Sayeed Ahmed, N.M. Madegowda, *Int. J. Chem. Kinet.* **15**, 775 (1983).
5. K. N. Mohana, Rangaswamy, K. M. Lokanath Rai, *Oxid. Commun.* **28**, 394, (2005).
6. S.K. Revathi, S. Ananda, Rangaswamy, K.N. Mohana, *Collect. Czech. Chem. Commun.* **69**, 1577, (2004).
7. C.R. Raju, K.N. Mohana, H.S. Yathirajan, K.S. Rangappa, *Indian. J. Chem.* **40A**, 613 (2001).
8. B.N. Usha, Rangaswamy, H.S. Yathirajan, *J. Indian Chem. Soc.* **61**, 812, (1984).
9. Sharon Alger, Karen Larson, Vicky Boyce, Helen Seagle, Anne-Marie Fontvieille, T. Robert, Ferraro, Russel Rising, Eric Ravussin, *Am. J. Clin. Nutr.* **57**, 120, (1993).
10. H.S. Yathirajan, Rangaswamy, D.S. Mahadevappa, *Collect. Czech. Chem. Commun.* **47**, 1826 (1982).
11. M.P. Raghavendra, K.S. Rangappa, K.M.L. Rai, *J. Carbohydr. Chem.* **16**, 343, (1997).
12. Feigl F Spot Tests in Organic Analysis, Elsevier, Amsterdam, New York, 1975, pp 244 and 245.
13. J.R.A. Pollock, R. Stevens Dictionary of organic compounds, Erye and Spottilwood Ltd., London, UK, 1965, p. 2820.
14. E. Bishop, V.J. Jennings, *Talanta* **1**, 197, (1958).
15. J.C. Morris, J.R. Salazar, M.A. Winemann, *J. Am. Chem. Soc.* **70**, 2036 (1948).
16. T. Higuchi, K. Ikeda, A. Hussain, *J. Chem. Soc. (B)* 546, (1967).
17. D.S. Mahadevappa, Rangaswamy, *Rev. Roumaine de chimie* **22**, 1233, (1977).
18. Rangaswamy, D.S. Mahadevappa, *Indian. J. Chem.* **14A**, 463, (1976).
19. F.F. Hardy, J.P. Johnston, *J. Chem. Soc. Perkin Trans II* **742**, (1973).
20. S.S. Narayanan, V.R.S. Rao, *Radio. Chim. Acta.* **32**, 221, (1983).
21. M. Subhashini, M. Subramanian, V.R.S. Rao, *Talanta* **32** 1082, (1985).
22. H.H. Cady, R.E. Connick, *J. Am. Chem. Soc.* **80**, 2646, (1958).
23. R.E. Connick, D.A. Fine, *J. Am. Chem. Soc.* **82**, 4187, (1960).
24. T. Davfokratova, Analytical Chemistry of Ruthenium, Academy of Sciences, USSR, 1963, pp. 54, 71 and 97.
25. J.R. Backhours, F.D. Dwyer, N. Shales, *Proc. Roy. Soc.* **53**, 146, (1950).
26. W.P. Griffith, The Chemistry of Rare Platinum metals, Interscience, New York, 1967, p. 4.
27. B. Singh, N.B. Singh, B.B.L. Saxena, *J. Indian Chem. Soc.* **61**, 319, (1984).
28. B. Singh, D.K. Singh, D. Singh, *J. Mol. Cat.* **78**, 207, (1988).
29. S. Ananda, B.M. Venkatesha, D.S. Mahadevappa, N.M.M. Gowda, *Int. J. Chem. Kinet.* **25**, 755 (1993).
30. Puttaswamy, R. Ramachandrapa, *Trans. Met. Chem.* **24**, 326, (1996).
31. Puttaswamy, R.V. Jagadeesh, Nirmala Vaz, Radhakrishna, J. Mol. Cat. A: Chemical, 229, 211 (2005).
32. D.A. Landskroner, K. J. Laidler, *Trans Faraday Soc.* **52**, 200, (1956).
33. E. S. Amis, Solvent Effects on Reaction Rates and Mechanisms, Academic Press, New York, 1966.
34. C.J. Collins, N.S. Bowman, Isotope Effects in Chemical Reactions, Van Nostrand Reinhold, New York, 1970 p.267.
35. K.B. Wiberg, *Chem. Rev.* **55**, 713 (1955); K.B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, 1964.
36. W.J. Albery, M.H. Davies, *J. Chem. Soc. Faraday Trans.* **68**, 167 (1972).
37. G. Gopalakrishnan, J.L. Hogg, *J. Org. Chem.* **50**, 1206 (1985).
38. N.S. Isaacs, *Physical Organic Chemistry*, Wiley, New York, 1987, p. 275.